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**DEVELOPMENT OF INNOVATIVE POLYOL
SYSTEMS FROM RECYCLED POLYETHYLENE
TEREPHTHALATE AND RENEWABLE RAW
MATERIALS FOR RIGID POLYURETHANE
FOAMS**

Doctoral Thesis

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EIROPAS SAVIENĪBA

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Polyols from recycled poly(ethylene terephthalate) flakes and rapeseed oil for polyurethane foams^{*)}

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Abstract: Bio/recycled polyols from rapeseed oil (RO) and poly(ethylene terephthalate) (PET) were prepared using a continuous, two-step synthesis method. The bio/recycled polyol properties were compared to RO and commercially available PET based polyols. Rigid polyurethane foams with a unified apparent density of 40–45 kg/m³ were prepared from these polyols. The thermal conductivity, thermal properties, water absorption and mechanical properties of foams were tested. The results indicated that the RO/PET polyols can be successfully used for preparing polyurethane foams as energy efficient thermal insulation material.

Keywords: rigid polyurethane foams, rapeseed oil, PET waste, renewable raw materials.

Poliole z recyklowanych płatków poli(tereftalanu etylenu) i oleju rzepakowego przeznaczone do wytwarzania pianek poliuretanowych

Streszczenie: Otrzymano biorecyklowane poliole z oleju rzepakowego i poli(tereftalanu etylenu), na drodze ciągłej dwuetapowej syntezy. Porównano ich właściwości z właściwościami polioliu uzyskanego z oleju rzepakowego i dostępnego w handlu polioliu na bazie poli(tereftalanu etylenu). Z syntetyzowanych polioli wytworzono sztywne pianki poliuretanowe o gęstości pozornej w zakresie 40–45 kg/m³. Oznaczono przewodność cieplną, właściwości termiczne, chłonność wody oraz właściwości mechaniczne otrzymanych pianek. Uzyskane wyniki wskazują, że poliole zsintetyzowane z oleju rzepakowego i poli(tereftalanu etylenu) mogą być stosowane do produkcji pianek poliuretanowych przeznaczonych do celów termoizolacyjnych.

Słowa kluczowe: sztywne pianki poliuretanowe, olej rzepakowy, odpady PET, surowce odnawialne.

Poly(ethylene terephthalate) (PET) is one of the most widely used packaging materials in Europe and also in the world. In Europe, 65 billion postconsumer PET bottles were recycled in 2013 according to Petcore Europe, in this way PET is the most recycled polymer in Europe [1]. PET recycling can be classified in four stages: primary recycling (preconsumer industrial scrap), secondary recycling (mechanical recycling), tertiary recycling (chemical recycling) and quaternary recycling (energy recovery). From the environmental and sustainability standpoint, chemical recycling is the most favorable process because, in chemical recycling, new raw materials are produced that in turn can be used again in refineries or petrochemical and chemical production. It also conserves petrochemical resources, energy and is a partial solution for the solid PET waste problem [2].

Chemical recycling of PET can be carried using different reactions: hydrolysis, glycolysis, methanolysis and

others. The most studied method is glycolysis using different glycols — ethylene glycol, diethylene glycol, propylene glycol and others [3]. Glycolysis offers the following advantages over other recycling methods — lower reagent amounts (it is not necessary to employ a large excess of reactant), lower temperatures and pressure [4]. PET glycolyzate can be used as a polyol for polyurethane (PUR) foam or polyisocyanurate (PIR) foam production. The use of these polyols improves the mechanical and thermal properties of the resulting PUR foams. Better thermal properties allow a reduction in the consumption of flame retardants in the final PUR formulation. However, these PET polyols also have major drawbacks — high viscosity polyols and incompatibility with the physical blowing agents. PET glycolyzate is not compatible with the physical blowing agents (pentanes and hydrofluorocarbons), which are currently allowed foaming agents under the Montreal Protocol. This results in unstable polyol systems that separate during storage and if such a system is used for the production of PUR/PIR foams, the dimensional stability and other properties of the resulting PUR/PIR foams are affected negatively [5–7].

Several authors have reported that vegetable oil based polyols show good compatibility with physical blowing

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agents. Yakushin *et al.* reported that polyols synthesized from rapeseed oil (RO) or sunflower oil amidated with diethanolamine show good compatibility with components conventionally used in polyol systems [8]. Guo *et al.* reported that a soy based polyol showed greater compatibility with cyclopentane than a commercially available petroleum derived polypropylene based polyol [9].

To decrease the viscosity and increase the compatibility of PET containing polyols with physical blowing agents, new type of polyols should be synthesized that would offer advantages from “both worlds” — aromatic moieties from PET and lipophilic nature of the vegetable oils. However, in the existing literature, there are not many papers that describe polyols from both renewable

bio/recycled polyols. The properties of the final bio/recycled polyols were investigated, as well as bio/recycled based PUR foams obtained, tested and compared to bio based foams from RO polyol and foams from PET based polyol.

EXPERIMENTAL PART

Materials

A short description and sources of the reagents used for the synthesis of RO/TEA, RO/PET polyols and PUR foams in this study are given in Table 1. All the reagents were used without any prior treatment.

Table 1. Reagents used for the synthesis of RO/PET polyols

Materials	Supplier	Description
PET flakes	PET Baltija, Latvia	Clear PET flakes
Rapeseed oil (RO)	Iecavnieks&Co, Latvia	I value = 117 I ₂ mg/100 g
Triethanolamine (TEA)	BASF, Germany	99.5 %
Zinc acetate dehydrate	Sigma Aldrich, Germany	≥ 98 %
Diethylene glycol (DEG)	Sigma Aldrich, Germany	99 %
Lupranol 3422	BASF, Germany	OH value = 490 mg KOH/g
Neopolyol 380 (NEO)	NEO GROUP, Lithuania	OH value = 370—390 mg KOH/g
Solkane 365/227	Solvay, Belgium	Pentafluorobutane / Heptafluoropropane (87/13)
PC CAT NP-10	Performance Chemicals Handels, Germany	
NIAX Silicone L6915	Momentive Performance Materials, Germany	
Trichloropropylphosphate	Lanxess, Germany	
Polymeric diphenylmethane diisocyanate IsoPMDI 92140 (pMDI)	BASF, Germany	NCO group content = 31.5 %

and recycled resources. Cakić *et al.* synthesized biorenewable polyols in a two stage synthesis: the first, glycolysis of PET using different molar ratios of the PET repeating unit to poly(ethylene glycol) PEG400 at different molar ratios; the second, transesterification of the oligoester polyols with different weight ratios of oligoester polyol to castor oil [10]. Beneš *et al.* carried out the depolymerization of PET using castor oil as a reagent and microwaves. They found that using castor oil as a reagent for PET depolymerization offers the following advantage — presence of long acylester chain in castor oil prevents the formation of cyclic oligomers that form when conventional PET depolymerization is carried out using different glycols [7].

The present paper describes polyols containing both renewable and recycled raw materials and synthesis using a continuous two-step method: (1) synthesis of rapeseed oil using transesterification with triethanolamine (TEA); (2) PET depolymerization with DEG at different molar ratios in the synthesized RO polyol media. The synthesized polyol from a combination of both, bio based raw materials and recycled PET, were named

Synthesis of RO/PET polyols

RO/PET polyols were synthesized using a two-step, continuous synthesis method. The reaction was carried out in a three neck 1.0 dm³ reaction flask equipped with a mechanical stirrer, a thermometer, a condenser and an argon inlet.

The first stage of the synthesis was to synthesize RO polyols using transesterification with triethanolamine (TEA), which was carried out at 170 ± 5 °C for 1 hour, 0.15 wt % zinc acetate was used as catalyst. The molar ratio was 1 M of RO to 2.9 M of TEA. A more detailed description of RO polyol synthesis is given in our previous work, Stirna *et al.* [11]. The end of the reaction was tested by the solubility of the obtained product in ethanol at the volume ratio (resin:ethanol = 1:1). When the product — RO/TEA polyol — was obtained, the temperature was increased to 230 °C and the second synthesis step — PET depolymerization — was carried out. To the mixture, PET flakes and DEG were added. The PET flakes were depolymerized at different molar ratios of PET to DEG using 0.5 wt % (based on the weight of PET) zinc acetate

as a catalyst. The molar ratios of PET to DEG were 1:2; 1:4 and 1:6. The reaction was carried out at 220–230 °C to conduct the glycolysis for 4 hours after which the flask was allowed to cool. Samples were named RO/PET-2, RO/PET-4 and RO/PET-6 where the number indicates the molar ratio of DEG.

Overall, the molar ratios of RO:TEA:PET:DEG were 1:2.9:3.2:6.5 for RO/PET-2 polyol, 1:2.9:2.1:8.5 for RO/PET-4 polyol and 1:2.9:1.6:9.5 for RO/PET-6 polyol.

To compare RO/PET polyols with vegetable oil based polyol, RO/TEA polyol was also synthesized as described above (first step of synthesis) and in our previous paper by Stirna *et al.* [11]. Also, commercial polyol NEO based on industrial PET scrap was chosen. NEO is synthesized using PET scraps and DEG. NEO was used without any prior treatment.

Preparation of polyurethane foams

The foams were prepared by the free-rising method in a mold, at room temperature. At first, the component was mixed in a 500 cm³ plastic beaker. Afterwards isocyanate was added and mixed for 15 s at a speed rate of 2000 rpm. Then, the mixture was quickly poured into an open mold (30×30×10 cm). The height of these foams was ~10 cm. The foams were conditioned for 24 h at room temperature.

Samples for different tests from prepared PUR foam blocks were cut using a band saw and afterwards they were conditioned for at least 24 h at room temperature.

Methods of testing

— The OH value was determined using the conventionally used acetic acetylation method. The acid value was determined according to DIN 53402. The hydroxyl and acid value of NEO was also tested in the laboratory.

— Viscosity measurements were carried out using a Haake Viscotester 6L/R plus at 20 °C.

— The moisture content in the polyol was tested using a conventionally used Karl Fischer method.

— The Fourier transform infra-red spectra measurements (FTIR-ATR) were made on a Perkin-Elmer spectrometer Spectrum One FTIR Spectrometer. The FTIR-ATR spectra of polyols were collected at a resolution of 4 cm⁻¹.

— The polyol compatibility with blowing agents was tested in plastic centrifuge tubes where 10 g of polyol was weighed and then 20 % of blowing agent was added. Then, the blends were centrifuged for 15 minutes at 55 rpm. The blends were then kept at ambient conditions for regular visual inspection.

— The compression strength and modulus of elasticity parallel and perpendicular to foaming direction of PUR foams were tested according to the requirements of ISO 844:2009 standard on testing machine Zwick/Roell Z100.

— The bulk density of obtained PUR foams was tested according to the ISO 845 standard.

— The thermal conductivity coefficient (λ , W/m·K) was tested using a Linseis Heat Flow Meter 200 according to ISO 8301 standard.

— The TGA and its derivative thermograms (DTGs) were studied using a Mettler Toledo TGA/SDTA 851e instrument. The heating rate was set to 10 °C/min under a flow of 20 cm³/min nitrogen and a temperature range was set from 25 to 1000 °C. The weight of the sample was ~8 mg.

— Water absorption was tested according to ISO 2896:2001 standard by immersing PUR samples in water for 7 days.

— Closed cell content was tested according to ISO 4590:2003, PUR samples with dimension (10×3.5×3.5 cm) were cut.

RESULTS AND DISCUSSION

Polyol characterization

The acid numbers, hydroxyl value, water content and viscosity of synthesized polyols are given in Table 2.

Table 2. Characteristics of polyols from RO and PET

Polyol	OH value mg KOH/g	Acid value mg KOH/g	Water content, %	Viscosity at 20 °C mPa·s
RO/TEA	363	2.5	0.12	160
RO/PET-2	233	3.2	0.23	1250
RO/PET-4	340	2.8	0.19	540
RO/PET-6	368	2.3	0.27	250
NEO	366	2.9	0.12	9640

All polyols used in this study have low acid numbers, which are less than 5 mg KOH/g, and thus all polyols are favorable for the production of rigid PUR foams. With an increase of the molar ratio of PET to DEG from 1:2 M to 1:6 M, the hydroxyl number of the derived polyols increased by 58 % and their viscosity decreased by 80 %. The results indicate that with increasing ratio of glycol to PET, the extent of depolymerization was greater. Aromatic polyol NEO showed the highest viscosity of all polyols. Except for RO/PET-2 polyol, the hydroxyl value of all polyols was in a comparable range. The water content of all polyols is admissible.

The polyols were also characterized by bio/recycled content (Table 3). The highest total bio/recycled content was for RO/TEA polyol — 67 % but this polyol does not contain PET. The total bio/recycled content of RO/PET polyols increased up to 57 % if the PET depolymerization was carried out at lower molar ratio of PET to DEG.

Depolymerization of PET by a two step continuous synthesis method with RO/TEA polyol and DEG was

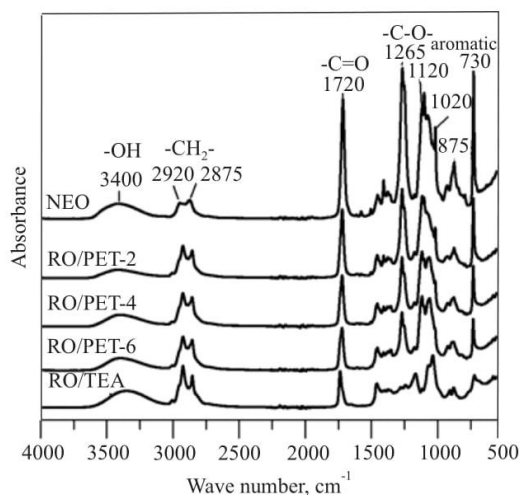


Fig. 1. FTIR-ATR spectra of polyols

confirmed using FTIR-ATR. The FTIR-ATR results of the RO/PET polyols obtained at different molar ratios are presented in Fig. 1. To compare the polyols, spectra of RO/TEA and NEO polyol were added.

Table 3. Renewable and recycled content in RO/TEA polyols

Polyol	Renewable content, %	Recyclate content, %	Total renewable + recyclate content, %
RO/TEA	67.0	-	67.0
RO/PET-2	33.5	23.8	57.3
RO/PET-4	33.5	15.6	49.1
RO/PET-6	33.5	11.6	45.1
NEO	-	45–48*	45–48

* Information obtained from the producers.

The band around 3400 cm^{-1} is due to the free hydroxyl groups present in all polyols. The band at 3400 cm^{-1} is stronger for RO/TEA, NEO and RO/PET-6 polyol. These results correlate with the higher hydroxyl values of these polyols in comparison to RO/PET-2 and RO/PET-4 polyols synthesized at lower glycol molar ratios. There is no absorption of aromatic groups for RO/TEA polyol. In the $3000\text{--}2850\text{ cm}^{-1}$ range, two bands can be observed due to symmetric and asymmetric stretching of CH_2 groups in all polyols. For polyols containing RO, the two bands in this region are more pronounced due to the presence of long fatty acid radicals.

For all polyols, there is a sharp band at 1720 cm^{-1} , which confirms that the bio/recycled polyols also contain an ester bond in their structure. It can also be seen that the peak around 1720 cm^{-1} becomes sharper and more intense with an increase in the amount of PET in the RO/PET polyols (Table 3), which is due to an increase in the number of ester linkages in the polyols.

In future, more experiments should be carried out to study the chemical structure of RO/PET polyols.

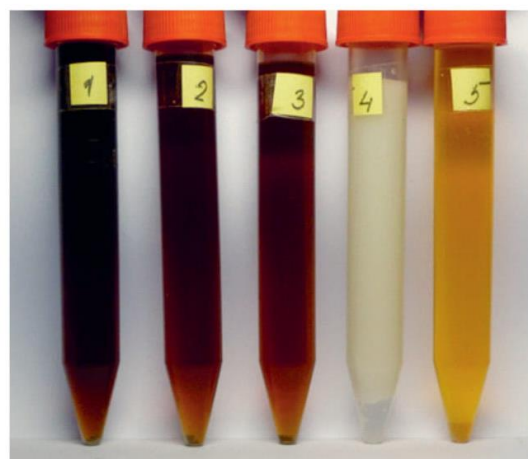


Fig. 2. Compatibility of polyols with blowing agent — Solkane 365/227; samples: 1) RO/PET-2; 2) RO/PET-4; 3) RO/PET-6; 4) NEO; 5) RO/TEA

Polyols compatibility with physical blowing agents

Experiments were carried out to test the compatibility of the polyols with physical blowing agents. Solkane 365/227 was chosen as a blowing agent. As expected, the aromatic polyester polyol NEO, based on PET scraps, showed poor compatibility with the blowing agent (Fig. 2, sample 4). All RO/PET polyols and also RO/TEA polyol showed complete compatibility with Solkane 365/227. This is due to the presence of long, hydrophobic and non-polar dangling chains in the polyol structure, which are introduced with RO.

The darker color residue at the bottom of sample 5 tube (RO/TEA polyol) is glycerol, which forms as a by-product during RO/TEA polyol synthesis. We have also reported this previously [11].

Formulation and foaming parameters of rigid PUR foams

Rigid PUR foam samples were prepared using synthesized polyols RO/PET-2, RO/PET-4, RO/PET-6, RO/TEA and commercially available NEO polyol. Foam samples were named accordingly to the polyol used and adding "PUR" before it. For example, PUR RO/PET-2 is a foam sample from polyol RO/PET-2. The detailed formulations of PUR samples is given in Table 4.

The amount of necessary pMDI was calculated according to isocyanate index 130. It is well known that the apparent density of PUR foams affects several foam properties, such as compression strength and thermal conductivity. Therefore, the amount of blowing agent Solkane 365/227 was adjusted to obtain PUR foams with a unified apparent density $40\text{--}45\text{ kg/m}^3$. This range of apparent density is suitable for rigid PUR foams used for thermal insulation in the construction industry.

Table 4. Formulation of rigid PUR foams

Component	Part by weight				
	PUR NEO	PUR RO/PET-2	PUR RO/PET-4	PUR RO/PET-6	PUR RO/TEA
Corresponding polyol			75		
Lupranol 3422			25		
Trichlorpropylphosphate			16		
NIAX Silicone L6915			1.5		
Water			2.2		
PC CAT NP-10	1.6	1.6	1.6	1.6	0.3
Solkane 365/227	14.0	16.0	16.0	16.0	15.0
pMDI	165.1	137.5	161.7	169.5	166.5

The foaming process was monitored by measuring the duration of start time (when foam begins to rise), gel time (indicating a transition of the mix from liquid to solid state) and tack-free time (when the foam solidifies completely). The results of the foaming parameters are presented in Table 5.

Table 5. Foaming parameters

Sample	Cream time, s	Gel time, s	Tack-free time, s
PUR NEO	70	100	135
PUR RO/PET-2	18	60	95
PUR RO/PET-4	23	53	80
PUR RO/PET-6	26	53	100
PUR RO/TEA	18	50	90

The results of the foaming parameters show that a lower amount of foaming catalyst is necessary for the PUR foam formulation when RO/TEA polyol is used (Table 4). The amount of catalyst PC CAT NP-10 was reduced in the PUR RO/TEA formulation to prolong the start time of foaming. It is necessary to decrease the start time otherwise the buildup of viscosity is too fast and it is not possible to pour the mixture into the mold. This is due to the fact that RO/TEA polyol also contains a tertiary amine group in its structure, which acts as a catalyst. So RO/TEA polyols can be characterized by a catalytic activity in urethane-forming reactions as reported in previous papers by our group [12]. Also, the synthesized bio/recycled polyols RO/PET show increased catalytic activity in comparison to NEO polyol. The start and gel

time of PUR foams was shorter for formulations where RO/PET polyols were used in comparison to the start and gel times of PUR foams from NEO polyol. All four PUR RO/PET formulations contained the same amount of foaming catalyst (Table 4).

Thermal conductivity of rigid PUR foams

Thermal conductivity is one of the most important physical properties of PUR foams and it determines their potential application. The thermal conductivity of PUR foams is from about 18 up to 28 mW/(m·K) [13]. It is influenced by several factors such as conduction through the polymer phase, conductivity through the gas trapped within the closed cell structure and the radiation between cells [14]. In the present study, the closed cell content of rigid PUR foam samples is ~95 %. The thermal conductivity of the obtained PUR foams is in a range from 19.5 to 21.5 mW/m·K (Table 6).

Over time, the thermal conductivity of PUR foams increases because the foaming agent with low thermal conductivity becomes diluted with air as it diffuses into the foam. Air has a higher thermal conductivity than foaming agent. The foaming agent also permeates the cell walls and escapes from the foam [15]. A small change (1.5–2.7 %) in the thermal conductivity of PUR NEO and for all PUR RO/PET samples is observed after 1 week. The best and the worst retentions of thermal conductivity were shown by foam samples PUR RO/PET-4 and PUR RO/TEA, respectively. As shown in Table 6, the thermal conductivity of PUR foams from RO/TEA polyol increased by 9.4 %.

Table 6. Thermal conductivity of rigid PUR foams

Sample	Closed cell content vol. %	Initial thermal conductivity mW/m·K	Thermal conductivity after 1 week, mW/m·K	Change in thermal conductivity after 1 week, %
PUR NEO	96 ± 1	19.49 ± 0.50	19.82 ± 0.50	1.7
PUR RO/PET-2	95 ± 1	20.54 ± 0.06	21.10 ± 0.06	2.7
PUR RO/PET-4	95 ± 1	20.65 ± 0.01	20.96 ± 0.01	1.5
PUR RO/PET-6	96 ± 1	20.86 ± 0.50	21.27 ± 0.50	2.0
PUR RO/TEA	95 ± 1	21.50 ± 0.25	23.52 ± 0.25	9.4

Water absorption of rigid PUR foams

Water absorption was tested by immersing PUR foam samples in water for 7 days. The results of water absorption are shown in Table 7.

Table 7. Water absorption of rigid PUR foams

Sample	Water absorption after 1 day, vol. %	Water absorption after 7 days, vol. %
PUR NEO	1.02 ± 0.05	2.11 ± 0.05
PUR RO/PET-2	1.58 ± 0.08	2.34 ± 0.13
PUR RO/PET-4	1.46 ± 0.10	2.56 ± 0.03
PUR RO/PET-6	1.56 ± 0.05	2.75 ± 0.36
PUR RO/TEA	1.97 ± 0.03	3.42 ± 0.08

The worst performance in water absorption experiments was observed for the PUR RO/TEA sample. It showed the highest water absorption after 1 day (1.97 vol. %) and also after 7 days (3.42 vol. %). PUR foams from RO/PET polyols and NEO polyol were more moisture-resistant.

Thermal stability of rigid PUR foams

The thermal stability of a material reflects the ability of its chemical structure to resist chain termination caused by heat. This greatly depends on the polyol structure.

Rigid PUR foams from aromatic polyols are thermally more stable than foams from aliphatic polyols [16]. Therefore, it can be expected that PUR foams from NEO and RO/PET polyols will show higher thermal stability than PUR foams from RO/TEA polyol. RO/TEA is an aliphatic polyol and does not contain any aromatic rings in its structure. TGA and DTG results are presented in Fig. 3 and Fig. 4, respectively. All PUR foams from RO/PET polyols show similar TGA and DTG curves, therefore only PUR RO/PET-4 was chosen for presentation.

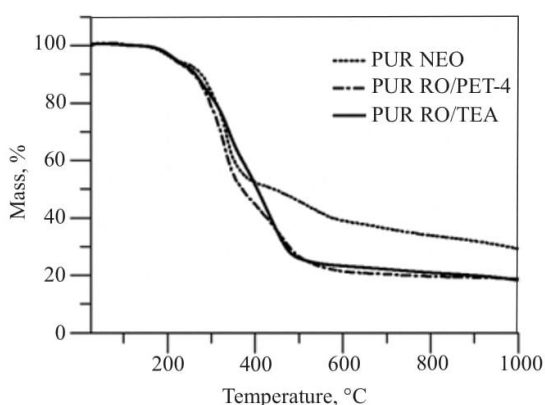


Fig. 3. TGA results of rigid PUR foams

The DTG curves show three peaks corresponding to three steps of degradation (Fig. 4) of PUR foams from NEO polyol and RO/PET-4 polyol. The three peaks are observed at about 200–210 °C, at ~330–340 °C and the

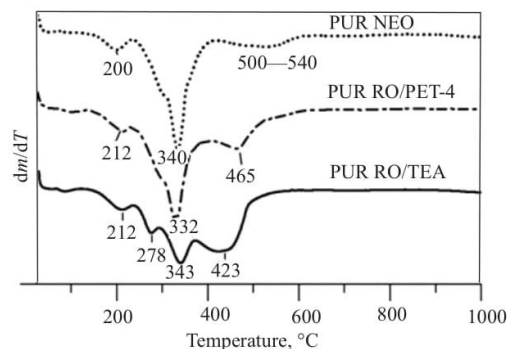


Fig. 4. DTG results of rigid PUR foams

final peak at ~450–500 °C. PUR RO/TEA also showed an additional peak at 278 °C. In the first step, low molecular weight compounds evaporate [16]. Also, allophanate and biuret crosslinks decompose [17]. In the second step, degradation starts at the urethane bond and other segments of the remaining structure [18]. Weight loss in the third stage is due to the degradation of the strongest bonds in the PUR backbone [19].

The thermal stability of PUR foams based on NEO polyol containing aromatic groups was higher than the thermal stability of PUR foams based on RO/TEA and RO/PET polyols. The char residues at 1000 °C for PUR foams from NEO, RO/PET-4 and RO/TEA polyols were 29.3 %, 18.8 % and 18.3 %, respectively (Fig. 3). The higher char residue of PUR NEO is due to the presence of aromatic groups in the polyol structure.

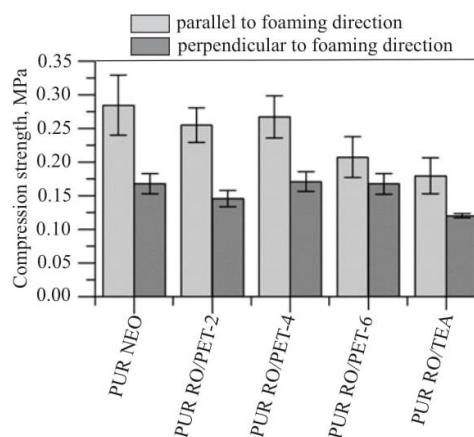


Fig. 5. Compression strength of rigid PUR foams

Compression strength of rigid PUR foams

It is well known that for rigid PUR foams obtained by the free rise method that anisotropy is observed. Therefore, compression tests were carried out in the foam rise direction and perpendicular to it. The mechanical properties of rigid PUR foams are significantly related to their apparent density. Due to this, all compression strength results were normalized with respect to a density of 45 g/m³ using the equations of Hawkins *et al.* [20]. The coefficients of anisotropy calculated from the compression strength results (Fig. 5) are in the range from 1.2 to 1.7.

PUR foams obtained from RO/PET polyols showed higher compression strengths than foams from RO/TEA. The highest compression strength (0.27 ± 0.03 MPa) of RO/PET foams was for the sample PUR RO/PET-4. Within the margin of experimental error, it reaches the same compression strength as for PUR NEO (0.28 ± 0.03 MPa).

CONCLUSIONS

The synthesis of polyols from recycled poly(ethylene terephthalate) and rapeseed oil was successfully achieved using a two-step continuous synthesis method. With higher molar ratios of diethylene glycol, the rapeseed/poly(ethylene terephthalate) polyols showed increased hydroxyl numbers and decreased viscosity. High reactivity and high bio/recycled content combined with excellent compatibility with blowing agents make these polyols suitable for the preparation of rigid polyurethane foams. Further studies on detailed chemical mechanisms are crucial to understand the chemical reactions and their effect on the properties of polyols and rigid polyurethane foams.

Rigid polyurethane foams from bio/recycled polyols showed decreased thermal conductivities and water absorptions in comparison to polyurethane foams obtained from rapeseed oil triethanolamine polyol. In addition, polyurethane foams from rapeseed/poly(ethylene terephthalate) polyols showed a better retention of thermal conductivity. The results show that the most favorable molar ratio of poly(ethylene terephthalate) to diethylene glycol is 1:4. Rigid polyurethane foams obtained using this polyol showed the best compression strength, water absorption, retention of thermal conductivity and foam samples were dimensionally stable without shrinkage. Overall, the results indicated that the rapeseed/poly(ethylene terephthalate) polyols can be successfully used for preparing polyurethane foams as energy efficient, thermal insulation material. Also, it is a promising and perspective material for the use in construction industry and domestic appliances *etc.*

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II

A.Ivdre, A.Fridrihsone-Girone, A.Abolins, U.Cabulis.

Effect of different concentration of rapeseed oil and recycled poly (ethylene terephthalate)
in polyols for rigid polyurethane foams.

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Effect of different concentration of rapeseed oil and recycled poly (ethylene terephthalate) in polyols for rigid polyurethane foams

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Abstract

In this research, polyols from rapeseed oil and recycled poly(ethylene terephthalate) were synthesized by two-step continuous synthesis with a different rapeseed oil and poly(ethylene terephthalate) concentration. All rapeseed oil/poly(ethylene terephthalate) polyols showed complete compatibility with blowing agent Solkane 365/227. The resulting polyols were used to prepare rigid polyurethane foams which were characterized with various techniques for determination of their physical, mechanical and thermal insulation properties. The effect of rapeseed oil and poly(ethylene terephthalate) concentrations in polyols on the characteristics of rigid polyurethane foams was investigated. The results showed that obtained rigid polyurethane foams were suitable for thermal insulation appliance. Also, the potential use of rapeseed oil as raw material combined with poly(ethylene terephthalate) to synthesize polyols with good compatibility with blowing agent was confirmed.

Keywords

Polyurethane foams, solubility, physical foaming/blowing agent, relative density, compression behaviors

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Introduction

It is well-known that poly(ethylene terephthalate) (PET) is one of the most versatile commodity thermoplastics widely used in a broad range of applications like apparel fibres, disposable soft-drink bottles etc. In 2012, the global annual production capacity of PET stood at over 28 million tons. During 2004–2011, the world PET production increased from nearly 11.3 million tons to around 18.6 million tons, registering an average annual growth of over 7%.¹ The increased consumption of PET is resulting in greater quantities of post-consumer and industrial PET waste. One of the main sources of PET waste is post-consumer soft drink bottles.^{2,3} Therefore, PET recycling has received a great deal of attention. In Europe, 1.8 million tons of PET plastic were recycled in 2013 according to Petcore Europe press release; in this way PET is the most recycled polymer in Europe.⁴

In general, PET waste can be recycled either physically or chemically. Chemical recycling can be realized by several processes including aminolysis,^{5–7} glycolysis,^{8–10} hydrolysis^{10–12} and alcoholysis.^{13,14} Glycolysis is carried out using different glycols like ethylene glycol (EG),^{15,16} diethylene glycol (DEG),^{17,18} triethylene glycol, 1, 4-butanediol,¹⁹ propylene glycol etc.²⁰ The catalyst used for this purpose is mainly metal acetate. In literature, glycolysis of PET in the presence of functional additives such as adipic acid, glycerol (GL), poly(propylene glycol) and hexanediol is studied.²¹

Chemical recycling of PET leads to the formation of monomer or oligomers that can be used for synthesizing new material. Product formed via PET glycolysis using EG as reactant is bis (2-hydroxyethylene) terephthalamide (BHET). Literature indicates that BHET has been widely used in various syntheses of polymeric materials such as unsaturated polyester resins and PET.²² BHET has also been used to obtain fatty amide derivatives²³ and benzothiazole derivatives.²⁴ The PET glycolysates find application in the manufacturing of unsaturated and saturated polyesters, alkyd resins,^{25,26} polyurethane (PUR) coatings,^{27,28} PUR and polyisocyanurate rigid foams.^{2,21}

Rigid PUR foams are widely used as a thermal insulation material in construction industry, domestic appliances and refrigerators. The monomers used to form PUR foams are isocyanates and polyols, which are mostly derived from petrochemical resources. Petrochemical polyols in PUR production partially or totally can be replaced by polyols from vegetable oils such as soybean, castor and palm oils. Also, renewable feedstock widely available in Northern Europe such as sunflower and rapeseed oil (RO) are used for polyol synthesis and rigid PUR foam production.²⁹ Only few investigations have been published about the polyols from both recycled PET and natural vegetable oils. Badri et al.³⁰ investigated PET waste glycolysis with ethylene glycol prior to blending with palm oil-based polyol. Beneš et al.³¹ reported the chemical recycling of waste PET using castor oil as a reagent, where acylester hydroxyl groups of castor oil ensures the depolymerisation of PET. Cakic et al.³² carried out PET glycolysis with poly(ethylene glycol) and produced saturated hydroxyl-functional polyester polyols with castor oil by transesterification process. Also, methods have been developed to synthesize aromatic polyester

polyols from PET and natural oils (corn oil and sunflower oil). Obtained polyols in these researches were compatible with hydrocarbon and hydrofluorocarbon blowing agents,³³ whereas polyols from PET prepared by the glycolysis usually are incompatible with some physical blowing agents.^{29,32} Polyol synthesis of RO and PET are innovative and should be investigated more widely.³⁴

The present paper describes polyester polyol synthesis of waste PET, RO and DEG. The influence of RO/PET molar ratio on polyol characteristics was investigated. The resulting polyols were used to prepare rigid PUR foams by reacting with isocyanate in the presence of catalyst, surfactant and physical blowing agent. The physical and mechanical properties, thermal conductivity and water absorption as well as foaming characteristics of the prepared PUR foams were investigated. The effect of different RO/PET polyols on the characteristics of rigid PUR foams was investigated.

Experimental

Materials

PET flakes from recycled plastic bottles were supplied from PET Baltia. RO ($I_2 = 117 \text{ I}_2 \text{ mg/100 g}$) was purchased from Iecavnieks & Co and used in all polyol synthesis. DEG (99%), which was used as a glycol in the depolymerization reaction, was purchased from Sigma Aldrich. Triethanolamine (TEA) (99.5%) from BASF was used as a material to obtain RO polyol. Zinc acetate dehydrate ($\geq 98\%$) from BASF was employed as the transesterification catalyst in polyol synthesis.

Rigid PUR foams were prepared from the synthesized polyols, high functional polyether polyol Lupranol 3422 ($\text{OH} = 490 \text{ mg KOH/g}$) from BASF, foaming catalyst CAT NP-10 from Performance Chemicals Handels, surfactant NIAx Silicone L6915 from Momentive Performance Materials, flame retardant trichloropropylphosphate (TCPP) from Lanxess and physical blowing agent Solkane 365/227 (pentafluorobutane: heptafluoropropane = 87:13) from Solvay. Distilled water was used as additional blowing agent. The isocyanate used was polymeric diphenylmethane diisocyanate (PMDI) ($\text{NCO group content} = 31.5 \%$) purchased from BASF. All reagents were used as received without purification.

Polyol synthesis

RO/PET polyols were synthesized using a two-step, continuous method. Reaction was carried out in a three-neck 1.0L reaction flask equipped with a mechanical stirrer, a thermometer, a condenser and an argon inlet.

The first step was RO transesterification with TEA at $170 \pm 5^\circ\text{C}$ for 1 h; 0.15 wt% zinc acetate was used as catalyst. The molar ratio was 1 M of RO to 2.9 M of TEA, and the end of the reaction was tested by the solubility of the obtained product in ethanol at the volume ratio 1:1.

Table 1. Composition of the synthesized polyols.

Polyol	RO (mol)	TEA (mol)	PET (mol)	DEG (mol)
RO/PET 1/1	1	2.9	1	4
RO/PET 1/2	1	2.9	2	8
RO/PET 1/4	1	2.9	4	16
RO/PET 1/6	1	2.9	6	24
RO/PET 1/8	1	2.9	8	32

PET: poly(ethylene terephthalate); RO: rapeseed oil; TEA: Triethanolamine; DEG: diethylene glycol.

In the second stage, depolymerization (glycolysis) of PET was carried out. The reaction mixture was heated up to the temperature of 230 °C and then PET flakes and DEG were added. The molar ratio 1 M PET to 4 M DEG was chosen based on Paberza et al.³⁴ earlier studies. Zinc acetate (0.5 wt% based on the weight of PET) was used as a catalyst. When all PET flakes were dissolved, the temperature of mixture was held at 225 ± 5 °C for 4 h.

Polyols were synthesized with different molar ratios of RO to PET. The molar ratios of RO to PET were 1:1, 1:2, 1:4, 1:6 and 1:8. RO/PET polyols were named according to RO-to-PET molar ratio. The compositions of polyols are given in Table 1.

Characterization of polyols

Hydroxyl number of the prepared products was experimentally determined by acetylating method according to DIN 53240. Acid number of the prepared products was determined according to DIN 53402. The moisture content in polyol was tested using conventionally used Karl Fischer method according to DIN 51777. Viscosity measurements were carried out using Haake Viscotester 6L/R plus at 20 °C.

The FTIR-ATR were made on a Perkin-Elmer Spectrum One FTIR Spectrometer. The FTIR-ATR spectra of polyols was collected within the wave number ranging from 4000 cm⁻¹ to 650 cm⁻¹ at a resolution of 4 cm⁻¹. Polyol compatibility with blowing agents was tested in plastic centrifuge tubes where 10 g of polyol was weighed and then 20% of blowing agent Solkane 365/227 was added. Then the blends were centrifuged for 15 min at 55 r/min and kept at ambient conditions for 8 weeks for regular visual inspection.

Preparation of rigid PUR foams

Rigid PUR foams were produced on a laboratory scale from a two-component (polyol and isocyanate) system with the isocyanate index equal to 130. The amount

Table 2. Composition of rigid PUR foams.

Component	Weight (g)
Corresponding RO/PET polyol	75.0
Lupranol 3422	25.0
Water	2.2
TCPP	16.0
PC CAT NP-10	1.6
NIAX Silicone L6915	1.5
Solkane 365/227	16.0
PMDI	Isocyanate index 130

PET: poly(ethylene terephthalate); RO: rapeseed oil; TCPP: trichloropropylphosphate; PMDI: polymeric diphenylmethane diisocyanate.

of necessary PMDI was calculated according to equation (1)

$$m_{PMDI} = \frac{II}{w_{NCO}} \cdot \left(\sum \frac{OH_n \cdot m_n}{1336} + 4.67 \cdot m_{H_2O} \right) \quad (1)$$

where II is the isocyanate index, m_{PMDI} , m_n , m_{H_2O} refer to the mass of PMDI, each polyol and summary water, respectively. w_{NCO} refers to the content of NCO groups of PMDI (31.5%) and OH_n is the hydroxyl value of each polyol (mg KOH/g).

The rigid PUR foams were prepared by blending polyols, blowing agents, fire retardant, surfactant and catalysts with a mechanical stirrer at 1000 r/min for 5 min to obtain a homogenous mixture. The precise amounts of the components are given in Table 2.

Such prepared polyol component was reacted with PMDI by mixing together at 2000 r/min for 7 s. The resulting reaction mixture was instantaneously poured into an open mould of dimensions $30 \times 30 \times 10$ cm and was allowed to rise freely. The process of rigid PUR foam formation was monitored by measuring the duration of cream time, gel time and tack-free time. All foam samples were allowed to cure at ambient conditions for 24 h before cutting it into test samples.

Obtained rigid PUR foam samples were named according to RO/PET polyol used and by putting "PUR" before it. For example, PUR RO/PET 1/1 is foam sample from polyol RO/PET 1/1 where RO/PET molar ratio is 1:1.

Characterization of rigid PUR foams

The measurements of closed cell content and apparent bulk density were carried out according to the standards ISO 4590 and ISO 845:2009, respectively. The tests

Table 3. Polyol characteristics.

Polyol	OH value (mg KOH/g)	Acid value (mg KOH/g)	Viscosity @20 °C (mPa·s)	Water content (%)
RO/PET 1/1	312	3.02	380	0.38
RO/PET 1/2	322	3.47	410	0.26
RO/PET 1/4	388	2.56	400	0.20
RO/PET 1/6	514	1.68	280	0.18
RO/PET 1/8	520	1.46	260	0.17

PET: poly(ethylene terephthalate); RO: rapeseed oil.

of rigid PUR foam compression properties were performed on testing machine Zwick/Roell Z100 according to the standard ISO 844:2009 at 10% relative deformation. Water absorption was tested immersing PUR samples in water for 28 days – according to the standard ISO 2896:2001. The thermal conductivity was tested with Linseis heat flow meter HFM 200 after 24 h when rigid PUR samples were cut out and periodically within 24 weeks. Temperature range was +10...+30 °C and dimensions of samples were 20 × 20 × 5 cm.

Results and discussion

General characterization of polyols

Synthesized RO/PET polyols were homogenous, yellowish brown liquids. The OH value, acid value, theoretical functionality, viscosity and water content in synthesized polyols are given in Table 3.

The OH value increases from 312 to 520 mg KOH/g by increasing PET content in polyol from 1 M to 8 M. This is due to the excess DEG and it correlates with results of FTIR. Polyols with such a high hydroxyl value are utilized to develop rigid PUR systems for foams with wide range of densities. Acid value of all the polyols used in this study is within the range, which is suitable for preparation of rigid PUR foams (<5 mg KOH/g). Higher acid value makes polyol systems more unstable because acid groups can react with amine groups of catalyst. The viscosity of synthesized polyols is ~20 times lower comparing with commercially available aromatic polyester, and it is ~3 time higher than RO/TEA polyol according to the results of Paberza et al.³⁴

Renewable and recycle content in polyols

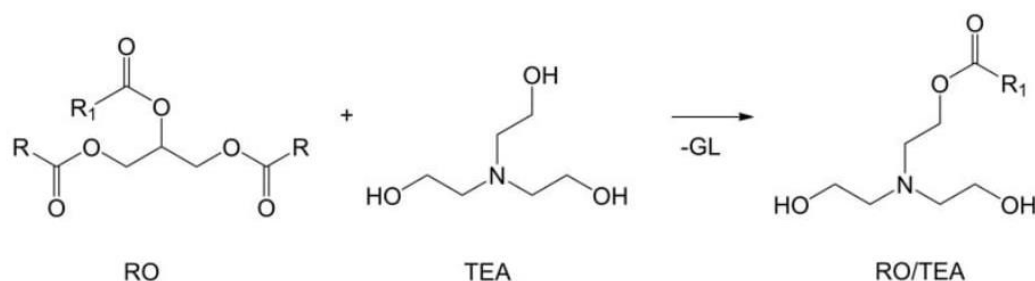
Renewable and recycle content in polyols was calculated and results are presented in Table 4.

With increasing RO/PET molar ratio from 1:1 to 1:8, the total renewable and recycle content in RO/PET polyols decreased from 55.5% to 38.6%. Hence,

Table 4. Renewable and recycled content in RO/PET polyols.

Polyol	Renewable content (%)	Recyclate content (%)	Total renewable + recyclate content (%)
RO/PET 1/1	45.5	9.9	55.5
RO/PET 1/2	34.5	15.1	49.6
RO/PET 1/4	23.2	20.3	43.6
RO/PET 1/6	17.5	23.0	40.5
RO/PET 1/8	14.1	24.6	38.6

PET: poly(ethylene terephthalate); RO: rapeseed oil.

**Scheme 1.** RO transesterification with TEA.

lower RO/PET molar ratio has to be chosen to reach higher total renewable and recyclate content in polyols.

Structural characterization of polyols

In the first step of polyol synthesis, RO transesterification with TEA is carried out according to Scheme 1. Transesterification yields GL as a by-product.

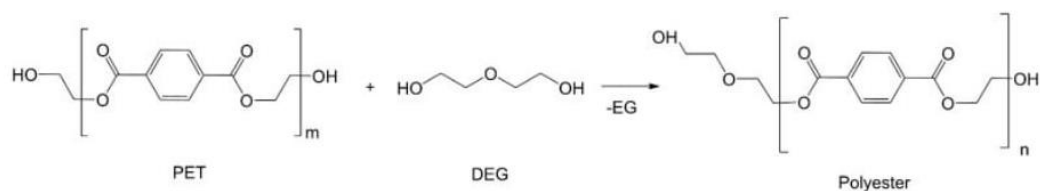
RO mainly consists of unsaturated fatty acids – oleic (56%), linoleic (26%) and linolenic (10%) acids;³⁵ therefore, the products of RO transesterification are mainly higher fatty acid ($\text{C}_8\text{--C}_{22}$) monoesters.³⁶

In the second stage of polyol synthesis, depolymerization of PET was carried out by glycolysis with DEG. Reaction is given in Scheme 2.

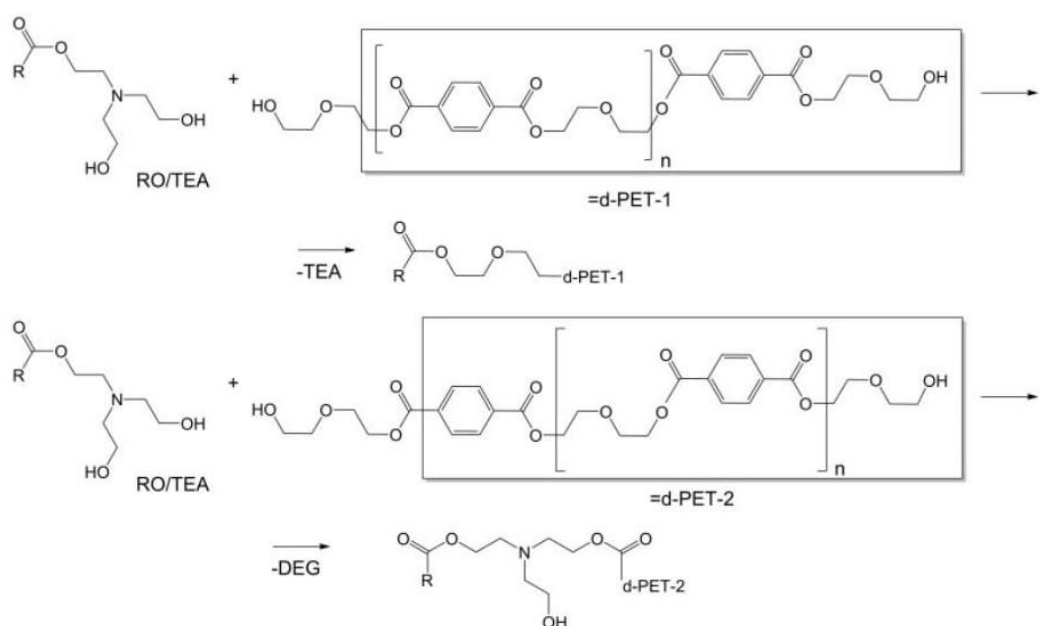
At the same time, obtained aromatic polyester from PET reacts with bio-based RO/TEA polyol obtained in the first stage of synthesis. The part of possible structures of transesterification products are given in Scheme 3.

Synthesized RO/PET polyols were investigated with FTIR-ATR method. The absorption spectra are presented in Figure 1. Also, spectrum of RO/TEA polyol from the first step of synthesis was taken and is shown in Figure 1 for comparison.

The broad band at 3400 cm^{-1} corresponds to the stretching vibration of --OH group. Absorption of this band increases with increasing RO/PET molar ratio in



Scheme 2. PET glycolysis with DEG.



Scheme 3. Aromatic polyester transesterification with RO/TEA polyol.

polyols and correlate with the results of OH value (Table 1). Asymmetric and symmetric $-\text{CH}_2-$ bands (at 2920 and 2855 cm^{-1} , respectively) are more intense for polyols which contain more RO. Absorbance in this region is due to the long-side chains in the structure of RO. All FTIR spectrum of polyols present a sharp band at 1720 cm^{-1} , which corresponds to the carbonyl bonds in ester group. The intensity of this peak for RO/PET polyols is higher than for RO/TEA polyol because additional ester bonds are introduced with depolymerized PET. Presence of aromatic structures from depolymerized PET is confirmed with small absorption bands of aromatic $-\text{C}=\text{C}-$ stretching vibrations at 1505 and 1410 cm^{-1} and the absorption band of bending and stretching vibrations of aromatic $\text{C}-\text{H}$ at 875 and 730 cm^{-1} , and the stretching vibration band of aromatic $\text{C}-\text{O}$ carbonyl group at 1265 and 1120 cm^{-1} . Also, a peak at $1075\text{--}1020\text{ cm}^{-1}$ indicates presence of aromatic structure. It corresponds to the symmetrical stretch of alkyl aryl ethers. These bands are most intensive for RO/PET 1/8 polyol, which has the highest content of PET. Peak at 875 cm^{-1} is partly overlapped with peak at 892 cm^{-1} . Peaks at 892 cm^{-1} and 920 cm^{-1} correspond to the $-\text{OC}_2\text{H}_4$ moieties of DEG

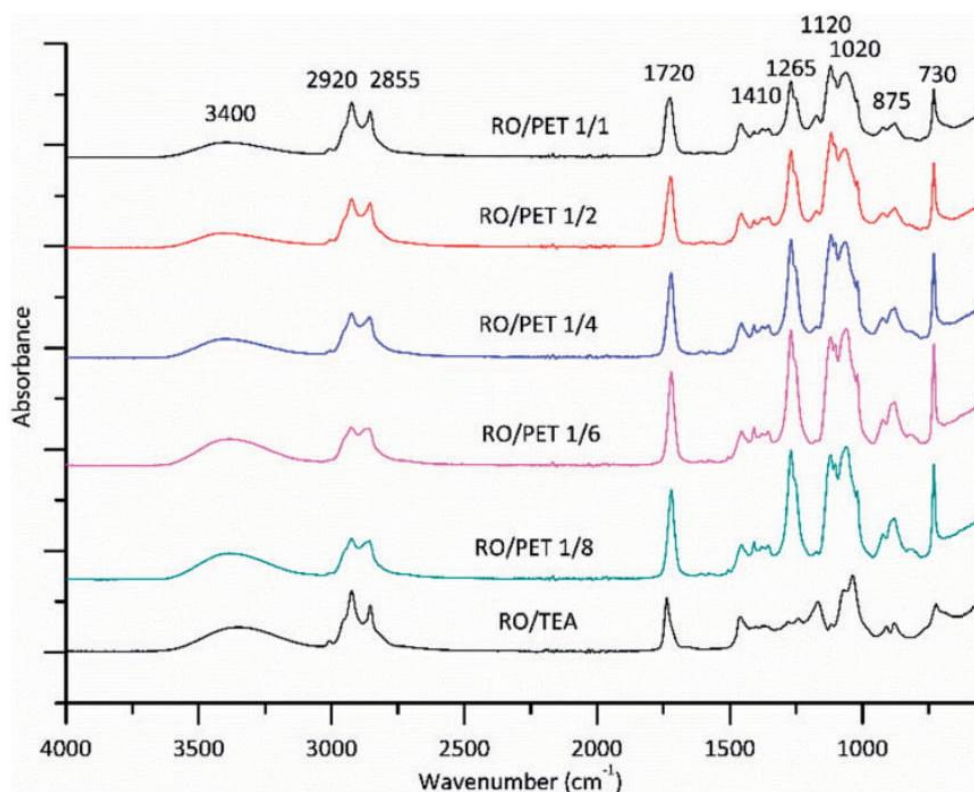


Figure 1. FTIR-ATR spectra of RO/PET polyols and RO/TEA polyol.

backbone and vibrations of C–O, respectively, which form the basis of the DEG detection according to investigations of Ahmed et al.³⁷

Polyols crystallization and polyols compatibility with physical blowing agent

Polyol systems for commercial appliance have to be homogenous, without phase separation during storage. Therefore, good compatibility between polyol and physical blowing agent is one of the most important properties of polyol. It also affects degree of foaming, cellular structure and dimensional stability of rigid PUR foams.³⁸ Paberza et al.³⁴ investigations showed that commercially available aromatic polyester polyol was incompatible with Solkane 365/227.

The solubility of blowing agent Solkane 365/227 in synthesized polyols was tested by mixing those compounds together and visually observing. Also, stability against crystallization was visually observed. The pictures of RO/PET polyols and Solkane 365/227 mixtures immediately after mixing and after 2 months are shown in Figure 2.

All RO/PET polyols showed complete compatibility with Solkane 365/227 (Figure 2a). That is due to the presence of long, hydrophobic and non-polar dangling chains in polyol structure which are introduced with RO. Crystallisation was visually observed for sample RO/PET 1/8 after 2 months (Figure 2b). Other samples stayed

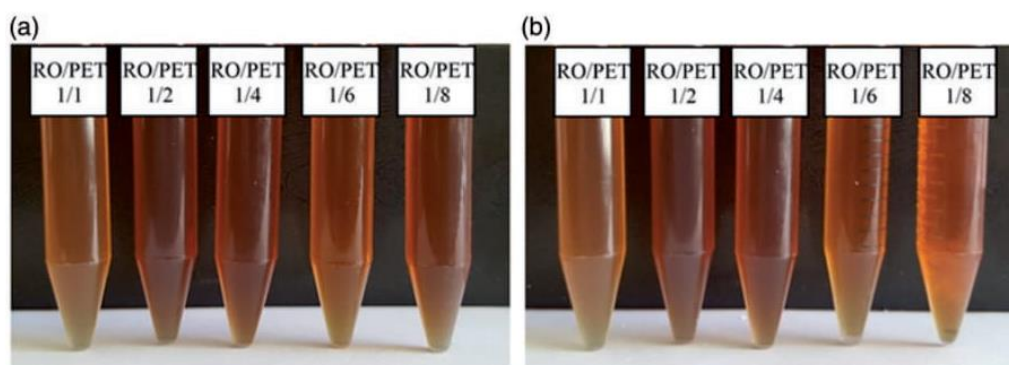


Figure 2. RO/PET polyols compatibility with Solkane 365/227 and stability: against crystallization (a) mixtures immediately after mixing; (b) after 2 months.

Table 5. Foaming characterization.

Sample	Cream time (s)	Gel time (s)	Tack-free time (s)
PUR RO/PET 1/1	15	40	80
PUR RO/PET 1/2	20	40	65
PUR RO/PET 1/4	23	47	67
PUR RO/PET 1/6	30	50	70
PUR RO/PET 1/8	30	50	67

PUR: polyurethane; PET: poly(ethylene terephthalate); RO: rapeseed oil.

without visible changes. So 1:6 M is the maximum RO and PET molar ratio to ensure both, polyol's good compatibility with Solkane 365/227 and stability against crystallization.

Rigid PUR foaming characterization

The process of rigid PUR foam formation was monitored by measuring the duration of cream time, gel time, and tack-free time. The cream time corresponds to the foaming start time when the PUR reaction mixture changes from a clear colour to a creamy one due to the introduction of the bubbles. Gel time is defined as the time during which the system remains in a fluid condition, and it is the starting point of a stable network formation by intensive allophanate crosslinking as well as urethane and urea linkages. Tack-free time indicates when the foam solidifies completely. Change in cream time, gel time and tack-free time indicates reactivity of the polyol system. Rigid PUR foaming characterization is given in Table 5.

Cream time increases and tack-free time becomes shorter with rising RO/PET molar ratio in synthesized polyols. This is due to the catalytic activity of RO/TEA polyol, which is obtained in the first step of synthesis, RO transesterification.

Table 6. Selected properties of PUR foams.

Sample	Apparent bulk density (kg/m ³)	Closed cell content (vol%)	Initial thermal conductivity (W/m·K)
PUR RO/PET 1/1	44.6	97	0.0216
PUR RO/PET 1/2	41.3	97	0.0217
PUR RO/PET 1/4	44.8	96	0.0202
PUR RO/PET 1/6	45.8	95	0.0206
PUR RO/PET 1/8	48.0	92	0.0197

PUR: polyurethane; PET: poly(ethylene terephthalate); RO: rapeseed oil.

RO/TEA polyol contains tertiary amine atom in its structure. It is reported previously by Stirna et al.³⁹ that tertiary amine atom acts as catalyst. With decreasing RO content, polyol is less catalytic active and foaming reaction is slower. Also, it is reported that higher OH value results in longer reaction times because as more OH groups are per molecule, the molecular mobility and foaming efficiency are reduced.⁴⁰

Thermal conductivity of rigid PUR foams

Rigid PUR foams with density in range from $45 \pm 4 \text{ kg/m}^3$ were obtained. Such a density was chosen because it is optimal for PUR thermal insulation material. The thermal conductivity of the prepared rigid PUR foams is one of the most important properties to evaluate materials' suitability for this appliance. In general, the thermal conductivity of rigid PUR foams depends on the foam density, cell size and closed-cell content and on the thermal conductivity of the gases trapped in the foam cells.⁴¹ Selected properties of rigid PUR foams are given in Table 6.

The thermal conductivity of obtained PUR foams is in range from 0.020 to 0.022 W/m·K and it slightly decreases by increasing RO/PET molar ratio. Closed-cell content was higher than 90 vol% for all samples, which is a typical value also for commercially used rigid PUR foams, for example, Elastopor H spray foam from BASF.⁴² From Table 6 results it is clear that the small difference in closed-cell content ($95 \pm 3 \text{ vol\%}$) and density ($45 \pm 4 \text{ kg/m}^3$) are not the main factors that affect thermal conductivity. It agrees with investigations of Septevani et al.,⁴³ where conclusion that closed-cell content is not the most important factor affecting thermal conductivity is made. Since the foaming agent with low thermal conductivity becomes diluted with air as it diffuses into the foam over time, thermal insulating properties of PUR foams get worse.⁴⁴ The thermal conductivity of Solkane 365/227, CO₂ and air are 0.0109,⁴⁵ 0.0153 and 0.0249 W/m·K, respectively.⁴⁶ As rigid PUR foams as insulation material is intended for long-term use, the retention of the thermal conductivity value is also an important property for them. Therefore, measurements of thermal conductivity were continued periodically 24 weeks more after rigid PUR foam preparation. Thermal conductivity of rigid PUR foams over time is shown in Figure 3.

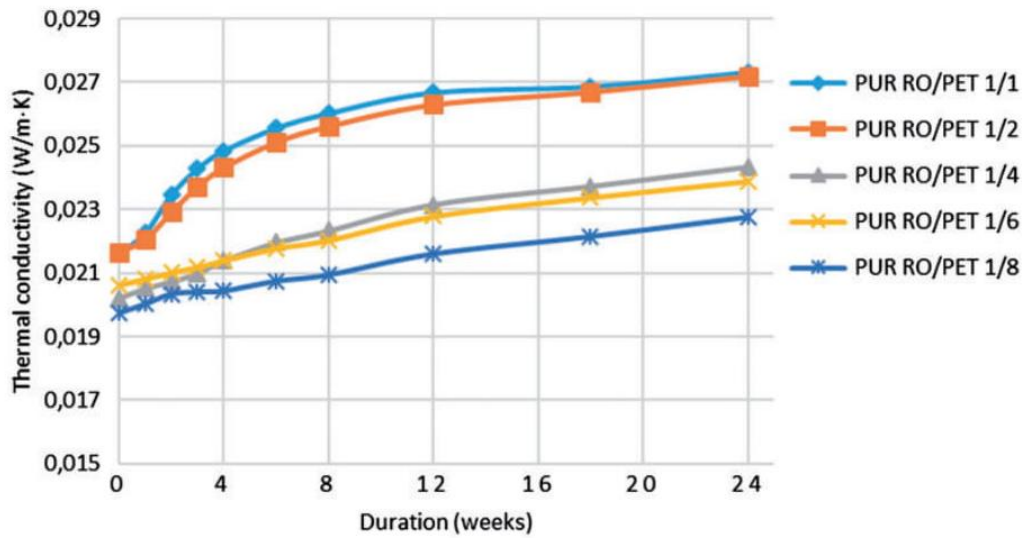


Figure 3. Thermal conductivity of rigid PUR foams over time.

Thermal conductivity increases less with increasing PET content in formulation. After 24 weeks thermal conductivity values of all samples still are according to typical thermal conductivity of PUR thermal insulation materials which is from about 0.018 up to 0.028 W/m·K; that is, two times lower than that of polystyrene, which is an alternative thermal insulation material.^{42,47} Rigid PUR foam from RO/PET 1/8 polyol showed the best retention of thermal conductivity. Change in thermal conductivity for this sample was only 15% in 24 weeks while for PUR RO/PET 1/1 it changed by 26%. Retention of thermal conductivity is enhanced because of the hard segments in polyol structure introduced from PET. Therefore, rigid PUR foams based on aromatic polyester polyol show even better retention of thermal conductivity.³⁴

Mechanical properties of rigid PUR foams

Compression strength test was carried out for obtained rigid PUR foams. The mechanical properties of rigid PUR foams are significantly related to their apparent density. Due to this, all compression strength results were normalized with respect to a density of 45 kg/m³ using equation of Hawkins et al.,⁴⁸ which is shown in equation (2)

$$\sigma_{norm} = \sigma_{exp} \left(\frac{45}{\rho} \right)^{2.1} \quad (2)$$

where σ_{norm} is the normalized strength (MPa), σ_{exp} is the raw strength (MPa) determined from the stress–strain curve and ρ is the apparent bulk density of sample (kg/m³). Results of normalized compression strength are shown in Figure 4.

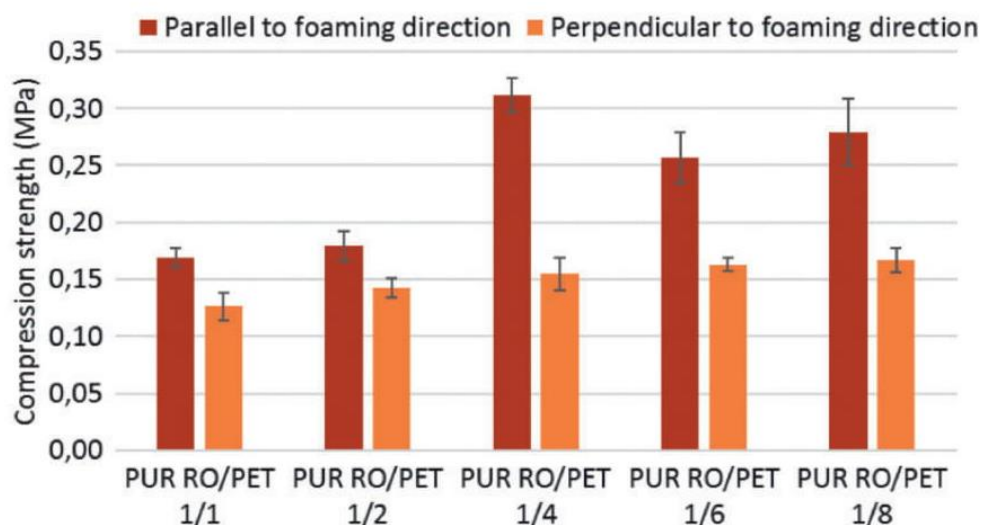


Figure 4. Compression strength of rigid PUR foams.

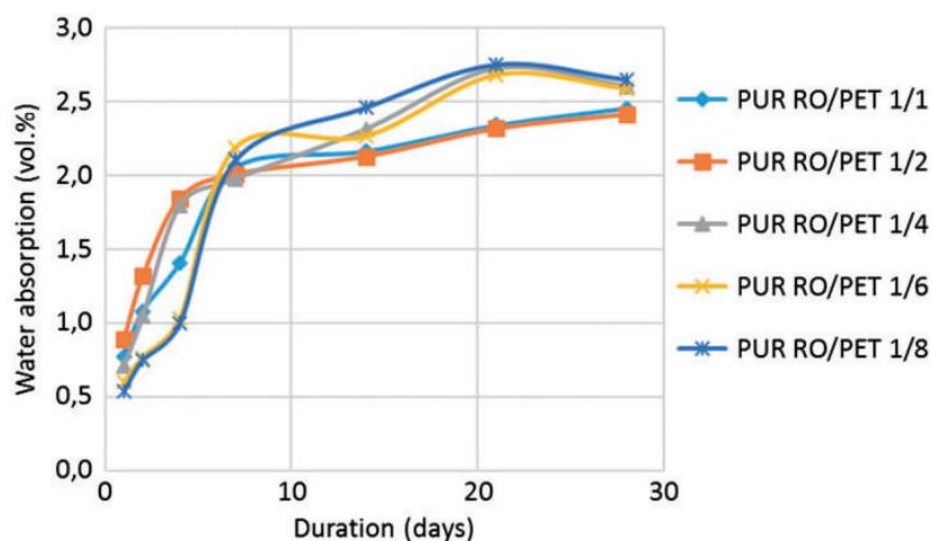


Figure 5. Water absorption of rigid PUR foams.

Difference between a compressive strength parallel and a perpendicular to foaming direction shows anisotropy of samples. Anisotropy of rigid PUR foams obtained by free rise method is very common. The coefficients of anisotropy calculated from compression strength results are in the range from 1.3 (sample PUR RO/PET 1/1) to 2.0 (sample PUR RO/PET 1/4). The highest compression strength (0.31 ± 0.01 MPa) of RO/PET foams was for the sample PUR RO/PET 1/4 where optimal ratio of hard segments and fatty acids side chains is reached. For comparison, commercially used rigid PUR foams Elastopor H from BASF with density $33\text{--}45\text{ kg/m}^3$ shows $0.15\text{--}0.20$ MPa high compressive strength.⁴⁸

Water absorption of rigid PUR foams

Water absorption was tested immersing PUR samples in water for 28 days. The change of samples volume was measured periodically during this period of time and kinetic curves are presented in Figure 5.

Different kinetic of water absorption is observed. For rigid PUR foams containing more RO (samples PUR RO/PET 1/1 and PUR RO/PET 1/2) water absorption in the first week is a little bit higher but in the long term they are slightly more water-resistant than rigid PUR foams with more PET in their formulation. Although RO contains long fatty acid side chains of hydrophobic nature in its structure⁴⁴ and hydrophobic properties exhibited by PUR/polyisocyanurate foams based on RO have been reported previously by Stirna et al.,⁴³ it does not affect the water absorption significantly for RO/PET foams. Overall, for all prepared materials, the water absorption was determined giving the favourable results of less than 3 vol% in 28 days.

Conclusions

Polyols from RO and recycled PET were synthesized by two-step continuous synthesis. Total renewable and recycate content in polyols was in range from 39% to 56%. With increasing PET content, OH value increases reaching 520 mg KOH/g and viscosity decreases to 260 mPa.s. All polyols showed complete compatibility with blowing agent Solkane 365/227 but polyol with RO and PET molar ratio 1:6 was the maximum molar ratio to ensure both polyols good compatibility with Solkane 365/227 and stability against crystallization.

Rigid PUR foams were obtained from synthesized polyols and characterized with various methods. With increasing PET content, the thermal insulation properties and compressive strength increases but long-term resistance to water absorption slightly decreases. All foams showed closed-cell structure and initial thermal conductivity in range from 0.020 to 0.022 W/m.K. The best complex of tested properties showed PUR composition based on polyol where RO and PET molar ratio is 1:4 M.

The potential use of RO as raw material combined with PET to synthesize polyols with good compatibility with blowing agent was confirmed. Also, complex of physical, mechanical and thermal insulation properties of obtained rigid PUR foams optimum gives potential to scale-up this synthesis and to use RO/PET polyols for commercial appliance.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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III

A.Ivdre, A.Abolins, I.Sevastyanova, M.Kirpluks, R.Merijs-Meri, U.Cabulis.
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Rigid Polyurethane Foams with Various Isocyanate Indices Based on Polyols from Rapeseed Oil and Waste PET

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Abstract: Developing polyols derived from natural sources and recycling materials attracts great interest for use in replacing petroleum-based polyols in polyurethane production. In this study, rigid polyurethane (PUR) foams with various isocyanate indices were obtained from polyols based on rapeseed oil and polyethylene terephthalate (RO/PET). The various properties of the prepared PUR foams were investigated, and the effect of the isocyanate index was evaluated. The closed-cell content and water absorption were not impacted by the change of the isocyanate index. The most significant effect of increasing the isocyanate index was on the dimensional stability of the resulting foams. This is due to the increased crosslink density, as evidenced by the increased formation of isocyanurate and increase of the glass transition temperature. Additionally, the influence on compression strength, modulus, and long-term thermal conductivity were evaluated and compared with reference PUR foams from commercially available polyols. Rigid PUR foams from RO/PET polyol were found to be competitive with reference materials and could be used as thermal insulation material.

Keywords: rigid polyurethane foams; bio-based polyols; renewable materials; thermal conductivity; dimensional stability; isocyanate index

1. Introduction

Polyurethanes (PURs) have been widely used for different applications, such as coatings, adhesives, sealants, elastomers, resins, and foams. Most of these PUR materials are obtained from petrochemicals which are non-renewable, have low sustainability, and cause environmental concerns for society [1]. Due to that, as well as increasing emphasis on issues concerning waste disposal and depletion of non-renewable resources, the development and production of polyols derived from natural sources and recyclable materials attracts great interest [2].

Over the past few decades, oils and fats of vegetable origin have served as a viable alternative to petroleum resources [3]. Researchers have managed to obtain PUR materials with up to 20%–35% of renewable material content [4]. Polyols from vegetable oils, such as soybean [5,6], castor [7,8], palm oils [9,10], sunflower [11,12], and rapeseed oil (RO) [13,14] have been synthesized and investigated as alternatives to petrochemical polyols in the production of PURs. Rapeseed is an especially important oil plant in the temperate climate region. Its production is showing a growing trend, both in Europe and around the world [15,16].

Typical methods used to produce polyols from vegetable oils are applied for RO too: epoxidation and opening of oxirane rings [13,17], transesterification with triethanolamine, and transamidation

with diethanolamine [17,18]. Hence, various RO polyols can be offered for the PUR market. According to Zieleniewska et al., investigations of PUR foams from RO polyols show competitive advantages such as lower water absorption (due to the hydrophobicity of fatty acids), higher thermal stability, and improved biological properties for rigid PUR foams. However, lower compressive strength and higher friability have been reported as disadvantages [13]. The incorporation of hard segments into the structure of PUR foam improves mechanical properties [19]. For this purpose, polyols from recycled polyethylene terephthalate (PET) can be successfully employed for PUR formulations to obtain rigid foams [20–22].

PET is one of the most versatile commodity thermoplastics, widely used in a broad range of applications, like fibres and disposable soft-drink bottles. The high popularity of PET as packaging material and its non-biodegradability creates huge amounts of waste. Therefore, effective recycling of PET is crucial [23,24]. PET waste can be recycled either physically or chemically.

One of the chemical recycling products of PET, that is suitable for obtaining PUR, is an aromatic polyester polyol. There are various chemical recycling pathways for aromatic polyester polyol synthesis: hydrolysis, aminolysis, methanolysis, and glycolysis [25]. Glycolysis is one of the most popular chemical recycling methods which has been commercialized [26]. Different depolymerization agents are employed (e.g., ethylene glycol [23,27], diethylene glycol (DEG) [28,29], propylene glycol [30], etc.) in glycolysis to obtain oligomers or oligoester diols/polyols with hydroxyl terminal groups. As mentioned before, aromatic polyester polyols improve the mechanical properties and thermal stability of PUR foams. Furthermore, it partly solves PET waste problems and decreases PUR dependence on petroleum feedstock. However, PET polyols' high viscosity, fast crystallization, and incompatibility with a blowing agent were reported as its drawbacks [31], whereas polyols from plant oils do not have such problems. The combination of PET and natural oils, such as RO and tall oil, eliminates the mentioned disadvantages of aromatic polyester polyols. Novel polyols are compatible with a physical blowing agent, less viscous, and more stable against crystallization. Therefore, these polyols are suitable for the preparation of rigid PUR foams [21,32,33].

Rigid PUR and polyisocyanurate (PIR) foams are one of the most energy-efficient thermal insulation materials, which are mainly used in civil engineering as well as in the refrigeration industry. PUR and PIR foams are also applied as impact absorption materials for structural and functional engineering applications [34]. PURs are made by the exothermic reactions between alcohols with two or more reactive hydroxyl groups (-OH) per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-NCO) per molecule (diisocyanates, polyisocyanates). Isocyanurate forms via trimerization of isocyanate as a side reaction during PUR formation [35].

The amount of PUR bonds and isocyanurate rings is closely related to a parameter called isocyanate index, which is the ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100. A theoretical equivalent amount is equal to one equivalent isocyanate per equivalent OH group. Higher isocyanate index incorporates more isocyanurate rings and increases the non-renewable material concentration in the end-product. The amount of isocyanurate rings in the polymer matrix affects the performance of PUR foams. The increase of glass transition temperature (T_g), dimensional stability, thermal stability, as well as thermal insulation with increasing isocyanate index value is reported [17,36]. Formulations for the production of rigid PUR foams normally have an index between 105 and 125, and those for rigid PUR-PIR foams have an index between 180 and 350 [37]. Hence, there is no precise limit where PUR foams end and PIR foams start. The influence of isocyanate index on the performance of rigid PUR and PIR foams, based on polyols synthesised from both PET and natural oil, have not been previously reported.

In the present study, rigid PUR foams were obtained from polyols based on RO and PET. Different isocyanate indices (from 110 to 180) were used for development of PUR foam formulations. The various properties (apparent density, foaming parameters, dimensional stability, water absorption, glass transition temperature, compression strength, and thermal conductivity) of the prepared PUR foams were investigated. For comparison, three series of reference rigid PUR foams were obtained from commercially available polyols. The isocyanate index effect on the foams'

performance was evaluated, as well as optimal isocyanate index as a compromise of sustainable material content, and foam performance was determined.

2. Materials and Methods

2.1. Materials

Aromatic polyester polyol based on RO and PET (RO/PET polyol, OH = 408 mg KOH/g) with RO/PET molar ratio 1:4 was synthesized, as described in our previous work [30]. Three base polyols for reference foams were chosen: aliphatic polyether polyol Lupranol 3300 (OH = 400 mg KOH/g, functionality $f = 3$) from BASF; aromatic polyester polyol Neopolyol 380 (OH = 370 mg KOH/g, $f = 3.3$ [4]) based on industrial PET waste and purchased from NEO Group (Lithuania); and RO/triethanolamine (RO/TEA) polyol (OH = 373 mg KOH/g, $f = 2.6$ [4]), which was synthesized by Latvian State Institute of Wood Chemistry via RO transesterification with TEA, and contains long dangling chains in its structure.

Rigid PUR foams were prepared by reacting synthesized RO/PET or reference polyols with different amounts of polymeric diphenylmethane diisocyanate (PMDI) (NCO group content = 31.5%) purchased from BASF. Other reagents used were: high functional polyether polyol Lupranol 3422 (OH = 490 mg KOH/g) from BASF, catalysts CAT NP-10 and 30 wt% solution of potassium acetate (KAc) in DEG from Performance Chemicals Handels, surfactant NIAx Silicone L6915 from Momentive Performance Materials, flame retardant Levagard PP (tris (2-chloroisopropyl)-phosphate) from Lanxess, and physical blowing agent Solkane 365/227 (pentafluorobutane:heptafluoropropane = 87:13) from Solvay. These materials were used without any additional prior treatment.

2.2. Preparation of Rigid PUR Foams

Rigid PUR foam series RO/PET was prepared from synthesized RO/PET polyol. In addition, three series of reference foams were prepared. As mentioned before, three base polyols for reference foams were chosen: Lupranol 3300, NEO 380, and RO/TEA. The obtained foam series were named LUPR, NEO, and RO/TEA, respectively. Chosen isocyanate indices were 110, 120, 130, 150, and 180. Foam samples were named SERIES NAME II = n , where n is the relevant isocyanate index. For example, RO/PET II = 120 is an RO/PET series rigid PUR foam with an isocyanate index of 120.

Polyols' systems were prepared by mixing all of its components according to the formulations presented in Table 1.

Table 1. Formulations of rigid polyurethane (PUR) foams

Component	Application	Amount, pbw ¹
Rapeseed oil/PET (RO/PET) or reference polyol	Base polyol	75
Lupranol 3422	Crosslinking agent	25
Levagard PP	Flame retardant	20
NIAx Silicone L6915	Surfactant	2.0
30 wt% potassium acetate (KAc) solution in diethylene glycol	Catalyst	1.0–1.5 ²
PC CAT NP-10	Catalyst	1.6–4.0 ³
Water	Blowing agent	2.2
Solkane 365/227	Blowing agent	16

¹ part by weight

² KAc was added only in PUR formulations with isocyanate indices 150 and 180

³ 4.0 pphp were added for reference foams based on Lupranol 3300 to enhance reactivity.

The necessary amount of PMDI was calculated according to the equation:

$$m_{PMDI} = \frac{II}{w_{NCO}} \cdot \left(\sum \frac{OH_n \cdot m_n}{1336} + 4.67 \cdot m_{H_2O} \right) \quad (1)$$

where II is the isocyanate index; m_{PMDI} , m_n , and m_{H_2O} refer to the mass of PMDI, each polyol, and summary water, respectively; w_{NCO} refers to the content of NCO groups of PMDI (31.5%); and OH_n is the hydroxyl value of each polyol (mg KOH/g).

The calculated amount of PMDI was added to a polyol system, and the resulting mixture was stirred vigorously at 2000 rpm for 10 s. Afterward, it was instantaneously poured into an open mold with the dimensions 30×30×10 cm to obtain free-rise foams. After preparing all foam samples, they were allowed to cure at ambient conditions for 24 h before any further tests.

2.2. Characterization of Rigid PUR Foams

The process of rigid PUR foam formation was monitored by measuring foaming parameters: the duration of cream time, gel time, and tack-free time. The closed-cell content and apparent density were measured according to the standards ISO 4590 and ISO 845, respectively. The compression strength of rigid PUR foams were tested on testing machine Zwick/Roell Z100 (standard ISO 844, maximum load-cell capacity 1 kN, test speed—10%/min, six specimens for each composition). Cylinder specimens with diameter and height of ≈20 mm were cut with a drill press using a crown drill bit. Water absorption was tested immersing PUR specimens into the water for seven days, according to ISO 2896. The dimensional stability measurements were acquired according to ISO 2796. Two modes were chosen: 28 days at 70°C, ambient relative humidity (R.H.); and 28 days at 70°C, R.H. = 97%. The initial thermal conductivity of the rigid PUR foams was measured, as well as thermal conductivity after 24 weeks. These tests were carried out with Linseis Heat Flow Meter 200 according to the ISO 8301 standard. The temperature range was +10...+30 °C, and dimensions of specimens were 200×200×30 mm. The FTIR data was collected using an attenuated total reflectance technique with a ZnSe and Diamond crystals on a Thermo Fisher Nicolet iS50 spectrometer. A total of 32 scans were averaged at 4 cm⁻¹ resolution for each spectrum. Dynamic mechanical analysis (DMA) was carried out with Mettler Toledo DMA/SDTA861^c: temperature range from 25 to 200 °C, ramp rate of 3°C/min, frequency of 1 Hz, amplitude 40 μm, and maximal force of 2 N. Compression oscillation mode was used. Three cylinder specimens with a diameter of ≈16 mm and a height of ≈8 mm were tested for each composition. Specimens were cut with a drill press using a crown drill bit. The maximum of the peak in the viscoelastic parameter $\tan \delta$ was used to define T_g .

3. Results and Discussion

3.1. Sustainable Material Content

Rigid PUR foams with different isocyanate indices were obtained by the free-rise method. Renewable and recycled material content was calculated and is shown in Figure 1.

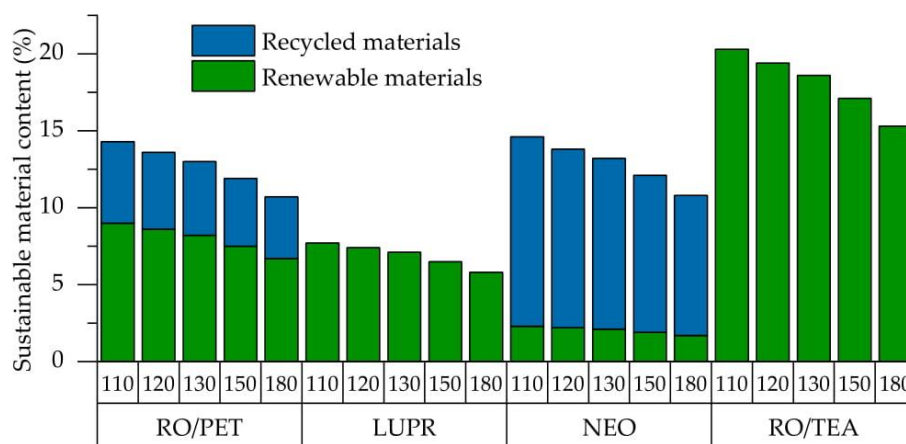


Figure 1. Sustainable material content in all series of rigid PUR foams

The amount of renewable and recycled materials in RO/PET foams is between 11% to 14%. In comparison, reference LUPR series foams contain up to 8%; NEO series, 15%; and RO/TEA series, 20%. The difference in sustainable material content between series of PUR foams depends mainly on the sustainability of the base polyol. The largest quantity of non-renewables in PUR formulations is made by PMDI. Hence, the sustainable material content decreases by rising isocyanate index.

3.2. Apparent Density and Closed-Cell Content

The obtained rigid PUR foams were characterized by apparent density and closed-cell content (Table 2). Closed-cell content of RO/PET PUR foams was higher than 95 vol.% (on average, 97 vol.%) and was not impacted by the isocyanate index. Reference foams, LUPR ($\rho = 40\text{--}43 \text{ kg/m}^3$), NEO ($\rho = 40\text{--}45 \text{ kg/m}^3$), and RO/TEA ($\rho = 41\text{--}48 \text{ kg/m}^3$) series, showed slightly lower closed-cell content: 93 vol.%, 95 vol.%, and 93 vol.% on average, respectively. Closed-cell content 92–98 vol.% is suggested as a typical rigid PUR foam characteristic [38]. All obtained rigid PUR foams are suitable for thermal insulation according to this indicator.

Table 2. Apparent density and closed-cell content of RO/PET series rigid PUR foams

Sample	Apparent density, kg/m^3	Closed-cell content, vol.%
RO/PET II = 110	39.1 ± 0.4	95.2 ± 0.2
RO/PET II = 120	38.5 ± 0.1	98.0 ± 0.4
RO/PET II = 130	44.3 ± 1.3	97.6 ± 0.3
RO/PET II = 150	39.1 ± 0.4	98.7 ± 0.2
RO/PET II = 180	41.7 ± 0.1	97.4 ± 0.4

3.3. Reactivity of Foam Formation

Reactivity of the polyol system is characterized by foaming parameters, such as cream time (the visible increase of foam volume), gel time (the transition from liquid to solid), and the tack-free time (when the outer surface of the foam is not sticky anymore). Gel time is the starting point of a stable network formation by intensive allophanate crosslinking as well as urethane and urea linkages [36]. Table 3 shows that all three foaming parameters increase with an increase in the isocyanate index. The absolute amount of foaming catalyst, PC CAT NP-10, was identical for all foams in the RO/PET series. Therefore, its part by weight to the total mass of foams decreased by increasing the isocyanate index, and that increased the cream time. The increasing tendency of gel time is due to the increased production of low molecular weight polymers, including the unreacted monomers, as the stoichiometric imbalance between the reacting groups is increased. Because of their low free energy, the low molecular weight species are typically exposed to the free surfaces, causing adhesiveness and prolonging tack-free time [36,39].

Table 3. Foaming parameters

Sample	Time, s		
	Cream	Gel	Tack-free
RO/PET II = 110	22	52	75
RO/PET II = 120	22	52	75
RO/PET II = 130	23	54	90
RO/PET II = 150	25	54	93
RO/PET II = 180	25	56	108

As mentioned earlier, the amount of foaming catalyst for reference foams was adjusted according to the reactivity of their polyol mixes. The series RO/TEA and RO/PET polyol systems were required to add less catalyst, as they showed higher reactivity. The higher reactivity was due to a tertiary amine group in the main polyol structure [32].

3.4. FTIR and DMA Results

It is expected that at a higher isocyanate index, the crosslinking density will increase. Two effects contribute to this. First, the functionality of PMDI is 2.7 and its molecular mass is relatively small (approx. 381 g/mol), so it will work as a crosslinking reagent by itself. Second, when an excess of isocyanate is added, allophanates, biurets, and isocyanurates can be formed via side reactions. That will add additional crosslink points in the PUR polymer matrix, which gives a decrease in M_c and an increase in elasticity. Additionally, the increase in T_g is expected for higher crosslinking [40].

FTIR analysis was carried out for RO/PET series to judge the amount of isocyanurate formation. An isocyanurate band appears at 1410 cm^{-1} , and it is shown in Figure 2.

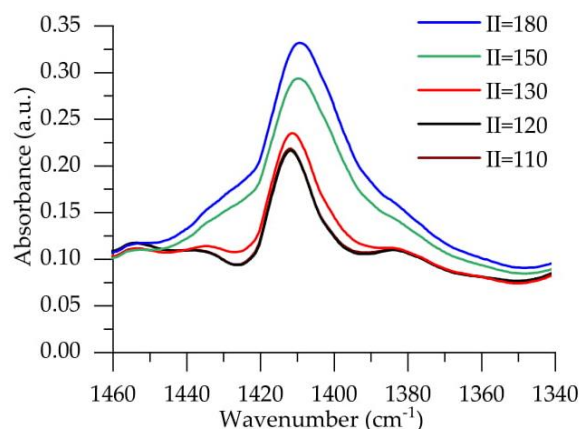


Figure 2. FTIR spectra for RO/PET rigid PUR foams, band at 1410 cm^{-1} .

The peak intensity for foams with $II = 110$ – 130 is very similar. It is clearly seen that for higher isocyanate indices, more isocyanurates are formed. As no trimerization agent is added for formulations with $II = 110$ – 130 , for those foams, crosslinking due to the formation of isocyanurate is closely similar. It agrees with the results of DMA. T_g was determined from damping factor curves, as shown in Figure 3. T_g of PUR foams for RO/PET $II = 120$ and $II = 130$ are similar: $121\text{ }^{\circ}\text{C}$ and $129\text{ }^{\circ}\text{C}$, respectively. A higher increase of T_g is observed by increasing the isocyanate index, and it reached $172\text{ }^{\circ}\text{C}$ for RO/PET $II = 180$.

FTIR and DMA results prove that crosslink density increases because more crosslinks are formed due to the formation of isocyanurates. Additionally, an increase in elasticity can be expected [36].

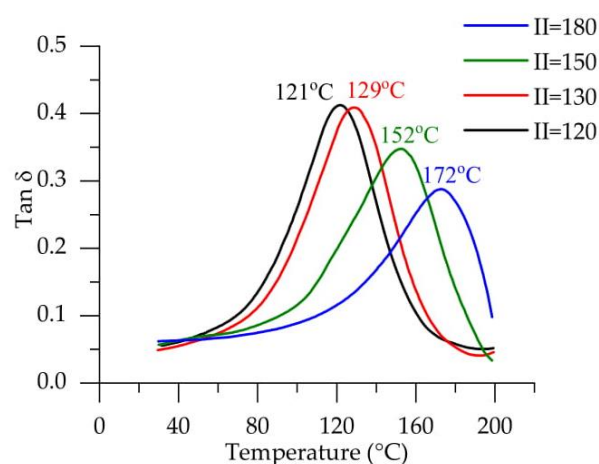


Figure 3. Damping factor curves of RO/PET series rigid PUR foams.

3.5. Compression Strength

Compression strength is strongly affected by apparent density. Therefore, compression strength and modulus values for all samples were normalized for an apparent density of 45 kg/m^3 using the equations of Hawkins et al [41]. Relating to the impact of isocyanate index, both decrease and increase in compression strength were reported. In the investigation of Javni et al., the soy polyol sample at the lowest index ($II = 110$) showed the highest compression strength because of the highest apparent density [42]. Additionally, Kim et al. showed a decrease of compression strength with an increase in isocyanate value (from 90 to 130) due to the decrease in apparent density [36].

In our case, the compression strength of RO/PET PUR foams slightly increases with an increase in isocyanate index (Figure 4a). It raises from 0.30 MPa for the sample with $II = 110$, to 0.37 MPa for the sample with $II = 180$. The same growing trend is observed for compression modulus, which raises from 6.35 MPa to 7.61 MPa (Figure 4b).

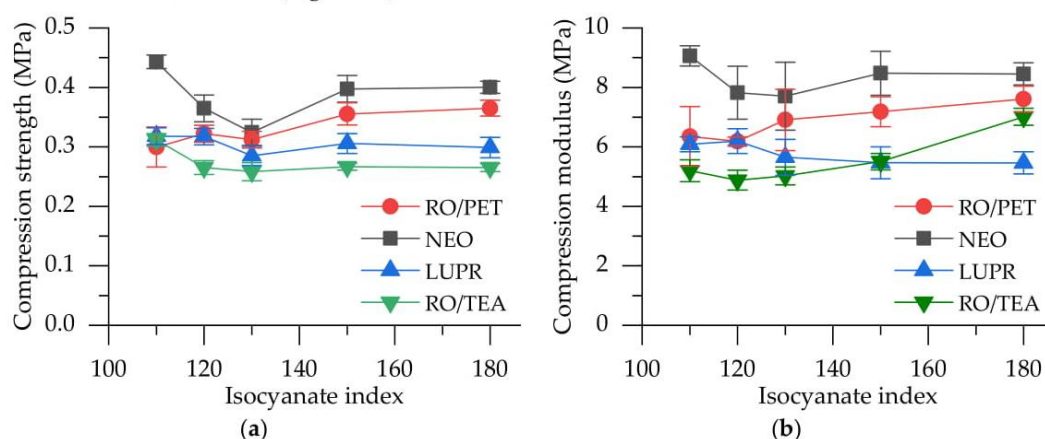


Figure 4. Physical-mechanical properties: (a) The compression strength of the RO/PET and reference rigid PUR foams; (b) Compression modulus of the RO/PET and reference rigid PUR foams.

Due to the enhancement of foam elasticity, anisotropic ratio (AR, strength ratio of parallel to perpendicular direction) for RO-PET 1/4 $II = 180$ is smaller ($AR = 1.79$) than for samples with lower isocyanate index ($AR = 1.85$ – 2.16). RO/PET shows higher compression strength than reference foams, LUPR and RO/TEA series, but slightly lower than the NEO series. NEO performance could be explained by the higher number of hard segments from recycled PET in its PUR foam matrix.

Reference foams show an unexpected decrease in compression strength and modulus with an increase in isocyanate index from 110 to 130. It could be related to the lack of isocyanate trimerization catalyst in their formulations, hence no addition crosslinks are formed and unreacted isocyanate remains in foams. Nevertheless, all samples are within commercially acceptable limits. According to Javni et al., typical industrial PUR rigid insulating foams have compression strength at 10% strain between 0.15 and 0.25 MPa [42].

3.6. Dimensional Stability and Water Absorption

The results of water absorption are presented in Figure 5. No impact of isocyanate index is observed for all series, with the exception of RO/TEA polyol based foam series, where a slight increase in water absorption for samples with $II = 130$, 150, and 180 is observed. PUR foams with base polyols containing aromatic structure (NEO and RO/PET series) show lower water absorption.

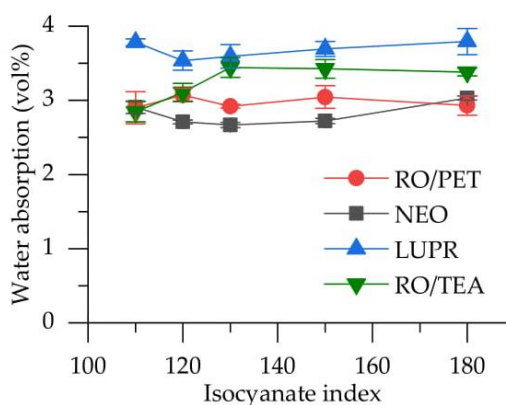


Figure 5. Water absorption after seven days of immersion

The increase of the isocyanate index improves dimensional stability due to the incorporation of the isocyanurate ring into the PUR foam matrix [43]. The results of dimensional stability are presented in Figure 6. Volume relative change after 28 days at 70°C, ambient R.H., decreases from 4.0% to 1.0% with increasing isocyanate index. At mode where R.H. = 97%, volume change for RO/PET series is below 15% and reaches 3.4% when II = 180.

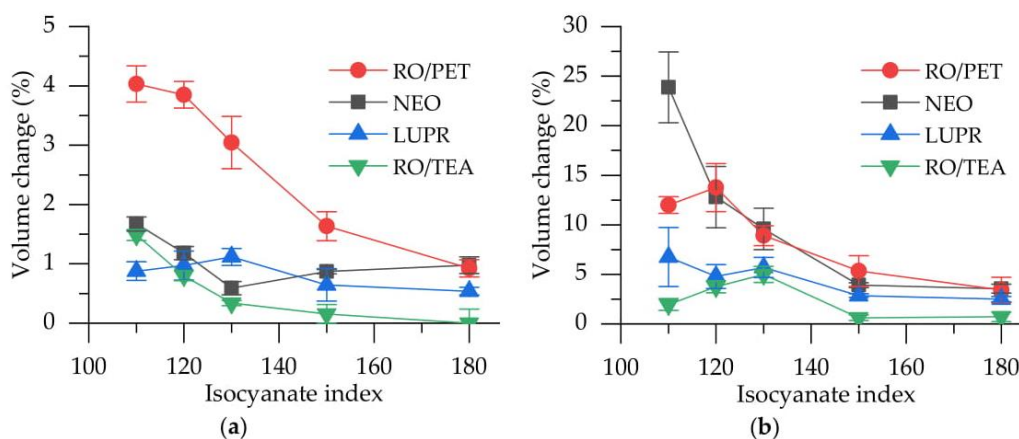


Figure 6. Dimensional stability—volume relative change at two modes: (a) 28 days at 70°C, ambient relative humidity (R.H.); (b) 28 days at 70°C, R.H. = 97%

Although RO/PET polyols show better compatibility with blowing agents [32], which could improve dimensional stability, it was not observed in the results of the present study. As the standard ISO 2796 gives various options for modes and test duration, it is quite difficult to compare our results with other investigations. For example, Kim et al. suggested that volume change at 80 °C and -30 °C less than 1% in one day is desired for sufficient strength [36]. All of our series foams at 70 °C in one day showed volume change less than 1%, except for RO/TEA II = 110 ($\Delta V = 1.7\%$). Overall, starting from II = 130 and up, the dimensional stability is considered to be within commercially acceptable bounds.

3.7. Thermal Conductivity

Initial thermal conductivity of rigid PUR foams with apparent density $42 \pm 3 \text{ kg/m}^3$ was measured, as well as thermal conductivity, after 24 weeks. The initial values are given in Figure 7a, where one can observe that foams from RO/PET polyol show as good thermal insulation property (average $\lambda = 20.7 \pm 0.7 \text{ mW/(m}\cdot\text{K)}$) as foams from commercially used NEO (average $\lambda = 21.2 \pm 0.7 \text{ mW/(m}\cdot\text{K)}$) and LUPR (average $\lambda = 21.9 \pm 0.2 \text{ mW/(m}\cdot\text{K)}$). Rigid PUR foams from RO/TEA polyol showed slightly worse results for thermal conductivity ($\lambda = 22.9 \pm 1.2 \text{ mW/(m}\cdot\text{K)}$).

Additionally, it can be observed that the isocyanate index does not affect the initial thermal conductivity.

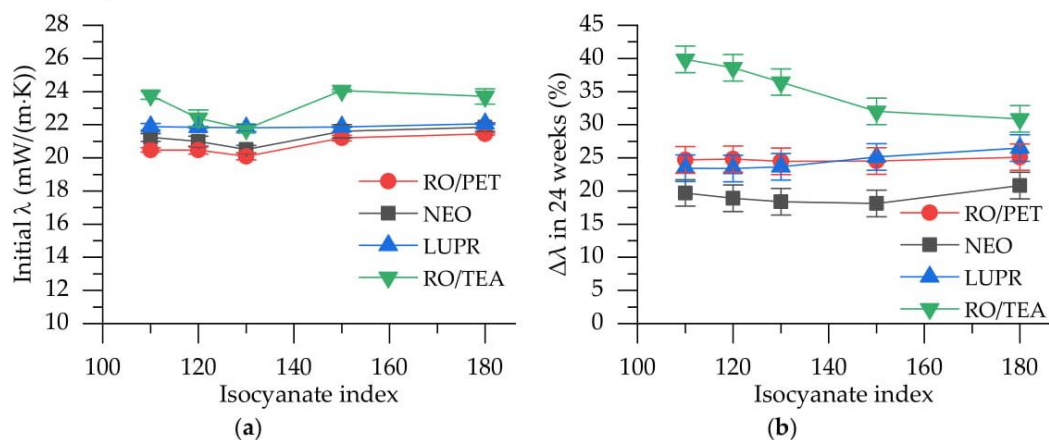


Figure 7. Results of thermal conductivity: (a) Initial thermal conductivity; (b) Thermal conductivity relative change in 24 weeks

To evaluate the retention of thermal conductivity in the long term, Figure 7b is given with results of thermal conductivity relative change in 24 weeks. The best retention of thermal conductivity was shown in NEO series PUR foams from PET-based aromatic polyester polyol. The same results were observed in previous investigations by our research group [21,32]. The retention of thermal conductivity depends on the blowing agent gas diffusion rate through rigid PUR foam material. This is related to the crosslink density of PUR polymer matrix, cohesion energy, and ability of macromolecular conformation of PUR polymer chains. NEO and RO/PET polyol structure have aromatic groups derived from PET polymer and additional carboxylic groups that allow the formation of hydrogen bonds between polymer chains. Both of these aspects contribute to a stronger and more neatly packed polymer matrix, which minimizes the outward flow of the carbon dioxide ($\lambda = 14.6 \text{ mW}/(\text{m}\cdot\text{K})$) and inward flow of air ($\lambda = 24 \text{ mW}/(\text{m}\cdot\text{K})$), thus enhancing long-term thermal conductivity retention [44]. Galakhova et al. reported that carbon dioxide leaves rigid PUR foams already after 2.5 months [45].

No impact of isocyanate index on the retention of thermal conductivity for rigid PUR foams series NEO, RO/PET, and LUPR is observed. Only for PUR foams based on RO/TEA polyol, does the increase of isocyanate index improve retention. RO/TEA polyol chemical structure introduces long dangling chains into the PUR polymer matrix, which causes a low packing degree of PUR macromolecules [46]. The excess of PMDI introduces aromatic groups and increases crosslink density. As mentioned above, a more neatly packed polymer matrix is formed and long-term thermal conductivity retention is improved.

4. Conclusions

Rigid PUR foams with isocyanate index 110–180 were obtained from polyols based on rapeseed oil and polyethylene terephthalate. Additionally, reference PUR foams were obtained from commercially available polyols: Lupranol 3300, Neopolyol 380, and rapeseed oil/triethanolamine polyol.

Closed-cell content of rapeseed oil/polyethylene terephthalate PUR foams was $\approx 97 \text{ vol.}\%$ and was not impacted by the isocyanate index. Additionally, no effect of the isocyanate index on water absorption was observed.

The values of foaming parameters increased with an increase in isocyanate index. The increasing tendency of gel time was due to the lower molecular weight polymers formed, which are typically exposed to the free surfaces, causing adhesiveness and prolonging tack-free time.

The increase of compression strength, compression modulus, and dimensional stability of RO/PET PUR foams with the increase of isocyanate index were caused by the higher ratio of crosslinking due to the formation of isocyanurate (evidenced by FTIR and DMA).

Overall, the optimum complex of the physical and mechanical properties of RO/PET PUR foams was achieved for formulations with isocyanate indices of 130–180. Therefore, it is possible to obtain commercially competitive rigid PUR foams with sustainable material content up to 13%.

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IV

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Polyols based on poly(ethylene terephthalate) and tall oil: synthesis and perspective in production of rigid polyurethane foams.

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Polyols Based on Poly(ethylene terephthalate) and Tall Oil: Perspectives for Synthesis and Production of Rigid Polyurethane Foams

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ABSTRACT: This study presents the synthesis of novel polyols made from tall oil (TO) and poly(ethylene terephthalate) (PET) with different TO/PET molar ratios. Rigid polyurethane foams based on these synthesized polyols were obtained and characterized to evaluate polyols' suitability for the development of light materials with insulating properties. The effect of TO/PET molar ratios on the physical, morphological and mechanical properties of the obtained foams, as well as their thermal insulation characteristics, were evaluated. Increasing amounts of PET in polyurethane foams resulted in higher compression strength and closed cell content, while water absorption was not affected. Results indicated that certain TO/PET polyols can be successfully used for preparing rigid polyurethane foams.

KEYWORDS: Rigid polyurethane foams, PET glycolysis, tall oil, renewable materials

1 INTRODUCTION

The production of polyols derived from natural sources and recycling materials is of great interest for the manufacturing of polyurethanes (PURs). Nowadays, global PUR production uses polyols and isocyanates based on hydrocarbons, whose availability remains uncertain in the near term, both for environmental and economic reasons [1, 2].

Tall oil (TO) and poly(ethylene terephthalate) (PET) scraps have great potential as raw materials for the production of polyols through chemical synthesis. The joint application of these natural and recycling materials may contribute to the reduction of the environmental impact.

Vegetable oils are very good feedstocks for synthesis of biobased materials because of their wide availability, low cost and large variety of potentially reactive groups in their structure [3, 4]. Specifically, the synthesis of polyols from different vegetable oils has attracted considerable attention since the late nineties. Many studies have been carried out about

the synthesis of biobased polyols from vegetable oils with applications in rigid PUR foams [5–13] and reinforced PUR composites [14–21]. One of the disadvantages of vegetable oils is that most of them are first generation biobased raw materials, so they are also used in food production. Therefore, polyol synthesis from TO, which is a second generation biobased raw material, is an excellent option [22]. However, only a few works about the utilization of TO for biobased PURs are readily available in the literature [23–26]. TO is a byproduct of the Kraft pulping process of pine wood. The crude oil, an oily dark liquid, is formed by the acidification of a black liquor soap skimming with sulfuric acid. Unlike vegetable oils consisting of triacylglycerols, TO contains higher amounts of unsaturated free fatty acids (36–48 wt%), mainly oleic acid (C18-1) and linoleic acid (C18-2), and resin acids or rosin (26–42 wt%) which are cyclic terpenes [27]. In this case, a TO-based polyol can be obtained by reaction of carboxyl groups present in fatty acids with triethanolamine (TEA) or diethanolamine via an esterification or amidization pathway [28]. Also, the esterification of TO with aromatic polyester polyols is found in the patent literature. In addition, these polyols were found to be compatible with trichlorofluoromethane blowing agent [29].

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PET is one of the most well-known thermoplastic materials because of its use in textile fibers and soft-drink bottles, which are its main applications. However, due to its increasing consumption and non-biodegradability, the higher amounts of waste PET produced result in disposal problems. Consequently, since the late 80s there has been a great interest in recycling this material through eco-friendly technologies. Chemical recycling offers the possibility to recover useful monomers or oligomers for further synthesis of new materials. In this sense, different chemical recycling methods, such as aminolysis, glycolysis, hydrolysis and alcoholysis, have been developed. Depolymerization of PET by glycolysis is carried out using mainly metal acetate as a catalyst and different glycols like ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol, 1,4-butanediol, propylene glycol, among others. Bis(2-hydroxyethylene) terephthalamide is the product formed via PET glycolysis using the excess EG as reactant [30–33]. This monomer can be used for rigid PUR formulation to improve the mechanical properties of the foams. However, PET glycolized products often are incompatible with some blowing agents commonly used in PURs.

Only a few reported studies have dealt with the polyols from both recycled PET and natural vegetable oils. Badri *et al.* [34] investigated PET waste glycolysis with EG prior to blending with palm oil-based polyol. Beneš *et al.* [35] reported the chemical recycling of waste PET using castor oil as a reagent, where acyl-ester hydroxyl groups of castor oil ensure the depolymerization of PET. Cakić *et al.* [36] carried out PET glycolysis with poly(ethylene glycol) and produced saturated hydroxyl-functional polyester polyols with castor oil by transesterification process. More recently, Paberza *et al.* [37] proposed a synthesis method for preparation of polyols from rapeseed oil and PET in two steps: rapeseed oil transesterification with TEA and PET glycolysis with DEG. The resultant polyols showed excellent compatibility with blowing agents and high reactivity. They were successfully used for preparing PUR foams with high bio/recycled content and good thermal insulation properties.

The main purpose of this study is the obtainment of polyester polyols from TO and PET, and the evaluation of the possibility to use these polyols in rigid PUR foam production. At first, TO/TEA polyol was synthesized from TO and TEA by esterification, and then polyol synthesis from TO/TEA polyol, PET and DEG were carried out at different TO/PET molar ratios. The resultant polyols were characterized and used for preparation of rigid PUR foams. Afterwards, the properties of these foams were investigated and the impact of TO/PET molar ratios on the foams' characteristics was evaluated.

2 EXPERIMENTAL

2.1 Materials

TO/TEA polyol (OH value = 344 mg KOH/g; acid value = 5.06 mg KOH/g) was synthesized from distilled TO (resin acids = 20 wt%; from Forchem) by the esterification with TEA (min. 99.5%; from BASF). PET flakes (bulk density 0.25–0.4 g/cm³; intrinsic viscosity 0.78–0.8 dl/g) from recycled bottles were supplied from PET Baltija. DEG (99%) from Sigma Aldrich was used as PET depolymerization agent. Zinc acetate dehydrate (≥98%) from BASF was employed as the transesterification catalyst in polyol synthesis.

Rigid PUR foams were prepared from synthesized TO/PET polyols, high functional polyether polyol based on sorbitol Lupranol 3422 (OH = 490 mg KOH/g) from BASF, reactive delayed action time amine-based foaming catalyst CAT NP-10 from Performance Chemicals Handels, surfactant NIAX Silicone L6915 from Momentive Performance Materials, flame retardant trichloropropylphosphate from Lanxess and physical blowing agent Solkane 365/227 (pentafluorobutane/heptafluoropropane = 87/13) (Solkane) from Solvay. The isocyanate used was polymeric diphenylmethane diisocyanate (PMDI) (NCO group content = 31.5%) purchased from BASF. All reagents were used as received without purification.

2.2 Synthesis of TO/PET Polyols

At first, TO/TEA polyol was synthesized from distilled TO by the esterification with TEA (molar ratio TO/TEA = 1/1.33) in pilot-scale (50 L) stainless steel chemical reactor with stirrer and heating. The synthesis was conducted at 175 °C and duration was controlled from the change in the acid number of polyol (ISO 660:2009). A more detailed description of TO/TEA polyol synthesis is described in our previous work by Cabulis *et al.* [23]. The reaction scheme is shown in Figure 1.

The TO/TEA polyol was further used to synthesize TO/PET polyols. These syntheses were carried out in a three-necked flask provided with a mechanical stirrer, a controlled argon atmosphere and a condenser. Syntheses were realized as follows: TO/TEA polyol was poured into the reaction flask and heated to 210 °C. The agitation was set at 300 rpm and zinc acetate (0.5 wt% of PET) was added. DEG was preheated at 70 °C and poured into the reaction mixture. Once the temperature was stabilized at 210 °C, PET flakes were added in two steps with an interval of 30 min. When complete miscibility of PET into the mixture was observed, the temperature of mixture was increased

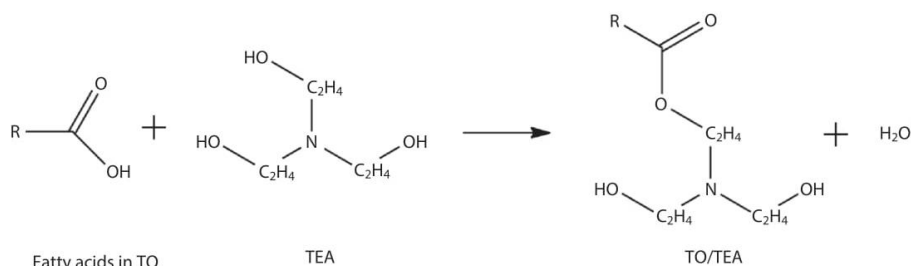


Figure 1 TO esterification with TEA; R – the fatty acid group [23, 24, 38].

Table 1 TO, PET and DEG molar ratios in synthesis of polyols.

Name of polyol	TO, mol	PET, mol	DEG, mol
TO/PET 1/1	1	1	2
TO/PET 1/2	1	2	4
TO/PET 1/4	1	4	8
TO/PET 1/6	1	6	12
TO/PET 1/8	1	8	16

and then held at 235 °C for 4 hours. After that, the flask was allowed to cool down.

Different TO/PET polyols were prepared using different TO/PET molar ratios, namely 1/1, 1/2, 1/4, 1/6 and 1/8, whose TO/PET/DEG molar ratios are shown in Table 1.

The reaction scheme of PET glycolysis with DEG is presented in Figure 2. This reaction consists of the transesterification of PET and the destruction of its polymer chain, resulting in the decrease of PET molecular weight [39].

In TO/PET polyol synthesis, transesterification between TO/TEA polyol and glycolyzed PET may take place. Two possible reactions of that are shown in Figure 3.

2.3 Characterization of Polyols

Hydroxyl (OH) value of the prepared TO/PET polyols was experimentally determined by acetylation method according to DIN 53240, and acid value (AV) was determined by the requirements of DIN 5340. The moisture content in polyol was tested using the Karl Fischer method according to DIN 51777.

Viscosity of polyols was determined according to DIN 53015 standard at 20 °C using a Falling Ball Viscometer KF 100 from Rheo Tec Messtechnik GmbH.

The FTIR-ATR spectra were made on a Thermo Fisher Nicolet iS50 FT-IR Spectrometer. The FTIR-ATR spectra of polyols were collected within the wave

number ranging from 4000 cm⁻¹ to 600 cm⁻¹ at a resolution of 4 cm⁻¹.

Polyol compatibility with blowing agents was tested in plastic centrifuge tubes where 10 g of polyol was weighed and then 20% of blowing agent Solkane was added. Then the blends were centrifuged for 15 minutes at 55 rpm and kept at ambient conditions for 8 weeks for regular visual inspection.

The TO/PET polyols were also characterized by resulting content of renewable and recycle, that was calculated as percentage by weight of TO and PET in polyol, respectively.

2.4 Preparation of Rigid PUR Foams

The foams were prepared at laboratory scale from a two-component (polyol and isocyanate) system by free-rising method in an open mold according to the formulations presented in Table 2.

The amount of necessary PMDI was calculated according to the isocyanate index 130 (the ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100). Rigid PUR foams were named the same as the TO/PET polyol in their formulation.

When PMDI was added to the polyol component, resulting mixture was stirred vigorously at 2000 rpm for 10 s and then instantaneously poured into an open mold of dimensions 30 × 30 × 10 cm. The process of rigid PUR foam formation was monitored by measuring foaming parameters: the duration of cream time, gel time, and tack-free time. All foam samples were allowed to cure at ambient conditions for 24 h prior to any further tests.

2.5 Characterization of Rigid PUR Foams

The closed cell content and apparent bulk density were tested according to the standards ISO 4590 and ISO 845, respectively. Compressive strength and modulus of elasticity were measured by the requirements of EN

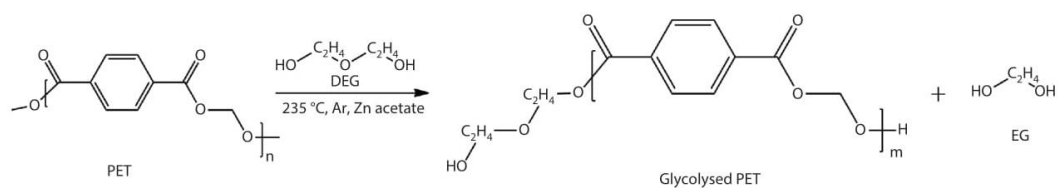


Figure 2 PET glycolysis with DEG [39, 44, 45].

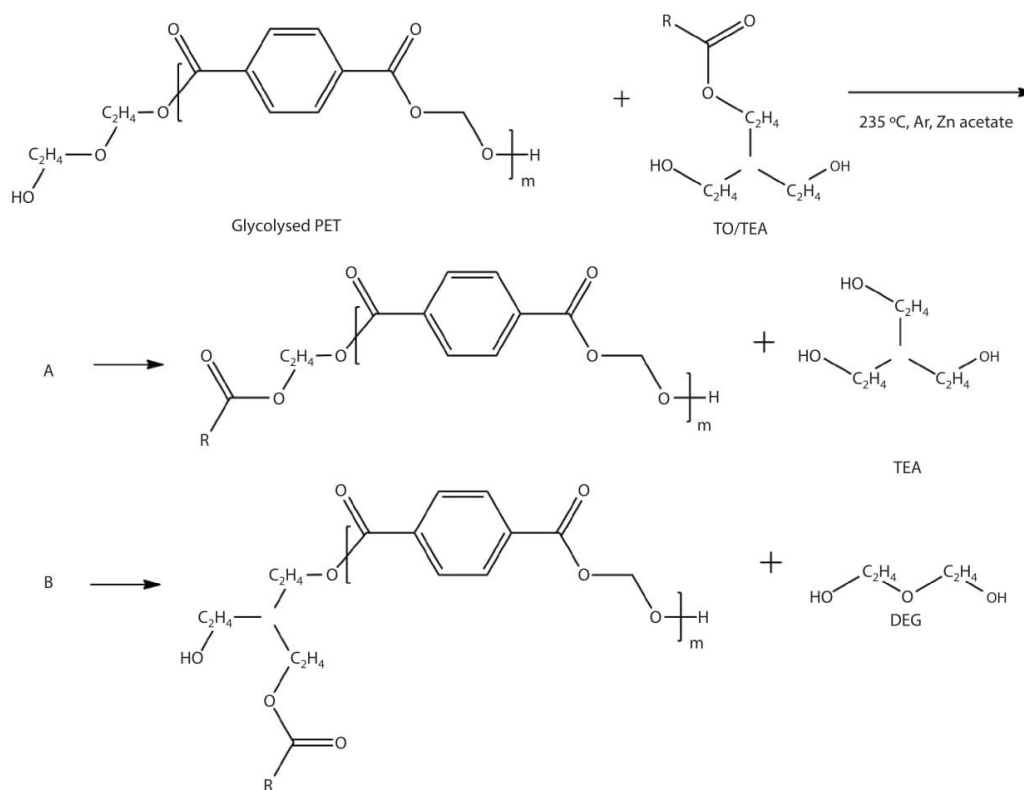


Figure 3 Possible reactions (A and B) between glycolysed PET and TO/TEA polyol.

Table 2 Rigid PUR foam formulation.

Component	Application	Amount, pbw*
TO/PET polyol	Synthesized polyol	75
Lupranol 3422	High functional polyol	25
Trichlorpropylphosphate	Flame retardant	20
NIAX Silicone L6915	Surfactant	2
Potassium acetate	Catalyst	1.2
PC CAT NP-10	Catalyst	1.2
Solkane	Blowing agent	25
PMDI		Isocyanate index 130

*parts by weight

ISO 844 using a Zwick/Roell Z100 testing machine for cylinder specimens with diameter and height of ~20 mm. The thermal conductivity of the rigid PUR foams was measured periodically for 10 weeks after foam preparation. These tests were carried out based on ISO 8301 standard, using a Linseis Heat Flow Meter 200. Temperature range was +10...+30 °C and dimensions of samples were 20 × 20 × 3 cm. Water absorption was tested by immersing PUR samples in water for 7 days, according to ISO 2896 standard.

3 RESULTS AND DISCUSSION

3.1 Polyol Characterization

3.1.1 Chemical Structure of Polyols

The chemical structure of the synthesized TO/PET polyols was studied by FTIR measurements. Similarity of the chemical structure of TO/PET polyols was expected because reagents in synthesis are the same but molar ratio differs. The FTIR spectra are shown in Figure 4.

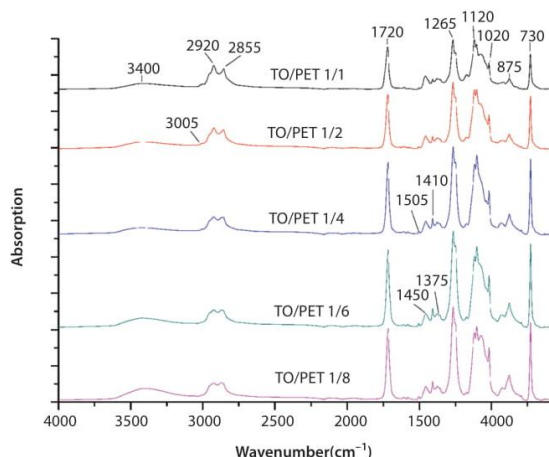


Figure 4 FTIR spectra of polyols.

The broad band at 3400 cm⁻¹ is due to the stretching vibration of -OH groups. Absorption intensity of this band correlates with OH values of polyols (Table 3). In the range of 3000–2850 cm⁻¹, two bands can be observed due to the symmetric and asymmetric stretching of -CH₂- groups mainly from TO fatty acids. Small peak at 3005 cm⁻¹ corresponds to cis-double bond stretching from oleic and linoleic acid in TO, therefore this peak increases for polyols with higher TO content. All FTIR spectra of polyols present a sharp band at 1720 cm⁻¹, which corresponds to the carbonyl bonds in ester group. For polyols with higher PET content the intensity of this peak, and also that of the ester bond peaks in the 1120–1020 cm⁻¹ region, are higher because additional ester and ether bonds are introduced with depolymerized PET. The stretching vibration bands of aromatic ArCO-O ester group occur at 1265 and 1120 cm⁻¹. Aromatic structure introduced with PET is shown in FTIR spectra by stretching vibrations of aromatic C-H at 875 and 730 cm⁻¹, and small absorption bands of aromatic -C=C- stretching vibrations at 1505 and 1410 cm⁻¹. Small peak at 892 cm⁻¹ (overlapped with peak at 875 cm⁻¹) corresponds to the -OC₂H₄ moieties of DEG backbone, and small peak at 920 cm⁻¹ is due to the vibrations of C-O in DEG. These two peaks form the basis of the DEG detection according to the investigation of Ahmed *et al.* [40]. A peak around 1450 cm⁻¹ indicates the presence of methylene groups, while an additional peak at about 1375 cm⁻¹ is caused by a methyl group.

3.1.2 Chemical and Physical Characteristics of Polyols

Synthesized TO/PET polyols were homogenous, transparent, yellowish brown liquids. General characteristics such as OH value, AV, water content and viscosity are shown in Table 3.

With increasing TO/PET molar ratio, OH value of polyols increases from 193 to 384 mg KOH/g due to excess of DEG. The AV for polyols with TO/PET molar ratio from 1/4 to 1/8 is ~1 mg KOH/g higher

Table 3 Chemical and physical characteristics of TO/PET polyols.

Polyol	OH value, mg KOH/g	AV, mg KOH/g	Water content, %	Viscosity @ 20 °C, mPa·s	Compatibility with Solkane (+/-)	Crystallization time, months
TO/PET 1/1	193	6.2	0.23	1170	+	not observed
TO/PET 1/2	246	5.5	0.11	1500	+	not observed
TO/PET 1/4	306	3.6	0.08	1850	+	not observed
TO/PET 1/6	292	3.4	0.07	2300	+	2
TO/PET 1/8	384	3.7	0.22	2750	+	2

compared with similar synthesized polyols from rapeseed oil and PET [37] because tall oil contains 20 wt% resin acids which increase the AV of resulting polyols. The AV for TO/PET polyols with higher TO content is even higher—5.5 and 6.2 mg KOH/g. Acid value higher than 5 mg KOH/g can make polyol systems with an amine type catalyst for PUR more unstable because acid groups can react with amine groups of the catalyst. Viscosity of polyols increases two times (from 1170 to 2750 mPa·s) by increasing TO/PET molar ratio from 1/1 to 1/8. For all polyols the viscosity as well as water content is in an acceptable range for obtaining PUR foam.

An investigation by Paberza *et al.* showed that commercially available aromatic polyester polyol from PET was incompatible with Solkane [37]. Good compatibility between polyol and physical blowing agent is important because homogeneity of polyol system affects characteristics of rigid PUR foams. Polyol systems for commercial appliance have to be homogenous and without phase separation during storage [41]. Therefore all synthesized polyols were visually observed. After 2 months, crystallization of TO/PET 1/6 and TO/PET 1/8 began. All other polyols did not crystallize during the observation time (4 months). In addition, all polyols were compatible with the blowing agent Solkane—the mixtures after the centrifugation were homogenous and remained stable during visual observation time (1 month).

3.1.3 Content of Renewable and Recyclate

The TO/PET polyols were synthesized from renewable resource, tall oil, and recycled part – PET. Resulting content of renewable and recyclate is presented in Figure 5.

Figure 5 shows that by increasing TO/PET molar ratio, the renewable content in polyols decreases from 34 wt% to 8 wt% but content of recyclate material increases from 20 to 40 wt%. Total renewable and recyclate amount in synthesized TO/PET polyols reached ~50 wt%.

3.2 TO/PET Polyols as Raw Material for Rigid PUR Foam Preparation

3.2.1 Rigid PUR Foam Characteristics

Perspectives for the use of synthesized TO/PET polyols in rigid PUR foam were evaluated by obtaining PUR foams and characterizing them in terms of thermal conductivity, water absorption and compression strength.

The process of rigid PUR foam formation was monitored by measuring foaming parameters, which are presented in Table 4. Results show a tendency for gel and tack-free time to decrease by using TO/PET polyol with higher PET content.

Rigid PUR foams from TO/PET 1/1 and TO/PET 2/2 polyols showed significant shrinkage, therefore were not used for further tests. Shrinkage of these rigid PUR foams could be explained by the low OH value of polyols. Formulations based on these polyols should be adjusted to get more stable rigid PUR foams. Rigid PUR foams from TO/PET 1/4, 1/6 and 1/8 polyols did not show shrinkage and were used for further tests. Table 3 also shows other foam characteristics such as apparent bulk density, closed cell content and water absorption. Density of obtained rigid PUR

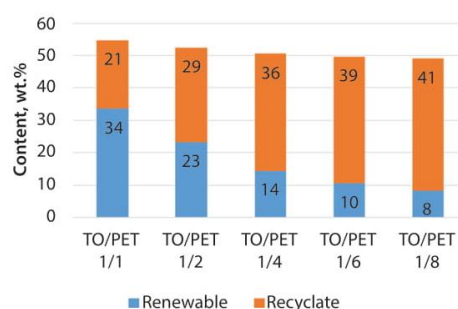


Figure 5 Content of renewable and recyclate in TO/PET polyols.

Table 4 Foaming parameters, density, closed cell content and water absorption of rigid PUR foams.

	TO/PET 1/1	TO/PET 1/2	TO/PET 1/4	TO/PET 1/6	TO/PET 1/8
Start time, s	20	20	17	20	22
Gel time, s	65	60	50	50	40
Tack-free time, s	90	80	65	70	57
Apparent bulk density, kg/m ³	48	43	44	42	41
Closed cell content, vol%	–	–	92	96	97
Water absorption in 7 days, vol. %	–	–	12.36	12.32	12.39

foams was in the range of 41 to 48 kg/m³, which is an appropriate value to use these foams as thermal insulation material. Closed cell content were in the range of 92 to 97 vol% and water absorption in 7 days was ~2.4 vol%.

3.2.2 Thermal Conductivity

Rigid PUR foams showed similar initial thermal conductivity (18.3–19.3 W/m·K) (Figure 6).

Thermal conductivity increases till 22.2–23.1 W/m·K in 10 weeks because of the air diffusion into foam. The lowest thermal conductivity during these 10 weeks of testing is shown by the rigid PUR foams obtained from TO/PET 1/6 polyol. Overall, thermal conductivity measurements indicate that these foams could be used as an insulating material in various construction applications.

3.2.3 Compressive Strength

As the mechanical properties of rigid PUR foams are significantly related to their apparent density, all compressive strength results were normalized with respect to a density of 45 kg/m³ using the equation of Hawkins *et al.* [42] (Eq. 1):

$$\sigma_{\text{norm}} = \sigma_{\text{exp}} \left(\frac{45}{\rho} \right)^{2.1} \quad (1)$$

where σ_{norm} is the normalized strength (MPa), σ_{exp} is the raw strength (MPa) determined from the stress-strain curve, and ρ is the apparent bulk density of sample (kg/m³). Results of normalized elastic modulus and compressive strength of obtained rigid PUR foams are shown in Figure 7 and Figure 8, respectively.

As seen from these figures, elastic modulus and compressive strength of foams increase by using polyols with higher TO/PET molar ratio in rigid PUR foam formulation. The highest elastic modulus (~9 MPa) and compressive strength (0.37 MPa) are shown by the

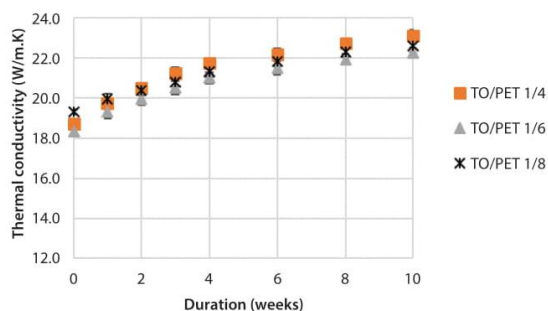


Figure 6 Thermal conductivity of rigid PUR foams.

rigid PUR foams prepared from TO/PET 1/8 polyol. This is consistent with the investigations of Cabulis *et al.* and Van Haveren *et al.* [23, 43] in which the introduction of the aromatic structure into the PUR polymer matrix improves mechanical properties of foams. Overall, the compressive strength of TO/PET rigid PUR foams meets the requirements of the construction industry for thermal insulation materials.

4 CONCLUSIONS

The combination of TO/TEA polyol and PET, which is a novel approach in the existing literature, was used in polyol synthesis. The TO/PET polyols were synthesized by using different TO/PET molar ratios (from 1/1 to 1/8) while PET/DEG molar ratio remains the same (1/2 in all synthesis). PET increases the OH value whereas TO grants polyols with good compatibility with hydrofluorocarbon-type blowing agent as well as increases their stability against crystallization and lowers viscosity. Moreover, total renewable and recycle content of ~50% in polyols was reached.

Synthesized TO/PET polyols were used as the main polyol component to obtain rigid PUR foams.

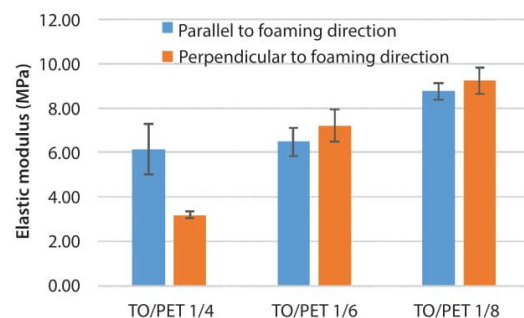


Figure 7 Elastic modulus of rigid PUR foams.

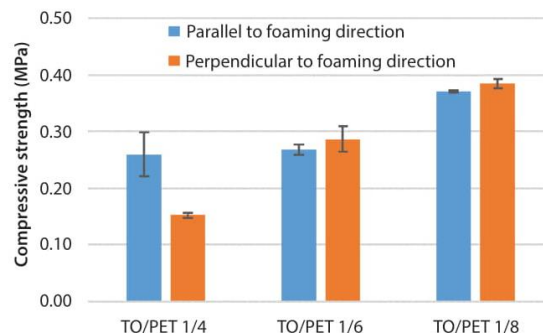


Figure 8 Compressive strength of rigid PUR foams.

The effects of TO/PET molar ratio on the properties of resulting foams were investigated. The shrinkage of foams made from polyols TO/PET 1/1 and TO/PET 1/2 suggests that improved rigid PUR foam formulations have to be developed to get more dimensionally stable materials. On the other hand, TO/PET polyols with TO/PET molar ratios of 1/4 to 1/8 were found as suitable polyols for preparing rigid PUR foams. The lowest thermal conductivity was shown by rigid PUR foams made from TO/PET 1/6 polyol. Aromatic structure of PET improved the foams' mechanical properties and slightly increased closed cell content; however water absorption was not affected. Overall, results indicated that certain TO/PET polyols can be successfully used for preparing rigid PUR foams with characteristics suitable for thermal insulation materials.

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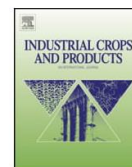
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Polyurethane rigid foams obtained from polyols containing bio-based and recycled components and functional additives



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ABSTRACT

We report the preparation of polyurethane (PU) rigid foams from bio-based and recycled components. Rapeseed oil (RO) and recycled polyethylene terephthalate (rPET) were used to synthesize PU polyols. Fifty-five percent of the content of the proposed PU polyols originates from renewable or recycled material. Glycerol (GL) and adipic acid (ADA) were added to improve the final properties of the foams. The GL/ADA content was varied from 1 to 6 wt.%. The hydroxyl value, acid value, water content, and viscosity of the synthesized polyols were measured. Using compression tests on PU rigid foams, we found that for some GL/ADA contents the rigidity increased almost 3-fold; whereas the strength increased almost 2-fold. The water absorption of the foams was below 3 wt.%. Optical microscopy of foam cross-sections revealed a mean cell sizes of 330 μm for PU with GL/ADA, and 420 μm for PU supplemented with GL/ADA and RO. FTIR measurements revealed enhanced hydrogen bond networking due to the incorporation of GL/ADA fragments and RO long aliphatic blocks in the PU chain backbone.

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1. Introduction

Polyurethane (PU) is a high consumption commodity polymer. The PU polymer family includes elastomers, thermoplastics, thermosets, and one- or two-component curable compositions. PUs have a broad range of applications, including in solid rubbers (Prisacariu, 2011), rigid and soft foams (Ashida, 2006), fibers and coatings (Szycher, 2012), and adhesives and sealants (Sonnenschein, 2014). PUs are characterized by a urethane group ($-\text{NH}-(\text{C}=\text{O})-\text{O}-$) in their backbone but can also contain aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, and isocyanurate groups (Szycher, 2012).

Initially, the crude oil is utilized to produce the raw ingredients for PU synthesis (Ionescu, 2005; Sonnenschein, 2014). Recently, natural raw components for PU fabrications have attracted considerable interest because of green chemistry and environmental concerns (Babb, 2012; Bobade et al., 2016). Vegetable oils can be chosen as bio-based and renewable feedstock to produce

polyol components for manufacturing PU materials (Li et al., 2015; Petrovic, 2008). The hydroxylated derivatives of the soybean (Orgilés-Calpena et al., 2014), coconut (Chethana et al., 2014), rapeseed (Kurańska and Prociak, 2016), sunflower (Omriani et al., 2016), palm (Pillai et al., 2016a), and castor (Kurańska et al., 2017) oils can be used for the synthesis of PU materials. For example, rapeseed oil (RO) is an abundant and inexpensive renewable natural compound (Islam et al., 2014; Meier et al., 2007). RO does not contain hydroxyl groups and cannot react with the isocyanate components, but can be easily chemically converted to a polyol. The main chemical modification routes for RO are ozonolysis (De Souza et al., 2012), epoxidation (Zhang et al., 2014), hydroformylation (Petrović et al., 2012), esterification (Valero and Gonzalez, 2012), and amidization (Kirpluks et al., 2013) reactions. All the functionalization methods mentioned above involve the formation of the polyol suitable for PU foam preparation (Lligadas et al., 2010; Pfister et al., 2011). The molecular weight (MW) and hydroxyl groups (OH value) present in the final polyol product depend on the applied modification method. Generally, the MW and OH values are in the range of 500–4000 g/mol and 50–300 mg KOH/g, correspondingly. Kurańska and Prociak (2016) and Kurańska et al. (2015, 2017) report that RO can be utilized as an excellent starting material to synthesize oligomeric polyols for the fabrication of flexible and PU rigid foams.

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Generally, butanediol (Ren et al., 2016), ϵ -caprolactone (Hou et al., 2016), and glycerol (Lee and Lee, 2016) are also proposed as chain extenders to modify the functionality and molecular structure of the polyol and network structure of PU materials.

The next trend for the production of PU, which is mostly driven by ecological sustainability concerns, relates to the utilization of recycled polymer materials (Kopczyńska et al., 2016; Sinha et al., 2010). Much study has been aimed at the recycling of linear polyesters, such as polyethylene terephthalate (PET) waste (Duldner et al., 2016; Patel et al., 2005). PET is the commodity plastic widely used to produce various consumer products (e.g., bottles, films, and fiber materials). PET is conventionally produced by the polycondensation reaction of terephthalic acid and ethylene glycol (Thomas and Visakh, 2011). Two principal strategies have been applied to recycle the PET waste—mechanical and chemical routes (Dutt and Soni, 2013).

The mechanical recycling of post-consumer PET waste is performed by the melt extrusion and reactive extrusion processing of the recycled polymer into bottles, packaging films, and fibers (Welle, 2011). The chemical recycling of PET is the depolymerization process to the monomer and oligomer substances, which is achieved by the thermal treatment of the plastic flakes in the solution (Karayannidis and Achilias, 2007). A large variety of solvents (organic solvents, glycols, ionic liquids, supercritical liquids, etc.), chemicals (alcohols, carbonic acids, anhydrides, etc.), and catalysts (metal–organic compounds, phase transfer compounds, hydrotalcites, metal oxides, etc.) are successfully utilized for that purpose (Geyer et al., 2016; Karayannidis and Achilias, 2007; Khoonkari et al., 2015; Sinha et al., 2010). The main reported chemical reactions to depolymerize the PET are glycolysis, methanolysis, hydrolysis, and aminolysis (Sinha et al., 2010). It is also reported that the depolymerization process of PET can be rigorously intensified with the assistance of ultrasonic and microwave treatment (Zeltins et al., 2016). Miscellaneous PET depolymerization products have been developed, including unsaturated polyester resins, alkyl resins, and polyols for polyurethane foams and coatings (Güçlü and Orbay, 2009; Patel et al., 2005; Viksne et al., 2000; Vitkauskienė et al., 2011a).

Depolymerization products of PET can be successfully utilized in the production of aromatic polyester polyols, which may be used for manufacturing PU foams (Kirpluks et al., 2016). Kirpluks et al. (2016) reported that the presence of aromatic blocks in the backbone structure of the polyol could enhance the final mechanical and thermal properties of PU foams. Unfortunately, the aromatic polyester polyols generated by the PET recycling process have limited compatibility with physical foaming agents because of the presence of hydrofluorocarbons and a tendency to crystallize. It has been proposed that the compatibility of such aromatic polyester polyols could be improved by the addition of ϵ -caprolactone, butanediol, polyglycols, glycerol, and adipic acid additives, which modify the branching and functionality of the molecular backbone of the aromatic polyester polyols (Kathalewar et al., 2013; Vitkauskienė et al., 2011b). The positive effects of castor and palm oils on the structure of the aromatic polyester polyols have been reported (Cakić et al., 2015; Pillai et al., 2016b). Thus, the final thermal and physical–mechanical properties of the PU materials can be improved (Sonnenschein, 2014).

Here we report new formulations of aromatic polyester polyols, which were synthesized from building blocks of RO and depolymerized PET oligomer, and their use in the manufacturing of rigid PU foams for thermal insulation applications. The synthesis of PU bio-based polyols was carried out in three steps: (1) the transesterification of RO with triethanolamine (TEA); (2) the industrial PET waste depolymerization by the transesterification reaction with diethylene glycol (DEG) in the presence of various concentrations of functional additives glycerol (GL) and adipic acid (ADA); and (3)

synthesis of the final PU polyol by the transesterification of the above-mentioned intermediary components. On average, the polyols blends that were processed into the PU rigid insulation foams consisted of 55% renewable and recycled components. The structure and mechanical properties of the processed PU rigid foams were investigated.

2. Material and methods

2.1. Raw materials

All raw components were used without any additional treatments. PET flakes of clear grade were obtained from PET Baltija, Latvia. RO (specifications: iodine value (IV)=117 I_2 mg/100 g sample; acid value=2.1 mg KOH/g; saponification value=192 mg KOH/g sample) was supplied by Iecavnieks & Co., Latvia. RO consists of unsaturated fatty acids, including oleic (56%), linoleic (26%), and linolenic acids (10%), as well as saturated fatty acids [palmitic (4%) and stearic acids (2%), and other fatty acids (2%)] (Kirpluks et al., 2013). Triethanolamine (TEA) (99.5%) was from BASF, Germany, and zinc acetate dehydrate (ZnAc) ($\geq 98\%$) and diethylene glycol (DEG) (99%) from Sigma Aldrich, Germany, and were used without any further purifications for the synthesis of PU polyols. Polyether polyols Lupranol 3422 (BASF, Germany; OH value=490 mg KOH/g), polymeric diphenylmethane diisocyanate IsoPMDI 92140 (pMDI) (BASF, Germany; NCO group content=31.5%), foaming agent Solkane 365/227 (Solvay, Belgium; Pentafluorobutane/Heptafluoropropane 87/13), and other reagents, such as the catalyst dimethylaminopropylidipropylamine PC CAT NP-10 (Performance Chemicals Handels, Germany), silicone surfactant NIAx Silicone L6915 (Mömentive Performance Materials, Germany), and flame retardant trichloropropylphosphate (Lanxess, Germany) were used without further purification for preparation of PU rigid foams.

2.2. Polyol synthesis

These synthesis reactions were carried out in a three-neck 1.0 L reaction flask equipped with a mechanical stirrer, a thermometer, a condenser, and an argon inlet. The aromatic polyester polyols were synthesized from PET. The glycolysis reaction of PET waste was performed by slowly heating the PET flakes (1 M) with DEG (2 M) at 190 °C in the presence of ZnAc catalyst (Vitkauskienė et al., 2011a); the blend was heated to 240–250 °C for 3 h; then, GL/ADA functional additives were introduced into the reaction blend.

The vegetable oil based polyol was synthesized by the transesterification reaction of RO (1 M) with TEA (2.9 M) according to Fig. 1. A more detailed description of the of bio-based polyol (RO/TEA polyol) synthesis is given in our previous works (Fridrihsone et al., 2013; Kirpluks et al., 2016; Kurańska et al., 2015; Stirna et al., 2013). RO/TEA polyol contains saturated and unsaturated fatty acid chain blocks with alkyl chain lengths of C_{16} – C_{18} . The reaction was carried out at 170 °C for 1 h in the presence of a catalyst (0.15 wt.% of ZnAc). The end of the reaction was tested by the solubility of the obtained product in ethanol at the volume ratio (resin:ethanol=1:1). The obtained polyol was characterized with viscosity 160 mPa s, hydroxyl value 363 mg KOH/g, acid value 2.5 mg KOH/g, number-average molecular weight 323 g/mol, number-average functionality 2.3, and 0.12% water content. These polyols are suitable for PU rigid foam production (Kurańska et al., 2015; Stirna et al., 2006).

The obtained aromatic polyester GL/ADA polyols were further transesterified with bio-based RO/TEA polyol by the weight ratio 1:1 at 180 °C for 1 h. The final polyol formulations contained 14 different combinations of GL/ADA and GL/ADA-RO concentration

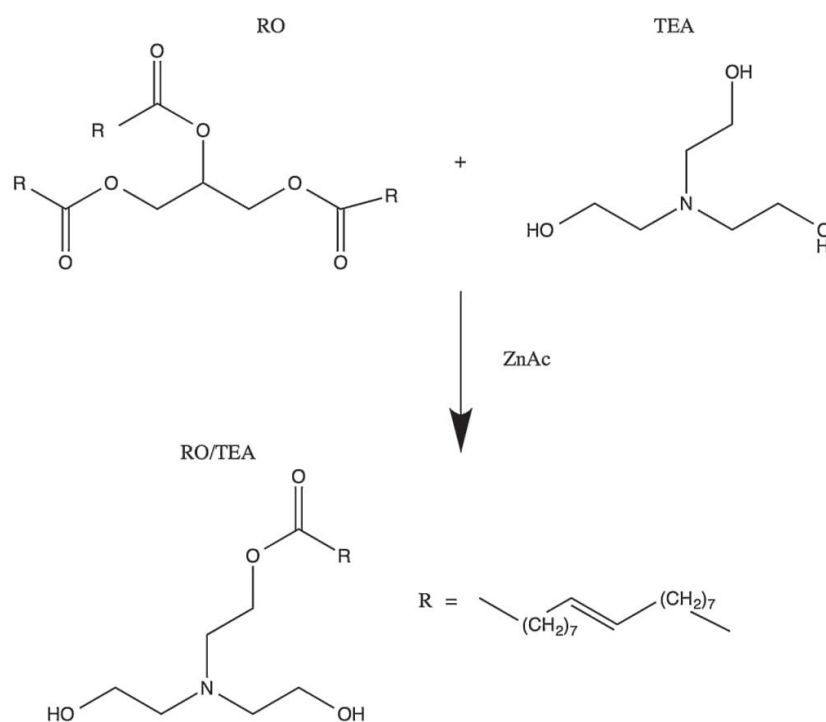


Fig. 1. Synthesis of RO/TEA polyol.

Table 1

The compositions of synthesized polyols from rPET, RO and additives.

Sample	Recycled component		Functional additives				Biobased component		Renewable and recycled content in obtained polyol	
	PET, mol	DEG, mol	GL		ADA		RO, mol	TEA, mol	Renewable content (%)	Recyclate content (%)
			wt.%	mol	wt.%	mol				
GL/ADA 0/1	1	2	0	0.00	1	0.03	–	–	–	46.9
GL/ADA 1/1	1	2	1	0.04	1	0.03	–	–	–	46.5
GL/ADA 1/3	1	2	1	0.04	3	0.08	–	–	–	45.6
GL/ADA 1/6	1	2	1	0.13	6	0.08	–	–	–	44.7
GL/ADA 3/3	1	2	3	0.04	3	0.17	–	–	–	44.3
GL/ADA 3/6	1	2	3	0.13	6	0.17	–	–	–	43.5
GL/ADA 6/6	1	2	6	0.26	6	0.17	–	–	–	42.3
GL/ADA-RO 0/1	1	2	0	0.00	1	0.03	0.31	0.90	33.5	23.5
GL/ADA-RO 1/1	1	2	1	0.04	1	0.03	0.31	0.91	33.5	23.2
GL/ADA-RO 1/3	1	2	1	0.04	3	0.08	0.32	0.93	33.5	22.8
GL/ADA-RO 1/6	1	2	1	0.13	6	0.08	0.33	0.95	33.5	22.4
GL/ADA-RO 3/3	1	2	3	0.04	3	0.17	0.33	0.96	33.5	22.2
GL/ADA-RO 3/6	1	2	3	0.13	6	0.17	0.34	0.97	33.5	21.8
GL/ADA-RO 6/6	1	2	6	0.26	6	0.17	0.35	1.00	33.5	21.2

ratios (Table 1). The possible structures of the obtained polyols are presented in Fig. 2. The acid numbers, hydroxyl values, water contents, and viscosities of the obtained GL/ADA and polyols are summarized in Table 2. The theoretical value of hydroxyl number is calculated from the equation $\text{OH}^* = (f \times 56,110)/M$ where M is the average molecular weight (g/mol), f is the functionality, the number of OH groups/mol, and 56,110 is the equivalent weight of KOH in milligrams (Kirpluks et al., 2013, 2016).

2.3. Preparation of polyurethane rigid foams

The obtained GL/ADA and GL/ADA-RO polyols were used to obtain the rigid PU foams. Formulation of PU rigid foams is corresponding polyol–70.0; Lupranol 3422–30.0;

Trichloropropylphosphate–16.0; NIAX Silicone L6915–1.5; Water–2.2; PC CAT NP-10–1.6; Solkane 365/227–16.0.

The necessary amount of pMDI was calculated according to isocyanate index 130, and it varied from 175 to 200 parts by weight, depending on OH value of corresponding polyol.

The PU foams were prepared on lab scale by 2-stage mixing of the components using the free-rising method in a mould at room temperature. First, the polyol system was mixed in a 500 mL plastic beaker. Next, the isocyanate was added and mixed for 15 s at a speed rate of 2000 rpm. Then, the mixture was quickly poured into an open plastic mould with dimensions $30 \times 30 \times 10$ cm. The foaming process was monitored by measuring the characteristic parameters: the duration of cream time, gel time, and tack-free time. The cream time indicates the rise start of foam, the gel time

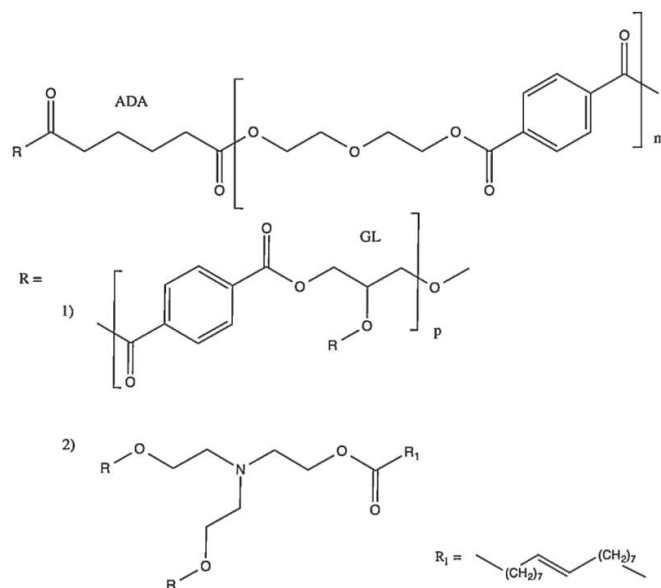


Fig. 2. Possible structure of polyols obtained from depolymerized PET and transesterified RO, containing fragments of GL and ADA.

Table 2
Properties of synthesized polyols.

Polyol	OH value (mg KOH/g)	OH ⁺ , theor value (mg KOH/g)	Acid value (mg KOH/g)	Water content (%)	Viscosity at 20 °C (mPa s)
GL/ADA 0/1	472	549	3.04	0.17 ± 0.03	3130 ± 40
GL/ADA 1/1	466	562	2.88	0.18 ± 0.01	2490 ± 33
GL/ADA 1/3	466	551	2.63	0.22 ± 0.03	2060 ± 10
GL/ADA 1/6	492	575	2.66	0.18 ± 0.02	1650 ± 37
GL/ADA 3/3	531	536	1.79	0.11 ± 0.02	1255 ± 69
GL/ADA 3/6	503	559	3.20	0.11 ± 0.01	1165 ± 26
GL/ADA 6/6	515	593	1.32	0.09 ± 0.04	1172 ± 13
GL/ADA-RO 0/1	405	461	4.02	0.11 ± 0.01	700 ± 87
GL/ADA-RO 1/1	408	467	4.20	0.14 ± 0.02	725 ± 53
GL/ADA-RO 1/3	417	461	2.90	0.09 ± 0.03	820 ± 40
GL/ADA-RO 1/6	399	474	2.83	0.13 ± 0.01	725 ± 12
GL/ADA-RO 3/3	449	454	2.49	0.10 ± 0.02	710 ± 21
GL/ADA-RO 3/6	440	466	2.70	0.16 ± 0.01	725 ± 15
GL/ADA-RO 6/6	400	483	3.17	0.11 ± 0.01	850 ± 22

is the transition of the mix from liquid to solid state, and tack-free time is when the foam solidifies completely. Specimens were then cut from the prepared PU foam blocks using a band saw for use in various physical–mechanical tests. The prepared PU foam blocks were conditioned at a room temperature for at least 24 h.

2.4. Characterization methods

The hydroxyl numbers (OH) of the polyols were determined using the acetic acetylation method without catalysis according to DIN 53240. The acid values were determined according to DIN 53402. The moisture content of the polyols was tested using the conventional Karl Fischer method and DIN 51777. Viscosity measurements were carried out using a HaakeViscotester 6L/R plus Rotational Viscometer (Thermo Scientific, Germany) at 20 °C. The Fourier transform infra-red spectra measurements (FTIR-ATR) were made on a Perkin-Elmer Spectrum One FTIR Spectrometer (Germany). The FTIR-ATR spectra of the polyols were collected at a resolution of 4 cm⁻¹.

The bulk density of the obtained rigid PU foams was measured according to standard test method ISO 845 for the apparent den-

sity of plastic foams. Water absorption was tested according to ISO 2896 by immersing the specimens in water for 28 days. Closed cell content was measured according to ISO 4590. PU samples with dimension (10 × 3.5 × 3.5 cm) were cut. Five specimens were analyzed for each composition. FTIR-ATR was used to study the bondings in prepared PU foams. FTIR-ATR spectra of the PU foams were collected at a resolution of 4 cm⁻¹ on a Nicolet 6700 (Thermo Scientific, Germany) in the region of 800–4000 cm⁻¹. Sixteen measurements of every specimen were performed, and the average spectrum is shown. Cells size distributions were calculated from the cellular structure images of foam cross-sections, which were taken using an optical microscope Leica DMR (Leica Microsystems, Germany) at 5× magnification. Leica Image Suite™ software was used to measure the cells. The compression strength and elasticity moduli of the PU foams were measured according to ISO 844 standard on testing machine Zwick Z100 (Zwick Roell, Germany), in the parallel (Z) and perpendicular (X) directions. Typically, ten specimens were analyzed for each composition, and the results were averaged.

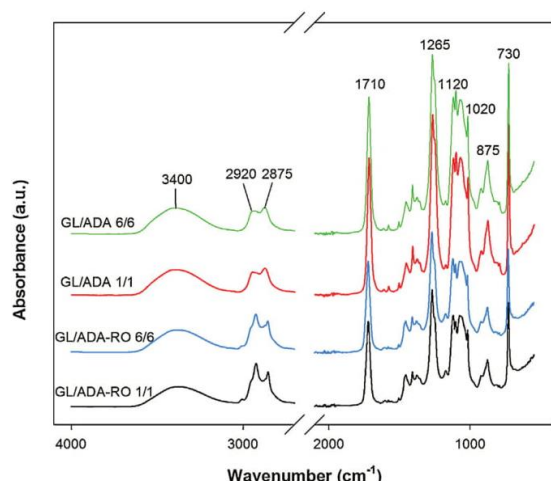


Fig. 3. FTIR spectra of obtained polyols.

3. Results and discussion

Viscosity is an indicator of the easiness of processing polyol. Polyols with low viscosity have many advantages (Ionescu, 2005) and can be easily processed into PU foams. High molecular weight polymers and branched chain cross-linked networks can also be obtained from low viscosity polyols. Generally, glycolysis of PET resulted in high viscosity oligomeric polyols (3130 mPa s for GL/ADA 0/1). We found that the addition of a small amount (1–6 wt.%) of GL and/or ADA decreases the viscosity of these polyols by about 3-fold (1165 mPa s for GL/ADA 6/6). The GL/ADA-RO polyols synthesized from GL/ADA and supplemented with 50 wt.% RO are characterized by much reduced viscosity values compared to the initial GL/ADA polyols. The GL/ADA-RO polyols' viscosity was in the range of 700–850 mPa s at 20 °C, which is appropriate for obtaining PU rigid foams (Kirpluks et al., 2013).

By increasing the content of functional additives (GL/ADA) in the concentration range from 0/1 to 6/6%, the OH values of the resulting polyols increase by 20% (from 472 to 515 mg KOH/g). The experimental obtained OH values of the produced polyols were lower than the theoretically calculated OH⁺ values. This is likely due to some dehydration of the hydroxyl groups and molecular chain branching (Ionescu, 2005; Szycher, 2012). After the transesterification reaction of GL/ADA and RO/TEA polyols, the OH values of the GL/ADA-RO products are reduced by a further ~20%. All of the processed polyols had low acid numbers, which are less than 4.5 mg KOH/g. These values are suitable for the production of PU rigid foams (Ionescu, 2005; Szycher, 2012). The water content of all of the polyols produced here were less than 0.25%, which is acceptable for obtaining the rigid foams (Ionescu, 2005; Szycher, 2012).

Table 1 shows the renewable and recycled content of the synthesized polyols. The GL/ADA formulations had no renewable component. The GL/ADA-RO polyols contain approximately 33% renewable part (RO) and about 22% of recyclate (rPET). The total renewable and recyclate content of the GL/ADA-RO polyols was about 55%, which exceeds the average values reported in the literature (Beneš et al., 2012; Cakić et al., 2015).

The FTIR spectra (Fig. 3) of the synthesized polyols confirmed the PET glycolysis with DEG and GL/ADA transesterification with RO/TEA. The FTIR spectra of the GL/ADA and GL/ADA-RO polyols were very similar, regardless of the concentration of functional additives used during their preparation. Hence, only the polyols

containing 1/1 and 6/6 of GL/ADA have been included as representatives in Fig. 3.

The presence of a recycled PET component in the polyol is mainly indicated by the absorption band intensities of aromatic C=C vibrations at 1578, 1505, and 1410 cm⁻¹, the absorption band of bending and stretching vibrations of aromatic C–H at 875 and 730 cm⁻¹, and the stretching vibration band of aromatic C=O carbonyl group at 1265 and 1120 cm⁻¹. The broad band at 3400 cm⁻¹ characterizes the free hydroxyl –OH groups in all polyols. There is also an important absorption band at 1710 cm⁻¹, which corresponds to the carbonyl C=O bonds in the ester groups. It can also be seen that the absorption intensity decreases for GL/ADA-RO polyols, which is in line with the decrease in the number of ester groups due to the transesterification reaction.

The regions of hydroxyl, aliphatic and aromatic group vibrations are shown in detail in Fig. 4, because these regions provide useful information about the linkages of the polyols (Sonnenschein, 2014). It shows that absolute absorption intensity at 3400 cm⁻¹ is stronger for GL/ADA polyols, which relates to higher hydroxyl absolute values of these polyols compared to the GL/ADA-RO polyol series. The GL/ADA content and ratio have little effect on the absorption intensities. The hydroxyl groups are consumed in the transesterification reaction, which results in a decrease in absorption intensity in this region. The OH value decreases from an initial value of 515 mg KOH/g for GL/ADA 6/6 to 400 mg KOH/g for GL/ADA-RO after reaction with RO/TEA.

In the 3000–2700 cm⁻¹ range (Fig. 4), two intense bands at 2920 and 2875 cm⁻¹ can be observed due to stretching of the –CH₂ groups of the aromatic and aliphatic structures in the chain backbone (Carta et al., 2003). For GL/ADA-RO polyols containing bio-based components, the characteristic intensities in this region are more pronounced due to the presence of long alkyl chain fragments from RO (i.e., fatty acid radicals in the molecular chain backbone). Another significant difference is the appearance of an absorption band at 875 and 730 cm⁻¹ corresponding to the aromatic groups from recycled PET oligomers (Fig. 4). These lower absorption band intensifies for GL/ADA-RO are consistent with the overall decrease in the recyclate (aromatic component) content in the GL/ADA-RO polyols.

The principal parameters used to characterize the stages of PU foam formation are the cream time, gel time, tack-free time, density, and closed cell content (Table 3). The observed closed cell content of the GL/ADA and GL/ADA-RO rigid foams was in the range of 90 to 96 vol.%. The cream time, which is measured as foam rise time due to the release of blowing gases, is approximately 30 s after mixing of the components. The gel time for all of the polyol formulations was in the range of 55–65 s. The gel time and cream time of the GL/ADA-RO containing bio-based and recycled components were comparable to the formulations with polyols GL/ADA (containing only recycled components). The tack-free time is measured at the point when the foam completely solidifies because of chain cross-linking and macromolecular network development. We observed no significant differences in the cream time, gel time, and tack-free time between the various GL/ADA, GL/ADA, and GL/ADA-RO polyols.

The tack-free time of some of the formulations containing GL/ADA-RO polyols was almost twice as long as for the GL/ADA polyols. This is consistent with the lower hydroxyl values and lower chain branching of the GL/ADA-RO polyols. Longer flexible segments and higher flexible segment content in the chains after the transesterification of RO/TEA and GL/ADA polyols results in the incorporation of bio-based RO radicals (fatty acid aliphatic chains fragments) into the molecular backbone of the GL/ADA-RO polyols. The possible chemical structure of the obtained PU molecular chain network is presented in Fig. 5.

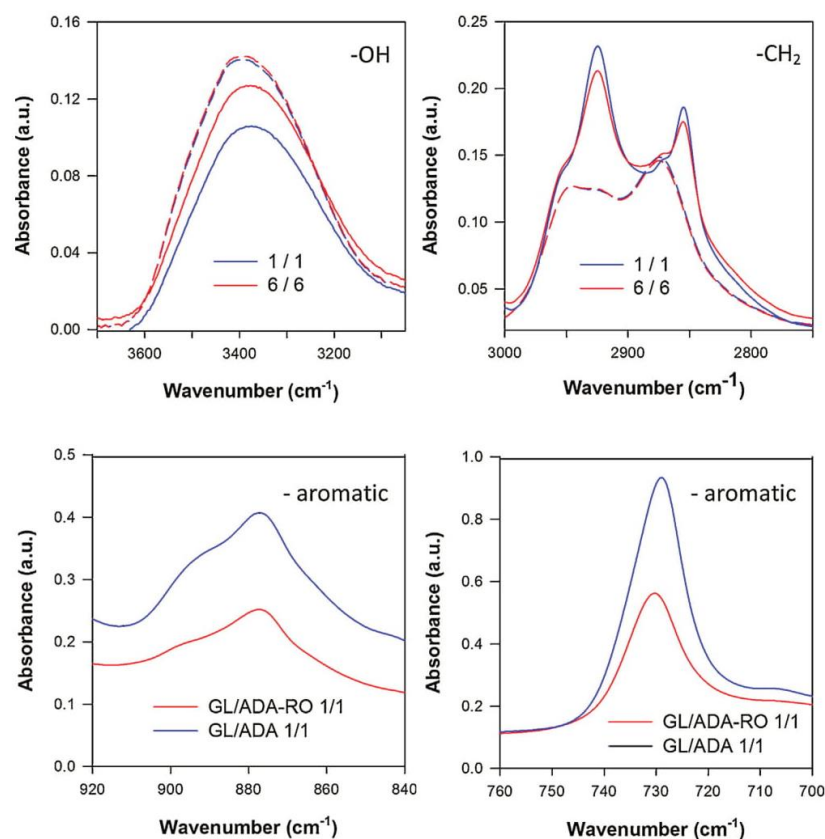


Fig. 4. FTIR spectra of -OH , -CH_2 and aromatic groups absorption bands for polyols; dashed line—GL/ADA, solid line—GL/ADA-RO.

Table 3
Parameters of PU rigid foam formation process.

Sample	Cream time (s)	Gel time (s)	Tack-free time (s)	Closed cell content (vol.%)	Density (kg/m^3)
GL/ADA 0/1	30	57	67	95.0 ± 0.6	42.6 ± 1.3
GL/ADA 1/1	31	55	67	96.2 ± 0.2	42.5 ± 0.7
GL/ADA 1/3	25	50	60	93.4 ± 0.4	42.8 ± 0.6
GL/ADA 1/6	25	50	60	97.3 ± 0.3	43.1 ± 0.6
GL/ADA 3/3	34	55	70	89.9 ± 0.9	45.9 ± 0.8
GL/ADA 3/6	32	57	71	90.5 ± 1.1	45.1 ± 0.7
GL/ADA 6/6	33	56	67	98.2 ± 0.6	45.9 ± 0.9
GL/ADA-RO 0/1	25	50	63	95.7 ± 0.5	38.3 ± 1.3
GL/ADA-RO 1/1	28	55	75	95.3 ± 0.6	37.7 ± 1.5
GL/ADA-RO 1/3	28	50	70	94.1 ± 1.0	38.8 ± 1.1
GL/ADA-RO 1/6	35	65	105	94.2 ± 0.3	47.2 ± 0.9
GL/ADA-RO 3/3	30	52	103	93.3 ± 1.3	44.7 ± 0.5
GL/ADA-RO 3/6	32	60	110	97.2 ± 0.4	46.4 ± 0.3
GL/ADA-RO 6/6	32	65	120	93.1 ± 0.2	52.5 ± 0.4

The effect of incorporation of fatty oil based aliphatic fragments (bio-based RO component) into the polyol molecular chain backbone was also confirmed in the cellular structure of the PU rigid foams. The GL/ADA and GL/ADA-RO foams are compared in Fig. 6. It can be seen that the addition of RO produces larger and more regular cells. This is due to the presence of aliphatic fragments in the backbone, which increase the overall flexibility of the molecular chain and decrease the viscosity of the polyol (Xu et al., 2015).

The results of optical microscopy's images analysis of the cellular structure of PU rigid foams are shown in Fig. 7. The average cell size of the PU GL/ADA foams was about $330 \mu\text{m}$. Whereas the GL/ADA-

RO foams have an average cell size of $420 \mu\text{m}$, approximately 30% larger than for GL/ADA foams. Altering the GL/ADA content in the polyol had little effect on the resulting cell size.

The water absorption kinetic curves for GL/ADA and GL/ADA-RO are shown in Fig. 8, which were all below 3 wt.%. The lowest water absorption values were obtained for the GL/ADA foams. The GL/ADA foams also had slightly higher closed cell content than the other foam types (Table 3) (Atta et al., 2013). The closed cell content for the GL/ADA and GL/ADA-RO foams ranged from 90 to 96 vol.%.

The mechanical properties of the PU rigid foams directly depend on the chemical structure of the polyols used in their production

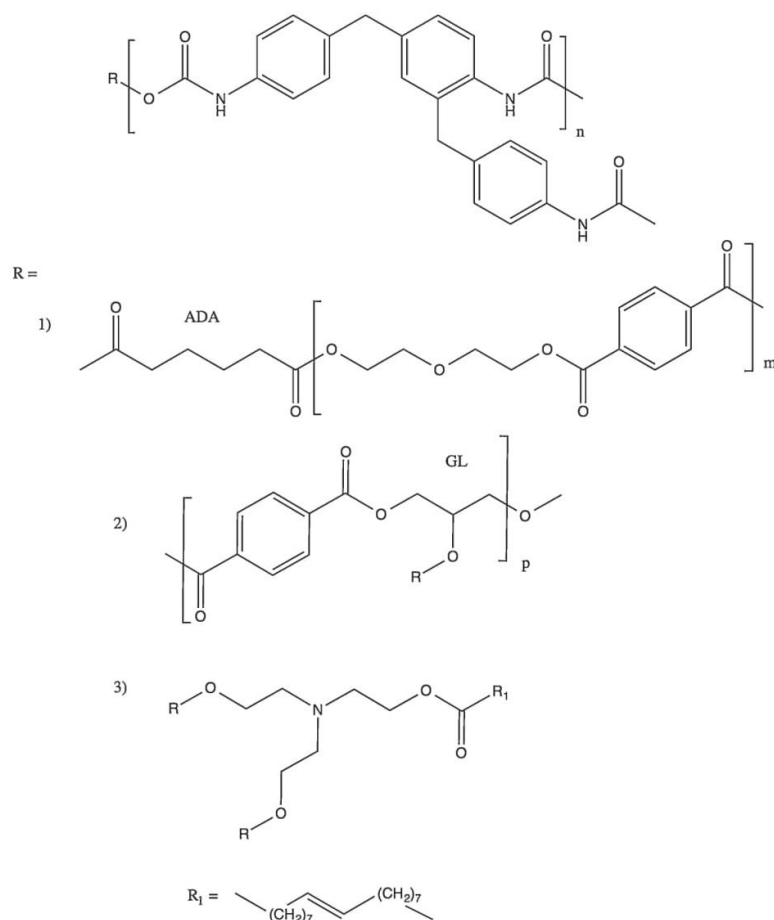


Fig. 5. Possible structure of prepared PU, containing fragments of rPET and RO.

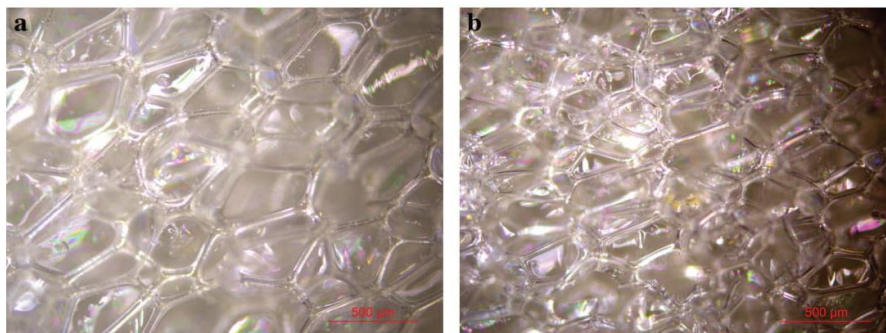


Fig. 6. OM images of PU foams (a) ADA/GL 0/1 and (b) ADA/GLA-RO 0/1.

(Szycher, 2012). Generally, compression tests of the rigid foams are carried out parallel (index z) and perpendicular (index x) to the foam rise direction (Stirna et al., 2011). This approach was used to measure the elasticity (E) and strength (σ) of prepared foams (Fig. 9). The obtained mechanical properties of foams are dependent on the density and developed cell anisotropy (Hamilton et al., 2013). Compression strength and elasticity in parallel to the foam

rise direction are larger than in the perpendicular to foam rise direction for all compositions, which is indicative of high anisotropy of the cell structure of the foams. For example, for the composition GL/ADA 1/1, the obtained E_x and E_z were 2.9 and 6.5 MPa, but for σ_x and σ_{null} these values were 0.16 and 0.33 MPa, respectively. Similar results were also obtained for commercial petrochemical PU rigid foams (Linul and Marsavina, 2015), which had an elas-

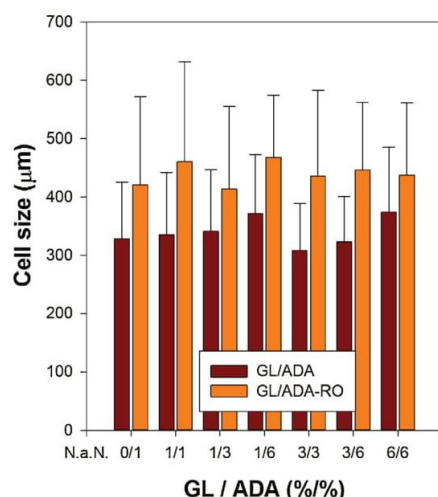


Fig. 7. Cell size of PU foams.

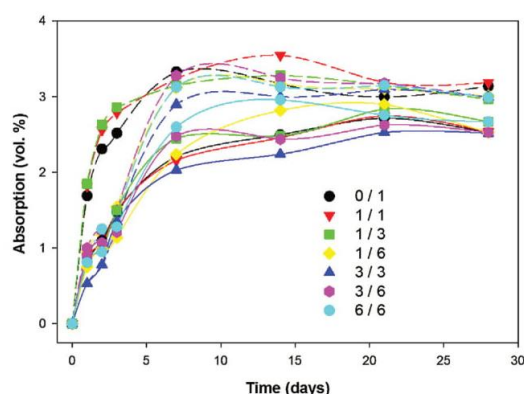


Fig. 8. Water absorption of PU foams; dashed line—GL/ADA, solid line—GL/ADA-RO.

ticity modulus of 4.2 MPa and yield strength of 0.38 MPa for PU rigid foams with a density of 40 kg/m³. These authors also stressed that the mechanical properties during compression are strongly dependent on the foam orientation, density, temperature, and loading rate (Linul et al., 2013). Kurańska et al. (2015) report that the type of bio-polyol and isocyanate index also strongly affects the rigidity of PU bio-based foams. For the RO-based polyol synthesized by epoxidation and opening of oxirane rings, the compression strength decreases with an increasing isocyanate index, but for the RO-based polyols synthesized by transesterification with TEA and transamidization with DEA, compression strength increases with an increasing isocyanate index (Kurańska et al., 2015).

We found that the E and σ parameters tended to increase significantly as greater amounts of functional additives are introduced into the polyols (Fig. 9). This is in line with previous PU rigid foam studies (Vitkauskienė et al., 2011a). For example, the E_z increased almost 3-fold, from 3.5 for GL/ADA 0/1 to 11.5 MPa for GL/ADA 3/3; the E_x increased almost 1.5-fold, from 2.9 for GL/ADA 0/1 to 4.4 MPa for GL/ADA 3/3. Whereas the σ_x increased almost 1.5-fold, from 0.15 for GL/ADA 0/1 to 0.23 MPa for GL/ADA 6/6; the σ_z increased almost 2-fold, from 0.18 for GL/ADA 0/1 to 0.35 MPa for GL/ADA 6/6.

The PU rigid foams prepared from GL/ADA polyols had a slightly higher compression strength (σ_x and σ_z) and elasticity coefficient (E_x and E_z) than foams prepared from GL/ADA-RO polyols (Fig. 9). It seems likely that the long flexible aliphatic chains (fatty acid chains C₁₆–C₁₈), which are present in the PU macromolecular network of the GL/ADA-RO foams (Fig. 5), have a plasticizing effect, resulting in improved viscoelasticity of the foams (Ashida, 2006). The distance between the cross-linking points in the PU network was greater for the GL/ADA-RO foams than the GL/ADA foams. The higher mechanical properties of the GL/ADA foams are also likely due to the higher concentration of ester and aromatic groups in the polyol and developed PU chain network (Ionescu, 2005). Thus, we assume that more efficient and stronger hydrogen bonding network occurs between the functional groups in the PU GL/ADA polymer than the PU GL/ADA-RO polymer (Li et al., 2014). Increasing the GL content of the polyols resulted in a branched chain structure with additional hydroxyl groups (higher OH value, Table 2) in the middle of the chains (Luo and Li, 2014). Then, the polyol reaction with isocyanate produced a dense PU polymer network with a short distance between the cross-linkings. The addition of ADA produces extra alkyl soft segments in the PU polymer network (Xu et al., 2015). These short soft segments in the PU macromolecular chain are favorable for the conformational mobility and development of the dense networks of hydrogen bonds (Ionescu, 2005). The influence of hydrogen bonding on the mechanical properties of rapeseed oil based PU has also been demonstrated by Stirna et al. (2011) and Gaidukov et al. (2013). Thus, the elasticity coefficient (E_x and E_z) and compression strength (σ_x and σ_z) tended to increase as introduced amount of ADA additive raised from 1 to 6 wt.% (Fig. 9). For example, the E_x increased almost 1.6-fold, from 2.9 for GL/ADA 0/1 to 4.7 MPa for GL/ADA 1/6; the E_z increased 1.8-fold, from 3.5 to 6.5 MPa; the σ_x increased 1.6-fold, from 0.15 to 0.24 MPa; the σ_z increased 1.5-fold, from 0.18 to 0.28 MPa, correspondingly.

The characteristic groups of the PU chain network can be clarified by FTIR spectroscopy. The existence of hydrogen bonds in PU can also be observed by FTIR spectroscopy (Sonnenschein, 2014). Possible reasons for hydrogen bond formation in PUs include ester–urethane, urethane–urethane, and urethane–amide hydrogen bonding. FTIR spectra were recorded for PU GL/ADA and PU GL/ADA-RO rigid foams. Changing the amounts of the functional additives (of ADA and GL) had little effect on the spectra. Representative spectra in the absorption mode are shown in Fig. 10.

The obtained FTIR spectra of the PUs are similar to those in literature (Hatchett et al., 2005; Hu et al., 2002; Stirna et al., 2006). The bands at 3300 cm^{−1} are characteristic of hydrogen-bonded N–H stretching, at 2925 cm^{−1} of aromatic C–H stretching, at 2854 cm^{−1} of aliphatic C–H stretching, at 1710 cm^{−1} of C=O ester groups, at 1615 cm^{−1} of C=O urethane group stretching, and at 1511 cm^{−1} of C=O aromatic rings.

Sharp peaks at 2925 and 2854 cm^{−1} due to methylene group vibrations were observed only for PU GL/ADA-RO foams; these peaks correspond to the long aliphatic fragments attributed from RO radicals incorporated into the polyol molecule chain backbone. PU rigid foams prepared with GL/ADA and PU rigid foams prepared with GL/ADA-RO exhibit the same intense absorption bands at 1615 cm^{−1}, which can be attributed to the urethane carbonyl groups. The PU GL/ADA-RO foams had a decreased absorption intensity at the band 1720 cm^{−1} compared to the PU GL/ADA foams, which is attributed to the lower content of ester carbonyl groups.

The presence of an absorption band at 2275 cm^{−1} clearly indicates that there are free isocyanate groups remaining in all PU rigid foams (Hu et al., 2002; Stirna et al., 2006). Carbodiimide group RN=C=NR formation is associated with the clear absorption band at 2137 cm^{−1}, which is the same for all PU foams (Hatchett et al., 2005; Hu et al., 2002; Stirna et al., 2006). The presence of aromatic structures and isocyanurate rings in the PU are indicated by the

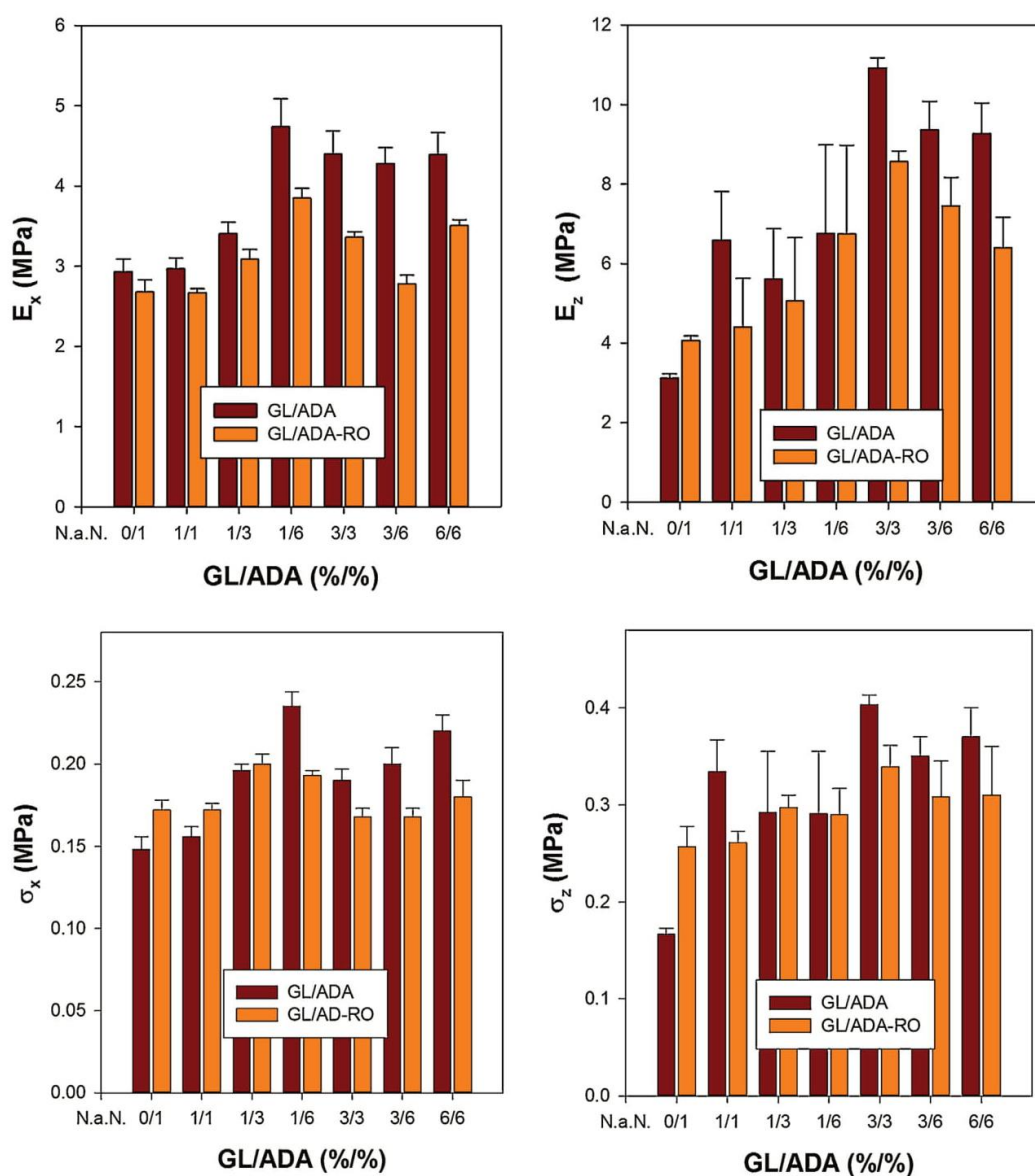


Fig. 9. Mechanical properties of PU foams.

absorption bands at 1597 and 1412 cm^{-1} respectively, which agree with the initially chosen isocyanate index 130. The formation of a cross-linked polymer network with urethane and isocyanurate chain fragments is a characteristic of the obtained PU rigid foams (Hatchett et al., 2005). The adsorption band at 1220 cm^{-1} indicates CN vibrations of urethane groups (Javni et al., 2000).

4. Conclusions

RO and recycled PET are renewable and recyclable components for the synthesis of polyols used for manufacturing bio-based PU rigid foams. Here, we show that modifying PU rigid foams by replacing 70 wt.% of the petrochemical polyol with RO-based polyols and

recycled PET can improve their mechanical properties. The proposed polyols consist of 33% renewable material and 22% recyclate. By varying the ADA and GL content of the foams, we were able to modify the chain structure, branching, and functionality of the polyols. These modifications significantly improved the mechanical properties of the obtained material. The increase in the additive concentration in the polyol allowed us to gradually enhance the mechanical characteristics of the foams. The enhanced mechanical properties were observed in material orientated parallel to the foam rise. The rigidity increased almost 3-fold, whereas the strength increased almost 2-fold. The prepared foams with the highest compression strengths contained 3 wt.% ADA and 3 wt.% GL. The use of bio-based polyol also increased PU foam cell size by

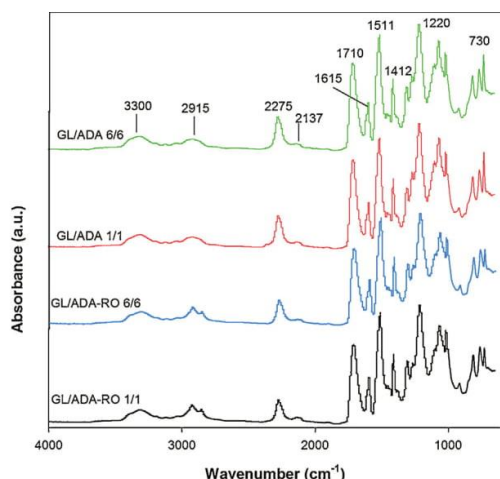


Fig. 10. FTIR-ATR spectra of PU foams.

approximately 30%. FTIR spectroscopy confirmed the higher concentration of long aliphatic chain blocks, and ester and aromatic groups, as well as the development of hydrogen bonding networks in the bio-based PU foams.

Acknowledgments

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VI

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Viscoelastic and thermal properties of polyurethane foams obtained from renewable and recyclable components.

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Viscoelastic and Thermal Properties of Polyurethane Foams Obtained from Renewable and Recyclable Components

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ABSTRACT: This article deals with the study of the viscoelastic and thermal properties of polyurethane (PU) rigid foams from biobased and recycled components. Rapeseed oil (RO) and recycled poly(ethylene terephthalate) (PET) were used to synthesize PU polyols. Addition of adipic acid (ADA) to polyol resulted in improved thermal and viscoelastic properties of foam materials. ADA content was varied from 1 to 6 wt%. Results of the dynamic mechanical spectra indicate an increase of the storage modulus E' and the loss modulus E'' in the whole temperature range for specimens with higher loading of ADA. In addition, damping factor shifted to higher temperatures, but damping intensity remained almost unaffected by the compositions. Scanning electron microscopy of the foams' cross sections testified that the average cells' size of 110 μm was unaffected by the ADA content in polyol.

KEYWORDS: Polyurethane rigid foam, rapeseed oil, recycled poly(ethylene terephthalate), viscoelastic properties, thermal properties

1 INTRODUCTION

Research and development in the field of biobased polymers has continued to be a hot topic over the last decades [1, 2]. The next trend for production of polyurethanes (PU), which is mostly driven by ecological sustainability concerns, is connected with the utilization of biobased and recycled raw materials for polyol synthesis [3, 4]. Quite frequently, rapeseed oil has been chosen as a renewable feedstock and the starting point to produce biobased polyols for PU preparation [5–7]. Its hydroxylated derivatives, synthesized by ozonolysis, epoxidation, hydroformylation, esterification and amidization reactions, are widely used for the preparation of soft and rigid PU foams [8]. In addition, many investigations have been dedicated to the recycling of linear polyester–poly(ethylene terephthalate) (PET) waste [9, 10]. The chemical recycling of PET is easily performed by the depolymerization process, which produces monomer and oligomer substances [4].

These depolymerization products can be successfully utilized in the production of aromatic polyester polyols, which can be used for manufacturing PU foams. This is achieved by the thermal treatment of PET flakes in a solution and reactions of hydrolysis, glycolysis, and aminolysis [11]. The effect of castor and palm oils on the structure of recycled PET polyols for PU preparation has been investigated [12–14]. Their limited compatibility is reported, which is partly solved by addition of diverse functional additives, enhancing the branching and functionality of polymer chains. For instance, the introduction of carboxylic acids, alcohols and glycols is very popular [15, 16]. Furthermore, it is obvious that the final exploitation properties of the polymer material will be strongly dependent on the chosen raw components [17].

As a result, thermal and mechanical properties are influenced by the concentration and chemical structure of the introduced reagents and additives [18, 19]. Enhanced chain branching and rigid/soft segments' incorporation into the polymer chain network interactions can significantly change the viscoelastic property of polymer foams [20]. The temperature changes can immediately influence the macromolecular flexibility

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and the chain segment conformational mobility, which reflect the polymer material's mechanical behavior [21]. The increased flexibility of the polymer chain, owing to the introduction of the flexible alkyl segment, essentially affects the polymer glass transition and increases the polymer material's compliance and damping characteristics [22–24].

Finally, viscoelastic properties as a function of temperature, time and frequency of the polymer material with a closed cellular structure, i.e., the foam subjected to an oscillating stress, significantly differ from those of the monolith polymer material [25, 26]. Since the foam is a complex system, the expansion during heating becomes very complex and directly depends on the cellular structure features [27]. For example, the size and anisotropy of the cells is essential. Polymer foam is discussed as a two-part structure consisting of a polymeric cell structure and the gas inside the cells [28]. Then, the cellular skeleton has the thermal expansion of the bulk polymer, while the thermal expansion of the polymer foams is connected with the volume change associated with the gas inside the closed cells. Theoretically, as the gas in the cells expands, it pressures the cell walls and changes the shape and size of the cells. The cell distortion depends on the contribution of the viscous properties of the polymer material [29, 30]. These findings make the thermal expansion and thermo-mechanical property investigations of polymeric foams very complicated, but very important, because closed-cell foams are often used for thermal insulation and protection [28].

In the present study, an attempt was made to better understand the viscoelastic behavior of closed-cell PU rigid foams, focusing on the tuned-up chemical structure of the experimentally obtained polyols from biobased and recycled components, responding to the different content of adipic acid (ADA) reagents. For this purpose, dynamic mechanical and thermo-mechanical tests were conducted, and the glass transition temperature, storage, loss modulus, and thermal expansion of the foam materials were investigated. In addition, thermal conductivity, differential calorimetric and thermal gravimetric measurements of the foams were performed to evaluate their thermal stability properties.

2 EXPERIMENTAL

2.1 Polyol Synthesis

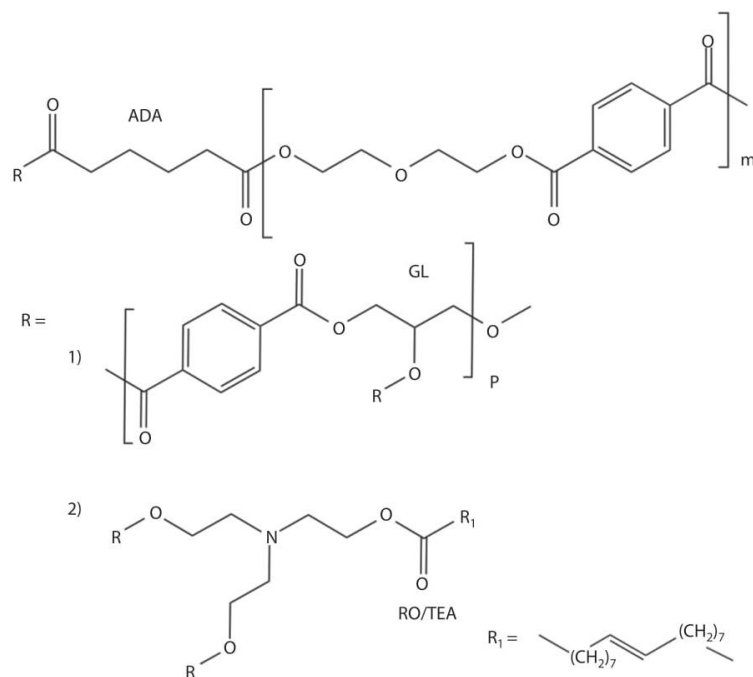
PET flakes of clear grade were obtained from PET Baltija, Latvia. RO (Iodine number = 117 mg/100 g) was supplied by Iecavnieks & Co, Latvia. Triethanolamine (TEA) (99.5%) was supplied by BASF, Germany; zinc

acetate dihydrate (ZnAc) ($\geq 98\%$), diethylene glycol (DEG) (99%), ADA (98%), and glycerol (GL) (99%) were obtained from Sigma-Aldrich, Germany. All reagents were used without any further purification for synthesis of PU polyols.

The polyols were synthesized according to the modified transesterification method by the use of PET flakes and RO. The synthesis was carried out in a three-neck 1.0 L reaction flask equipped with a mechanical stirrer, a thermometer, a condenser and an argon inlet. The details of the synthesis have been reported previously [31]. Possible structures of the prepared polyols are given in Scheme 1. The final biobased polyols' concentrations of ADA were 1, 3 and 6 wt%, while the GL content was equal to 1 wt% and the RO/TEA ratio was kept constant for all formulations.

2.2 PU Foam Preparation

The PU rigid foams with an apparent density of about 45 kg/m³ and a closed-cell content of about 90% from the experimentally synthesized novel polyols were manufactured by the following procedure. Firstly, the polyol system was blended. It contained the obtained polyol, polyether polyols Lupranol 3422 (BASF, Germany; OH value = 490 mg KOH/g), foaming agent Solkane 365/227 (Solvay, Belgium; Pentafluorobutane/Heptafluoropropane 87/13), catalyst dimethylaminopropyldipropylamine PC CAT NP-10 (Performance Chemicals Handels, Germany), silicone surfactant NIAx Silicone L-6915 (Momentive Performance Materials, Germany), and flame retardant trichloropropylphosphate (Lanxess, Germany). All the raw components were used without further treatment. The formulation of the obtained blend was similar to that reported in [31] and was as follows: the obtained biobased polyol – 70; petrochemical polyether polyol – 30; flame retardant – 16; surfactant – 1.5; water – 2.2; catalyst – 1.6; foaming agent – 16. The components' content is given as part per weight (ppw). PMDI 92140, supplied by BASF, Germany, was chosen as an isocyanate component. It is a polymeric methylene diphenylene diisocyanate (PMDI) with NCO% of 31.5, a density of 1.20 g/cm³, and a viscosity of 30 mPa·s at 25 °C. The necessary amount of MDI was calculated according to the isocyanate index 130. Isocyanate was added and mixed at a speed rate of 2000 rpm for 15 s. Then, the mixture was quickly poured into an open plastic mold with dimensions of 30 × 30 × 10 cm. The free-rising method in a mold at room temperature was chosen. The prepared foam blocks were conditioned at room temperature for at least 24 h. After that, the specimens for tests were cut from the prepared blocks using a band saw. During the foaming process, the cells became elongated in the



Scheme 1 Possible chemical structure of the polyols' chain network, containing blocks of ADA, GL, RO/TEA and PET.

rise direction. Furthermore, this cell design exhibits anisotropy properties in the foam rise and transverse directions. For further analysis, only specimens cut in the rise direction were used.

2.3 Characterization of PU Foams

Force and displacement amplitudes as well as phase shifts were determined with a Mettler Toledo DMA/SDTA861e dynamic mechanical analyzer. The specimens ran in a temperature range of 20–200 °C, an applied force of 500 mN, an elongation of 30 µm, a frequency of 1 Hz, and a heating rate of 1 °C/min. Compression oscillation mode was used.

Differential calorimetric tests were carried out on a Mettler Toledo DSC 823e instrument. Specimens of about 10 mg were heated in a temperature range of 0–200 °C. The heating ran at a rate of 10 °C/min under nitrogen atmosphere.

Thermogravimetric tests were performed on a Mettler Toledo TGA/SDTA 851e instrument. Specimens of about 10 mg in weight were heated in air at room temperature up to 800 °C. The foam thermal stability was evaluated from the weight-loss heating curves by calculating the thermal degradation temperature.

A Linseis PT1000 thermo-mechanical analyzer (TMA) was used to measure the dimensional changes of the material as a function of temperature in a temperature range of 20–250 °C, an applied force of 0–150 mN, and a heating rate of 1 °C/min. The specimens' thickness was about 20 mm. The dilatometric mode of the thermo-mechanical test was used to calculate the linear thermal expansion coefficient.

The cellular structure of the foams was examined with a Tescan Mira TS 5136 MM scanning electron microscope (SEM) at different magnifications and a voltage of 25kV.

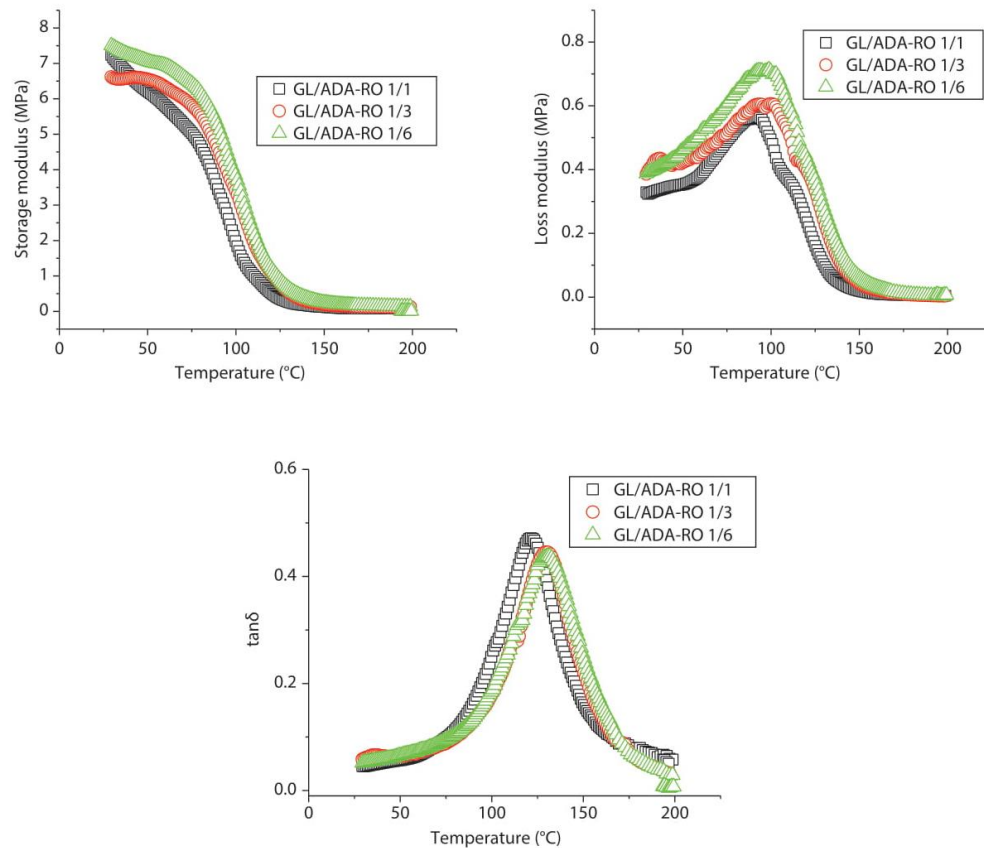
The thermal conductivity of the rigid PUR foams was measured periodically for 8 weeks after the foam's preparation. These tests were carried out based on the ISO 8301 standard using a Linseis Heat Flow Meter 200. The temperature range was 10–30 °C and dimensions of samples were 20 × 20 × 3 cm.

3 RESULTS AND DISCUSSION

Closed-cell rigid PU foams within the free-rise foaming process were obtained. The foams were characterized by the composition and basic characteristics given in Table 1 [31].

Table 1 Composition and characteristics of PU foams.

Sample	Recycled component		Biobased component		Closed-cell content (vol%)	Density (kg/m ³)
	PET (mol)	DEG (mol)	RO (mol)	TEA (mol)		
GL/ADA-RO 1/1	1	2	0.31	0.90	95.3	37.7
GL/ADA-RO 1/3	1	2	0.32	0.93	94.1	38.8
GL/ADA-RO 1/6	1	2	0.33	0.95	94.2	47.2

**Figure 1** Dynamic mechanical spectra of PU foams.

3.1 Viscoelastic Properties of PU Foams

The dynamic mechanical spectra (Figure 1) of the PU foams were recorded versus the temperature at the heating operation mode. Obviously, the polymer material's viscoelasticity improves and rigidity drops, while the operation temperature increases due to the dominance of the macromolecular chain viscous flow (Table 2). Modulus values were normalized with

respect to a density of 40 kg/m³ using the equation of Hawkins *et al.* [32]. Storage modulus E' was found to increase in a broad temperature range after the addition of ADA to the polyols.

There is an almost 1.5-fold increase in E' for GL/ADA-RO 1/3 at 150 °C. It characterizes the enhanced stiffness of the polymer foam after the ADA incorporation, while E' is directly proportional to the energy stored elastically and reversibly. Meanwhile, the loss

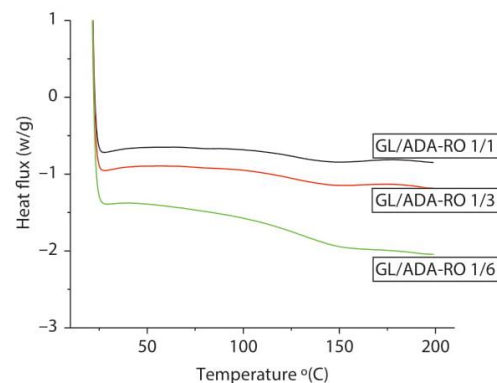
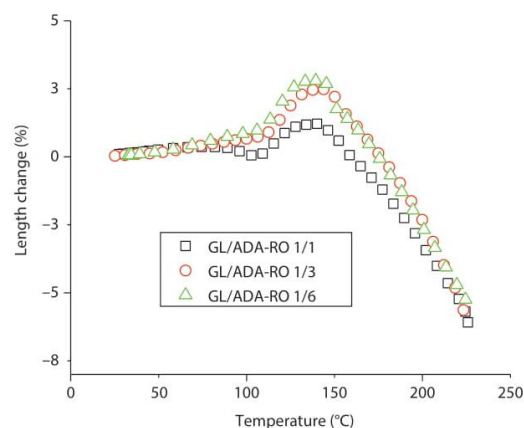
Table 2 Storage modulus, loss modulus and loss factor of PU foams.

Sample	E' (MPa)			E'' (MPa)			tan δ
	50 °C	100 °C	150 °C	50 °C	100 °C	150 °C	
GL/ADA-RO 1/1	6.86	2.88	0.16	0.40	0.60	0.03	0.47
GL/ADA-RO 1/3	6.95	4.11	0.25	0.45	0.63	0.07	0.44
GL/ADA-RO 1/6	5.28	3.32	0.23	0.35	0.54	0.08	0.43

modulus E'' characterizes the energy transformed into heat and irreversibly lost owing to the viscoelastic and / or viscous deformation of the polymer chains [22]. E'' is also significantly improved (Table 2) after the incorporation of flexible aliphatic short segments of ADA into the chain backbone. For example, E'' increases almost 1.3-fold at 50 and 100 °C, and almost 3-fold at 150 °C. Also, the increase of E' and E'' observed at all tested temperatures is connected with the possible increased crosslinks' density and intersegmental interactions that resulted in higher rigidity of the polymer chain network after the soft segment incorporation [33]. The loss modulus of PU foams GL/ADA-RO 1/1, GL/ADA-RO 1/3 and GL/ADA-RO 1/6 has a local maximum at 91, 95 and 100 °C, respectively. It testifies that higher energy is required and dissipated by the macromolecular chains for occurring viscoelastic deformation [34], while some decrease of modulus values for GL/ADA-RO 1/6 relates to the increase in the viscoelasticity of the foam materials due to the increase in the content of the flexible aliphatic segments of ADA in the chain network. The next important viscoelastic characteristic of the material is the damping effectivity that relates to the relative height loss–damping factor ($\tan\delta$), which is calculated as the ratio of E'' to E' . We also observed some decrease of the peak height intensity of $\tan\delta$ from 0.47 (GL/ADA-RO 1/1) to 0.43 (GL/ADA-RO 1/6). It shows that the polymer chain network deforms with extensive internal friction [35]. This drop in the effectivity of the energy dissipation after the incorporation of soft dangling segments also greatly confirms the enhancements of the material's viscoelastic characteristics due to the restrained conformation mobility of the chain segments between the entanglement sites [36], strong interactions between the soft-hard segments of the developed chain network [37], and the dense packing density of the soft segments [38].

3.2 Thermal Properties of PU Foams

In order to obtain the glass transition temperature T_g of the polymer, DMA (Figure 1) and DSC (Figure 2) curves were used. Meanwhile, the thermal stability of rigid PU foams was evaluated as the softening

**Figure 2** DSC curves of PU foams.**Figure 3** TMA curves of PU foams.

temperature T_{soft} and thermal degradation temperature T_{deg} , obtained from TMA (Figure 3) and TGA (Figure 4), respectively.

It is observed that T_g (DMA) tends to increase by about 8 °C with the GL/ADA-RO 1/6, but T_g (DSC) rises by only about 2 °C with the same foam composition. The general increase of T_g relates to the previously confirmed mechanism of the enhancements of the material's viscoelastic characteristics due to the

restrained conformation mobility of the chain segments between the entanglement sites in the cross-linked polymer chain network [39], which also agrees with the viscoelasticity property investigations of PU foams conducted by Aou *et al.* [40]. It is also reported that the incorporation of soft segments can lead to the development of additional hydrogen bonding [41] and even to the formation of two domain morphologies [35] of PU foams.

Figure 3 shows TMA curves of PU foams. It is described as a continuously changed specimen size during the thermal heating of the specimens. The coefficient of thermal expansion (CTE) was calculated from the slopes of the thermal expansion curves. The resulting CTE values at 30 and 120 °C are summarized in Table 3. It testifies that CTE is directly dependent on the temperature and the GL/ADA-RO composition. At 30 °C, the CTE value increases almost 1.4-fold from 5.12 to $7.08 \cdot 10^{-5}$ ($1/^\circ\text{C}$); while at 120 °C, it increases almost 2.2-fold from 55.1 to $119.0 \cdot 10^{-5}$ ($1/^\circ\text{C}$). A glass-rubber transition of the polymer shell is observed as the change of the thermo-mechanical curve slope at about 100 °C. The further heating up to the temperature of 140 °C results in a continued expansion of the rubbery state foam specimen with a higher rate till

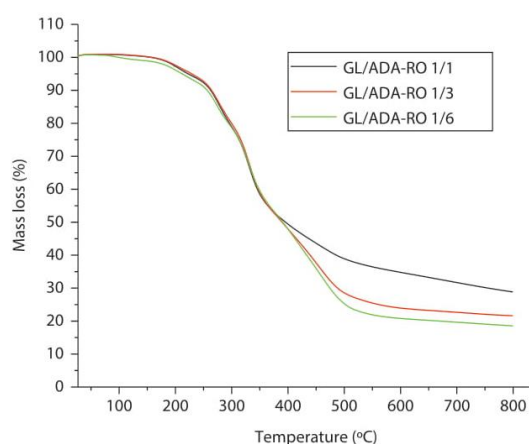


Figure 4 TGA curves of PU foams.

the softening point. The softening of the polymer corresponds mainly to the viscous deformation of the polymer chains [22]. It should also be noted that the gas pressure inside the foam's cell has a more pronounced contribution to the increase of the specimen size expansion rate for the soft rubbery polymer shell cell than for the rigid polymer shell cell [27]. The T_{soft} is calculated from the thermal curves of the specimen's length change at the onset decrease point of the specimen dimension (Figure 3). The measured T_{soft} of the obtained PU foams is about 140 °C; further increase in temperature results in a rapid softening of the polymer shell of the cellular materials and the overall rapid size shrinkage of the foams. Accordingly, only minor changes in the specimen weight at 140 °C were observed, as was testified by the TGA measurements (Figure 4). The T_{deg} relates to the polymer chain breakdown due to thermal heating. The T_{deg} of PU foams is about 330 °C. ADA loading does not affect the thermal degradation behavior of PU foams till about 400 °C. The subsequent heating of the foams till 800 °C reveals a lower relative weight (about 20%) of residual char for the specimen with GL/ADA-RO 1/6 in comparison to the specimen (about 40%) with GL/ADA-RO 1/3. Finally, it can be concluded that the thermal stability (T_{deg}) and softening point (T_{soft}) of the PU foams remain almost unaffected by the ADA content in the polyol.

In addition, the obtained PU rigid foams have sufficient properties to be used for different thermal insulation applications. The time-dependent thermal conductivity of the prepared PU foam is shown in Figure 5. The increase of the ADA content in the formulations decreases the thermal conductivity of the foams by 10%, and this decrease is reasonable for thermal insulation materials. While the obtained cellular structure of the PU foams is very regular, the average cell size is about 110 μm (Figure 6). Altering the ADA content in the polyol had no effect on the foam cells' size and shape. The observed decrease in thermal conductivity can be related to the enhanced foam cell wall material's viscoelastic properties. It can also relate to the observed increase in glass transition (up to 8 °C) due to the restrained conformation mobility

Table 3 Characteristic phase transition temperatures and coefficients of thermal expansion of PU foams.

Sample	T_g ($^\circ\text{C}$)		T_{soft} ($^\circ\text{C}$)	T_{deg} ($^\circ\text{C}$)	CTE $\cdot 10^{-5}$ ($1/^\circ\text{C}$)	
	DMA	DSC	TMA	TGA	30 °C	120 °C
GL/ADA-RO 1/1	121	117	140	330	5.12	55
GL/ADA-RO 1/3	129	119	140	332	5.65	108
GL/ADA-RO 1/6	129	119	140	331	7.08	119

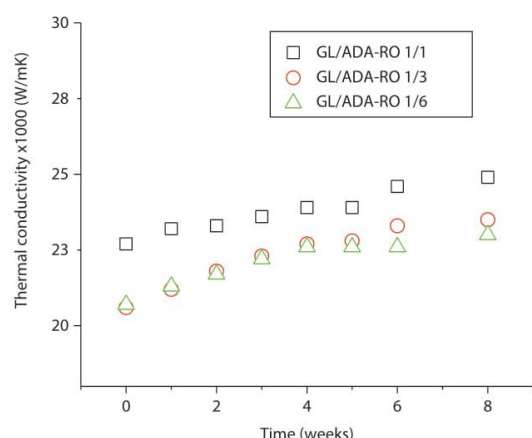


Figure 5 Time-dependent thermal conductivity of PU foams.

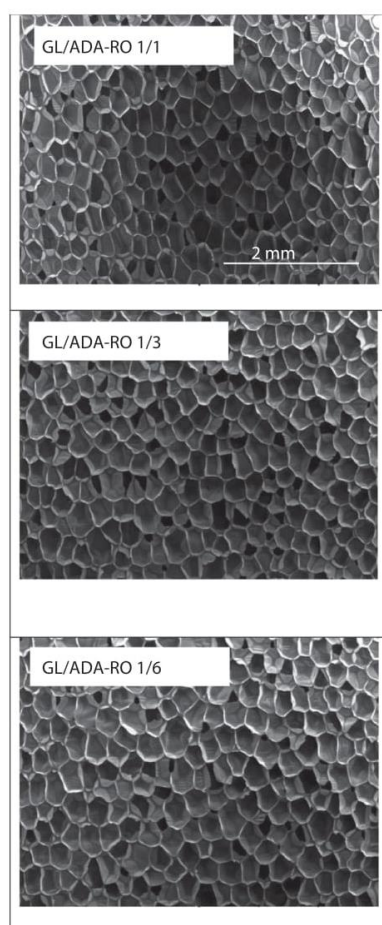


Figure 6 SEM images of PU foams.

of the chain segments between the entanglement sites in the crosslinked polymer chain network and a possible development of additional hydrogen bonding, thereby substantially limiting the diffusion of the foaming agent Solkane 365/227 out of cells.

4 CONCLUSIONS

Viscoelastic and thermal properties of rigid PU foams from biobased and recycled components are reported. RO and recycled PET were used to synthesize PU polyols. The addition of ADA resulted in improved thermal and viscoelastic properties of rigid PU foam materials. The increase in the ADA content from 1 to 6 wt% in the polyol allowed a gradual enhancement of the thermal and viscoelastic characteristics of rigid PU foams. It was observed that the incorporation of flexible short aliphatic segments into the polymer chain backbone significantly improved the viscoelastic properties of the obtained material. The E' and E'' increased up to 1.5-fold after the addition of ADA. The $\tan\delta$ shifted to higher temperatures, but damping intensity remained almost unaffected by the compositions. Finally, the ADA loading affected the thermal behavior of the prepared PU foams. The value of CTE increased with higher content of ADA in the formulation, while the thermal conductivity coefficient significantly decreased to 10% and glass transition temperature increased up to 8 °C after the incorporation of 6 wt% of ADA. The SEM investigations testified to the uniformity of the cell size and shape for all PU foam compositions. The average cell size was 110 μm .

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