

**RIGA TECHNICAL UNIVERSITY**  
Faculty of Materials Science and Applied Chemistry  
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Doctoral Student of the Study Programme “Chemical Engineering”

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

**Summary of the Doctoral Thesis**

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# **DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE**

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on December 3, 2020 at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3/7 P.Valdena Street, Room 272.

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## **DECLARATION OF ACADEMIC INTEGRITY**

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Aiga Ivdre ..... (signature)

Date: .....

The Doctoral Thesis is prepared as a thematically unified set of scientific publications. It contains 6 publications written in English. Total volume of the Doctoral Thesis is 74 pages. The summary contains an introduction; 3 chapters; conclusions; 19 figures; 6 tables; the total number of pages is 40. The Bibliography contains 72 titles.

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## ABBREVIATIONS AND SYMBOLS

ADA – adipic acid

DEG – diethylene glycol

DMA – dynamic mechanical analysis

$E$  – elastic modulus

EG – ethylene glycol

GL – glycerol

GL/ADA – aromatic polyester polyols based on polyethylene terephthalate with glycerol and adipic acid as functional additives

GL/ADA-RO – aromatic polyester polyols based on polyethylene terephthalate and rapeseed oil with glycerol and adipic acid as functional additives

$I$  – isocyanate index

Index  $x$  – perpendicular to foaming direction

Index  $z$  – parallel to foaming direction

KAc – potassium acetate

$\lambda$  – thermal conductivity

LUPR – polyurethane foam series based on Lupranol 3300 polyol

$\mu$  – viscosity

NEO – polyurethane foam series based on Neopolyol 380 polyol

$OH_v$  – hydroxyl value

PET – polyethylene terephthalate

PMDI – polymerized diphenylmethane diisocyanate

PIR – polyisocyanurate

PU – polyurethane

$R.H.$  – relative humidity

RO/PET – rapeseed oil / polyethylene terephthalate

RO/TEA – rapeseed oil / triethanolamine

$\sigma$  – compression strength

$\tan\delta$  – damping factor

TEA – triethanolamine

$T_g$  – glass transition temperature

TO/PET – tall oil/polyethylene terephthalate

# INTRODUCTION

## Actuality of the Topic

As society's responsibility for the environment increases, the more and more legislative and directive emphasis is placed on the use of sustainable resources (both renewable and recycled) as valuable raw materials for the production of various materials. This also applies to polyurethane (PU) foams, which are mainly produced from petroleum raw materials. Rigid PU foams are widely used as one of the most effective thermal insulation materials, which reduces energy consumption in various industries. Its use in thermal insulation is growing, and cheaper and better solutions are being sought for PU production. The main raw materials for PU production are polyol and isocyanate. The use of recycled materials and renewable raw materials in the production of polyols has several advantages: production is more environmentally friendly and it is possible to improve the properties of the final product. In the dissertation rapeseed and tall oil were selected as renewable raw materials and polyethylene terephthalate (PET) flakes from PET bottles as recycled raw material.

Nowadays vegetable oils are already used in the production of polyols. The most used one is soybean oil. Soybean is not an oilseed crop typical for the Europe, but rapeseed oil as a raw material could be a competitive polyol resource. It is one of the most popular oil crops in Europe, including Latvia. Tall oil, on the other hand, is one of the most commercially important by-products of pulp and paper production.

PET is one of the most versatile plastics, mainly used in the production of textile fibers and soft drink bottles. The recycling of used PET bottles is a worldwide concern because, although PET bottles do not pose a direct risk to the environment, they do not decompose in the environment and thus constitute a significant volume of solid waste streams. At present, the recycling of used PET bottles continues to develop rapidly in the world and also in Latvia, where PET is separated from the waste stream and mechanically recycled or processed to obtain PET granules and PET flakes of various qualities. Aromatic polyester polyols suitable for PUR production can be obtained from PET chemical processing.

The polyols available on the market obtained exclusively from the recycled industrial PET waste have several very significant disadvantages: high viscosity, incompatibility with physical foaming agents, and crystallization at room temperature. High viscosity and crystallization make it difficult to obtain PU foams using industrial spraying and casting equipment – preheating of polyol and higher pump capacities are required. Incompatibility with physical foaming agents and crystallization at room temperature do not allow stable long-term storage of polyol systems – delamination and heterogeneity of the systems negatively affect the properties of the PU foams obtained from them. On the other hand, most of the polyols from vegetable oils that are available on the market do not contain an aromatic group in their chemical structure, thus the thermal and mechanical properties of PU foams obtained from them are weaker. It would be possible to obtain polyols with improved properties by using both PET and vegetable oils as raw materials.

## **Aims and Objectives**

The Thesis aims to develop innovative polyols suitable for the production of rigid PU foam from recycled PET flakes and renewable raw material resources (rapeseed oil and tall oil) and to evaluate the effect of polyols on the most important properties of rigid PU foams as a thermal insulation material.

According to the aim of the work, the following tasks have been set:

- 1) to develop a methodology for the synthesis of polyols based on tall oil and PET (TO/PET polyols), as well as from rapeseed oil and PET (RO/PET polyols) with and without functional additives;
- 2) to characterize the developed polyols, to assess their compatibility with physical foaming agents, and to determine their long-term storage stability;
- 3) to develop polyol systems (formulations) based on the synthesized polyols and to obtain rigid PU foams with isocyanate 130 ( $II = 130$ );
- 4) to obtain PU foams based on RO/PET polyols with different isocyanate indices;
- 5) to characterize and evaluate the influence of rapeseed oil, tall oil, PET, functional additives, and the isocyanate index on the properties of rigid PU foams;
- 6) to compare the obtained PU foams from the developed polyols with the PU foams obtained from rapeseed oil, tall oil, and commercially available polyols (reference polyols).

## **Scientific Significance and Novelty**

As a result of research, the synthesis methods were developed for TO/PET polyols and RO/PET polyols with and without functional additives – cross-linking agent glycerol (GL) and chain extender adipic acid (ADA). The most optimal synthesis conditions and raw material ratios have been determined to obtain low viscous innovative polyols, which are stable against crystallization and form a stable homogeneous system with physical foaming agents and other components of the polyol system.

The effects of rapeseed and tall oil, PET, functional additives, and isocyanate index on the compressive strength, elastic modulus, water absorption, closed-cell content, thermal conductivity, and other characteristics of rigid PU foam as a thermal insulation material have been studied. The most suitable polyols and recommended isocyanate indices for obtaining rigid PU foams have been determined in comparison with rigid PU foams from reference polyols. Properties of developed rigid PU foams correspond to application of thermal insulation material.

## **Practical Significance**

The synthesis of innovative polyols based on PET and rapeseed oil, as well as from PET and tall oil have been developed. The resulting low-viscosity polyols are compatible with physical foaming agents and do not crystallize at room temperature. Thus, it is possible to create polyol systems that exhibit long-term stability.

The suitability of polyols in the production of rigid PU foams has been proven. The properties of the obtained final materials are suitable for use as thermal insulation materials. They are rated as competitive with commercially available rigid PU foams.

## **Main Thesis to Defend**

1. It is possible to synthesize low-viscosity polyols from rapeseed oil and PET, as well as from tall oil and PET, that are stable against crystallization during long-term storage, as well as are compatible with foaming agents.
2. RO/PET and TO/PET polyols are suitable for the production of rigid PU foams.
3. It is possible to vary and improve the properties of rigid PU foams by using functional additives such as GL and ADA in the synthesis of polyols.
4. The aromatic structure of RO/PET and TO/PET polyols allow obtaining rigid PU foams with improved properties compared to the PU foams based on rapeseed oil and tall oil polyols without the aromatic structure.

## **Structure and Volume of the Thesis**

The Thesis is a compilation of scientific publications focusing on the synthesis of innovative polyols from recycled PET and renewable raw materials and the use of developed polyols for the production of rigid PU foams. Three types of polyols and PU foams were obtained and characterized:

1. Based on rapeseed oil and PET without functional additives, varying:
  - a) PET and diethylene glycol (DEG) ratio (publication No. 1);
  - b) RO/PET ratio (publication No. 2);
  - c) isocyanate index (publication No. 3).
2. Based on tall oil and PET (publication No. 4).
3. Based on rapeseed oil and PET with functional additives GL and ADA (publications No. 5 and 6).

## Publications and Approbation of the Thesis

The scientific achievements and main results of the Thesis are discussed in 6 publications indexed in Scopus, as well as reported in 4 international scientific conferences.

### Scientific publications

1. **A. Paberza**, A. Fridrihsone-Girone, A. Abolins, U. Cabulis. Polyols from recycled poly(ethylene terephthalate) flakes and rapeseed oil for polyurethane foams. *Polimery*, **2015**, 60(9), 572–578.
2. **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. *Journal of Cellular Plastics*, **2018**, 54(2), 161–177.
3. **A. Ivdre**, A. Abolins, I. Sevastyanova, M. Kirpluks, R. Merijs-Meri, U. Cabulis. Polyurethane/Polyisocyanurate Foams with Various Isocyanate Indices Based on Polyols from Rapeseed Oil and Waste PET. *Polymers: Cellular Polymeric Materials*, **2020**, 12, 738.
4. **A. Ivdre**, G. D.Soto, U. Cabulis. Polyols Based on Poly(ethylene terephthalate) and Tall Oil: Synthesis and Perspective in Production of Rigid Polyurethane Foams. *Journal of Renewable Materials*, **2016**, 4, 285–293.
5. G. Gaidukova, **A. Ivdre**, A. Fridrihsone, A. Verovkins, U. Cabulis, S. Gaidukovs. Polyurethane rigid foams obtained from polyols containing bio-based and recycled components and functional additives. *Industrial Crops and Products*, **2017**, 133–143.
6. S. Gaidukovs, G. Gaidukova, **A. Ivdre**, U. Cabulis. Viscoelastic and thermal properties of polyurethane foams obtained from renewable and recyclable components. *Journal of Renewable Materials*, **2018**, 6(7), 755–763.

### The results of the Thesis were presented at the following conferences

1. **A. Ivdre**, G. D. Soto, U. Cabulis. Polyols Based on Tall Oil and Rapeseed Oil in Combination with PET for Production of Rigid Polyurethane Foams. *BiPoCo 2016*, Szeged, Hungary, 28 August – 1 September 2016.
2. A. Abolins, **A. Paberza**, A. Fridrihsone-Girone, U. Cabulis. Recycled PET flakes and rapeseed oil as feedstock for rigid polyurethane foams. *Baltic Polymer Symposium 2015*, Latvia, Sigulda, 16–18 September 2016.
3. **A. Paberza**, A. Fridrihsone-Girone, A. Abolins, U. Cabulis. Rigid polyurethane foams as thermal insulation material based on recycled PET and rapeseed oil. *6th Workshop Green Chemistry and Nanotechnologies in Polymer Chemistry*, Portugal, Bragansa, 15–17 July 2015.
4. U. Cabulis, M. Kirpluks, **A. Paberza**, A. Fridrihsone-Girone, I. Vitkauskiene. Balance between renewable and recyclable feedstock for rigid polyurethane foams. *6th Workshop Green Chemistry and Nanotechnologies in Polymer Chemistry*, Portugal, Bragansa, 15–17 July 2015.

# 1. LITERATURE REVIEW

Vegetable oils are promising feedstocks for the synthesis of biobased materials due to their wide availability, low cost, and a large variety of potentially reactive groups in their structure [1], [2]. Polyols from vegetable oils, such as soybean [3], [4], castor [5], [6], palm [7], [8], sunflower [9], [10], and rapeseed oil [11], [12] have been synthesized and investigated as an alternative to petrochemical polyols in the production of PUs. 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 [13], [14].

Typical synthesis pathways to produce polyols from vegetable oils such as epoxidation and opening of oxirane rings [11], [15], transesterification with triethanolamine (TEA), and transamidation with diethanolamine [15], [16] are also applied for rapeseed oil. Hence rapeseed polyols with various chemical structure and properties can be offered for the PU market. According to Zieleniewska *et al.*, the investigations of PU foams from rapeseed oil polyols, in comparison with petroleum-based PU foams, show competitive advantages such as lower water absorption (due to the hydrophobicity of fatty acids), higher thermal stability, and improved renewable material content for rigid PU foams. However, lower compressive strength and higher friability have been reported as disadvantages [11]. Hard segment incorporation into the structure of PU foams would allow to avoid these disadvantages and improve the mechanical properties of the foam [17]. For this purpose, polyols from recycled polyethylene terephthalate (PET) can be successfully employed in PU formulations [18], [19].

One of the disadvantages of vegetable oils is that most of them are first-generation biobased raw materials, so they are also used in the food and feed production. Therefore, polyol synthesis from tall oil, which is a second-generation biobased raw material, is with additional advantage [20]. Tall oil is a byproduct of the Kraft pulping process of pine wood. Unlike vegetable oils consisting of triacylglycerols, tall oil contains higher amounts of unsaturated free fatty acids (36–48 wt. %), mainly oleic acid and linoleic acid, and resin acids or rosin (26–42 wt. %), which are cyclic terpenes [21].

A tall oil-based polyol can be obtained by reaction of carboxyl groups present in the fatty acids with triethanolamine (TEA) or diethanolamine via an esterification or amidization pathway [22]. Also, the esterification of tall oil with aromatic polyester polyols is found in the patent literature. Moreover, these polyols were found to be compatible with the trichlorofluoromethane blowing agent [23].

The high popularity of PET as a packaging material and its non-biodegradability creates huge amounts of solid waste, therefore effective recycling of PET is crucial [24], [25]. In 2017, 58.2 % (1.9 million tonnes) of the more than three million tonnes of PET bottles in the European market were collected for recycling [26]. PET waste can be recycled either physically or chemically. One of the chemical recycling products of PET is an aromatic polyester polyol that is suitable for obtaining PU. There are various chemical recycling pathways for aromatic polyester polyol synthesis: hydrolysis, aminolysis, methanolysis, and glycolysis [27]. The glycolysis is the most popular chemical recycling method, which has been commercialized [28]. Different depolymerization agents have been employed, for example, ethylene glycol (EG) [24],

[28], DEG [29], [30], propylene glycol [32], etc. in the 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 PU foams. Moreover, they partly solve PET waste problems and decrease PU dependence on the petroleum feedstock. However, PET polyols' high viscosity, fast crystallization, and incompatibility with a blowing agent have been reported as their drawbacks [33], whereas polyols from plant oils do not exhibit these disadvantages. It has been proposed that the compatibility of such aromatic polyester polyols could be improved by the addition of  $\epsilon$ -caprolactone, butanediol, polyglycols, GL, and ADA additives, which modify the branching and functionality of the molecular backbone of the aromatic polyester polyols [33], [34]. The positive effects of castor and palm oils on the structure of the aromatic polyester polyols have been reported [35], [36]. Thus, the final thermal and physical-mechanical properties of the PU materials can be improved [38]. Hence, the combination of PET and natural oils, such as rapeseed and tall oil, could also eliminate the mentioned disadvantages of aromatic polyester polyols and improve their suitability for the production of rigid PU foams.

Rigid PU and polyisocyanurate (PIR) foams are one of the most effective thermal insulation materials of the conventional, which are mainly used for civil engineering as well as for the refrigeration industry. PUs are produced in the exothermic reactions between alcohols with two or more reactive hydroxyl groups ( $-\text{OH}$ ) per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group ( $-\text{NCO}$ ) per molecule (diisocyanates, polyisocyanates) (Fig. 1.1). Whereas isocyanurate forms via trimerization of isocyanate as a side reaction during PU formation [39].

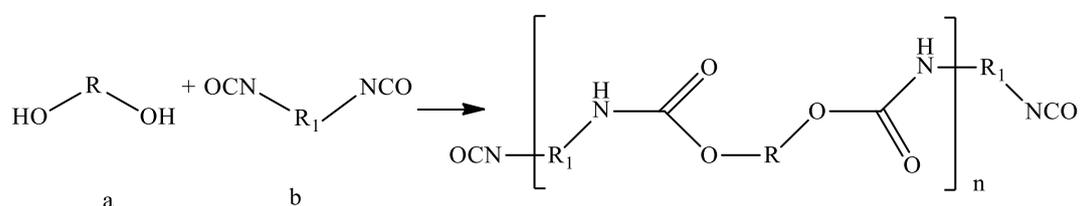


Fig. 1.1 The basic reaction for urethane formation: a – diol; b – diisocyanate [40].

The amount of PU 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 content in the end-product. The amount of isocyanurate rings in the polymer matrix affects the performance of PU foams. The increase in glass transition temperature ( $T_g$ ), dimensional stability, thermal stability as well as thermal insulation properties with increasing isocyanate index value is reported [15], [39]. The rigid PU foams formulations normally have an index between 105 and 125, and formulations for rigid PU-PIR foams have an index between 180 and 350 [42]. The influence of the isocyanate index on the performance of rigid PU and PIR foams based on polyols synthesised from both, PET and natural oil polyols, has not been previously reported.

## 2. METHODS

### 2.1. Experimental Design

Figure 2.1 shows an experimental design for the synthesis of rapeseed oil and PET polyols without functional additives, as well as for the production of rigid PU foams from the synthesized polyols. First, three polyols were synthesized using three different PET/DEG ratios for PET depolymerization. From them, the most optimal ratio was selected and five polyols with different ratios of rapeseed oil and PET were synthesized. PU foams with isocyanate index  $II = 130$  were obtained from all polyols. A series of PU foams with different isocyanate indices ( $II = 110-180$ ) was created from the most promising RO/PET polyol. Reference PU foams obtained from the following base polyols were used for comparison: aliphatic polyether polyol Lupranol 3300, aromatic polyester polyol Neopolyol 380, and rapeseed oil / TEA (RO/TEA) polyol. The reference PU foam series were named LUPR, NEO, and RO/TEA series respectively.

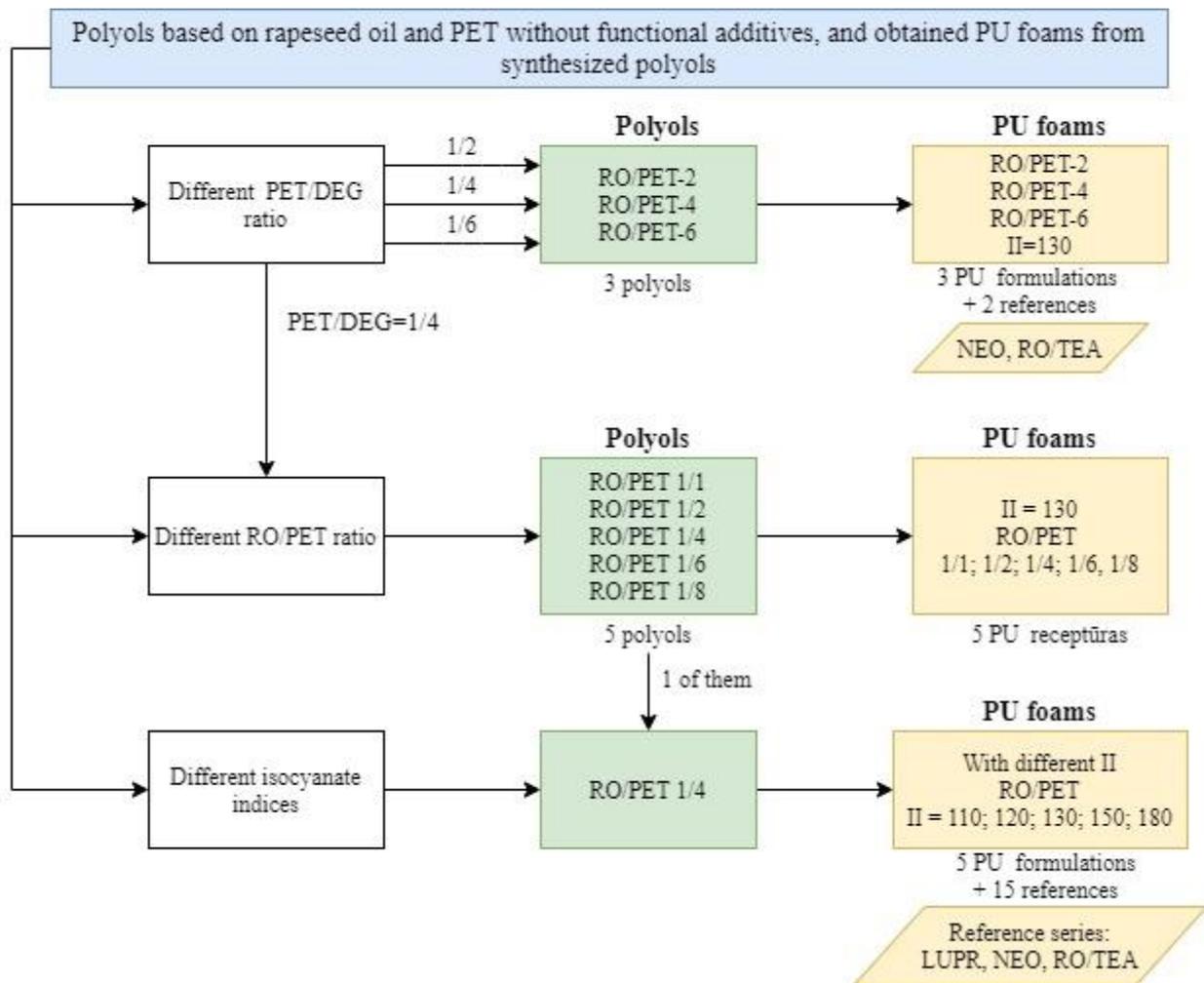


Fig. 2.1. Schematic experimental plan for RO/PET polyol synthesis and PU foam development.

Five TO/PET polyols were synthesized from tall oil and PET and series of PU foams with  $II = 130$  were obtained (Fig. 2.2).

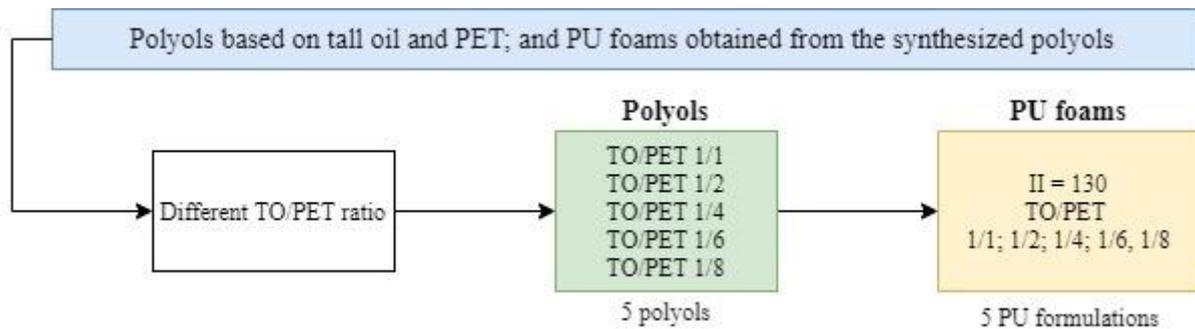


Fig. 2.2. Schematic experimental plan for TO/PET polyol synthesis and PU foam development.

Schematic plan of the experiments for the synthesis of rapeseed oil and PET polyols with functional additives GL and ADA is shown in Figure 2.3. First, seven polyols were synthesized by depolymerizing PET with DEG and adding GL and ADA in various ratios. The resulting polyols were named GL/ADA polyols. Afterwards, these polyols were transesterified with RO/TEA polyol and seven new polyols were obtained, named GL/ADA-RO polyols. Fourteen PU formulations with  $II = 130$  were developed and PU foams were obtained. For three of the rigid PU foam formulations, the viscoelastic and thermal properties were described in more detail in a separate publication [43].

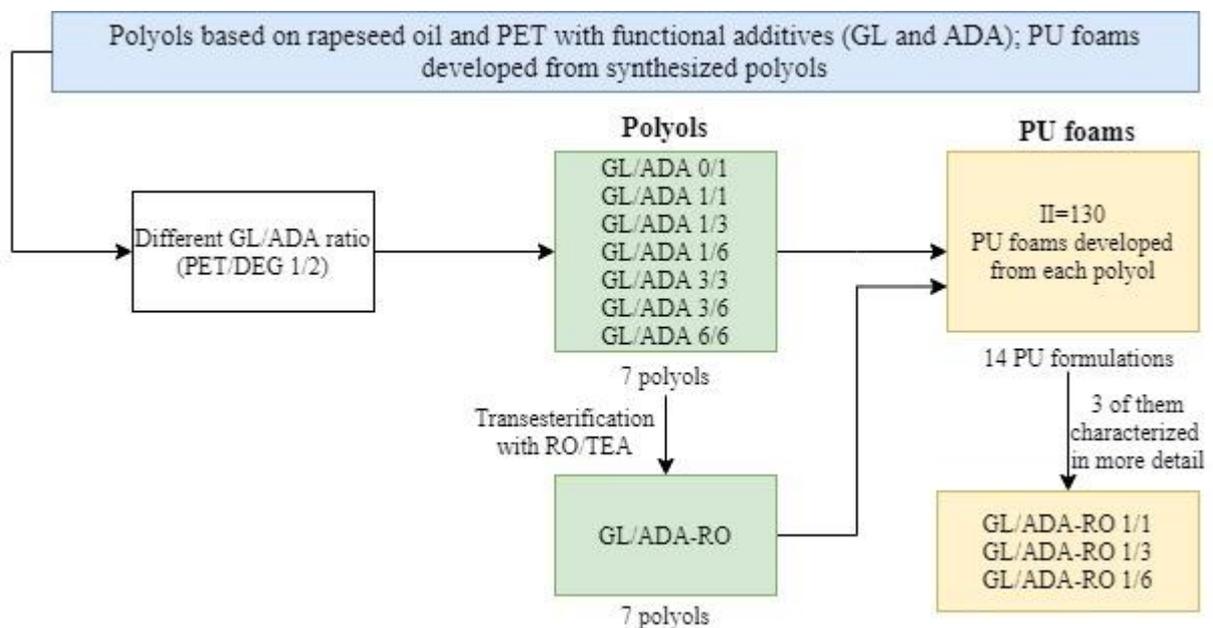


Fig. 2.3. Schematic experimental plan for GL/ADA and GL/ADA-RO polyol synthesis and PU foam development.

## 2.2. Synthesis and Characterization of Polyols

All polyols were synthesized in a 1 L three-necked flask equipped with a mechanical stirrer, a thermometer, and an argon inlet capillary.

RO/PET polyols were obtained in a continuous two-step synthesis.

1. In the first step, rapeseed oil was transesterified with TEA at  $170\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  for 1 hour in the presence of the catalyst zinc acetate. The molar RO/TEA ratio was 1 : 2.9, zinc acetate was added 0.15 % by weight of the raw materials (rapeseed oil and TEA). The idealized reaction scheme is given in Figure 2.4.

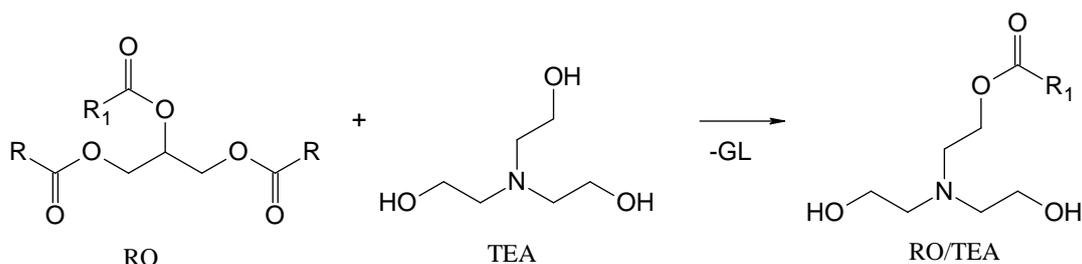


Fig. 2.4. Rapeseed oil transesterification with TEA.

2. In the second step, the temperature was raised to  $230\text{ }^{\circ}\text{C}$  and PET, DEG, and additional Zn acetate (0.5 % by weight of PET) were added to the reaction mixture. The temperature of  $220\text{--}230\text{ }^{\circ}\text{C}$  was maintained for 4 hours. The idealized reaction scheme is given in Figure 2.5. At the same time, the aromatic polyester was transesterified with RO/TEA polyol.

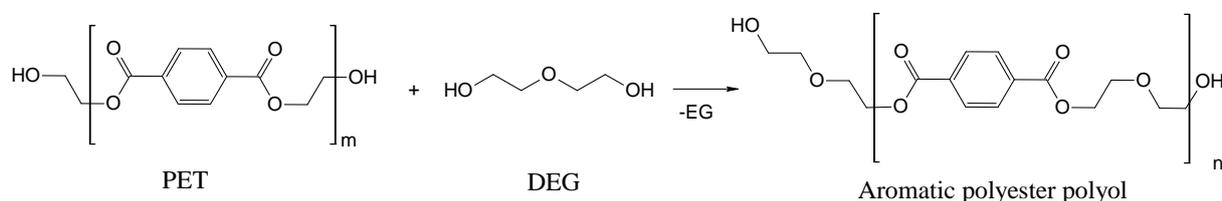


Fig. 2.5. PET glycolysis with DEG.

To obtain GL/ADA-RO polyols, three sequential syntheses were required.

1. In the first synthesis, aromatic polyester polyols were obtained by glycolysis of PET with DEG in the presence of zinc acetate. First, DEG was heated to  $190\text{ }^{\circ}\text{C}$ , zinc acetate, and GL were added. ADA was added after 20–30 minutes, PET was added after another 20–30 minutes. The reaction temperature was raised to  $240\text{--}250\text{ }^{\circ}\text{C}$ . When all the PET had melted, the synthesis was continued for another 1 h. In total, the mixture was heated for 3 h at  $240\text{--}250\text{ }^{\circ}\text{C}$ .
2. In the second synthesis, RO/TEA polyol was synthesized separately as described above.
3. In the third synthesis, RO/TEA polyol was transesterified with the obtained GL/ADA polyols at  $180\text{ }^{\circ}\text{C}$  for 1 hour, polyol weight ratio 1 : 1.

TO/PET polyols were synthesized similarly to RO/PET polyols, but in 2 separate syntheses.

1. At first, tall oil transesterification with TEA (TO/TEA = 1/1.33 M) was carried out (reaction scheme in Fig. 2.6). Tall oil was heated to  $175\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  under argon, then

TEA heated to 70 °C was added. The esterification was carried out for 4 to 5 hours at 175 °C ± 5 °C until the acid number was less than 5 (mg KOH)/g. The vacuum distillation was then carried out at a pressure of 0.267 bar.

- Zinc acetate and DEG heated to 70 °C were added to the TO/PET polyol at 210 °C. PET flakes were added in 2 portions at 30 min intervals. After the PET flakes had dissolved, the temperature was raised to 235 °C, and the synthesis was continued for 4 h. Then the reaction mixture was allowed to cool down to room temperature.

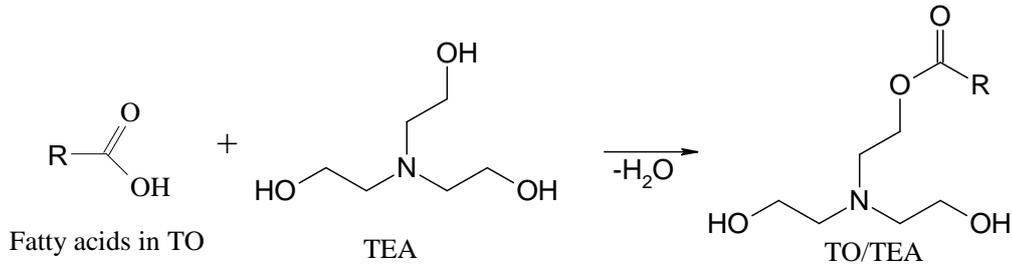


Fig. 2.6. Tall oil esterification with TEA.

The synthesized polyols were characterized by the methods summarized in Table 2.1.

Table 2.1

Methods for Characterization of Polyols

Parameter	Description/standard
Hydroxyl value ( $OH_v$ )	Acetylation method, DIN 53240
Acid value	DIN 53402
Water content ( $w_{H_2O}$ )	Carl Fisher method, DIN 54777
Viscosity	Haake Viscotester 6L/R 20 °C
Chemical structure	FTIR-ATR; Perkin-Elmer Spectrum One FTIR spektrometers, 4000 $cm^{-1}$ to 650 $cm^{-1}$ , resolution 4 $cm^{-1}$
Compatibility with blowing agents	To 10 g of polyol add 20 % Solkane 365/227 or pentane, centrifuge for 15 min at 55 rpm. It is then visually observed for phase separation
Long-term stability	Visual observation at room temperature for 3 months

### 2.3. PU Foam Formulation, Obtaining, and Characterization

The formulations of polyol components (Table 2.2) included the synthesized base polyol, the high-functionality polyol as a crosslinking reagent – Lupranol 3422, the flame retardant Levagard PP (trichloropropyl phosphate), the catalysts PC CAT NP-10 and potassium acetate (KAc) in DEG solution, foaming agent Solkane 365/227, and water. To compare the obtained foams with each other, the formulations were similar for all series. The amount of foaming agents was adjusted so that the apparent density of the obtained PU foams would be ~40–45  $kg/m^3$ . The chosen density is optimal for PU thermal insulation materials.

PU foams were obtained by reacting a polyol component with polymerized diphenylmethane diisocyanate (PMDI) by mixing with a mechanical stirrer (2000 rpm) for 5 to 10 s. After mixing the components, the resulting mixture was poured into a mold (0.5 L cups or 30 cm × 30 cm × 15 cm box) and allowed to foam freely. The foaming height in the box did not exceed 8 cm. After 24 h, the samples were cut to the required size for further testing.

Table 2.2

## Polyol Component Formulations for Rigid PU Foams

Raw materials	Amount, pbw				
	PET/DEG $II = 130$	RO/PET $II = 130$	RO/PET $II = 110-180$ and references	GL/ADA and GL/ADA-RO $II = 130$	TO/PET $II = 130$
Base polyol	70	75	75	70	75
Lupranol 3422	30	25	25	30	25
Levagard PP	16	16	20	16	20
NIAX Silicone L6915	1.5	1.5	2.0	1.5	2
30 % KAc solution in DEG	0	0	1.0-1.5 <sup>1</sup>	0	1.2
PC CAT NP-10	1.6	1.6	1.6-4.0 <sup>2</sup>	1.6	1.2
Water	2.2	2.2	2.2	2.2	0
Solkane 365/227	16	16	16	16	25

<sup>1</sup> only for  $II = 150$  and  $II = 180$  formulations

<sup>2</sup> 4,0 pbw were added for LUPR series to improve reactivity

The required amount of PMDI is calculated according to Formula (3.1) formula:

$$m_{\text{PMDI}} = \frac{II}{w_{\text{NCO}}} \left( \sum \frac{OH_{\text{skn}} m_n}{1336} + 4.67 m_{\text{H}_2\text{O}} \right), \quad (3.1)$$

where  $II$  – isocyanate index;  $m_{\text{PMDI}}$  – mass of PMDI, g;  $w_{\text{NCO}}$  – content of NCO groups in PMDI, % ( $w_{\text{NCO}} = 31.5\%$ );  $OH_{\text{vn}}$  – polyol n hydroxyl number, (mg KOH)/g;  $m_{\text{H}_2\text{O}}$  – mass of water, g.

The methods used for the characterization of PU foams are summarized in Table 2.3.

Table 2.3

## Methods Used for Characterization of Rigid PU Foams

Parameters	Description/standard
Foaming parameters	Start, gel and tack-free time by visual observation
Apparent density	ISO 845
Closed-cell content	ISO 4590
Thermal conductivity	ISO 8301
Compression strength and elastic modulus	ISO 844 – Compression strength and modulus of elasticity were normalized to an apparent density of 45 kg/m <sup>3</sup> using Hawkins <i>et al.</i> equations [44]: $E_{\text{norm}} = E_{\text{exp}} \left( \frac{45}{\rho} \right)^{1.7} \text{ and } \sigma_{\text{norm}} = \sigma_{\text{exp}} \left( \frac{45}{\rho} \right)^{2.1}, \text{ where}$ $E_{\text{norm}}$ – normalized modulus of elasticity; $E_{\text{exp}}$ – experimental modulus of elasticity; $\rho$ – apparent density of the foam; $\sigma_{\text{norm}}$ – normalized compression strength; $\sigma_{\text{exp}}$ – experimental compression strength
Anisotropy	Is calculated by dividing the compressive strength parallel to the foaming direction by the compressive strength perpendicular to the foaming direction
Water absorption	ISO 2896 by immersion for 7 days
Dimensional stability	ISO 2796, 2 modes: 1) 28 days at 70 °C temperature, dry conditions; 2) 28 days at 70 °C temperature, relative humidity $R.H. = 97\%$
Chemical structure	FTIR-ATR; Perkin-Elmer Spectrum One FTIR spectrophotometer 4000 cm <sup>-1</sup> to 650 cm <sup>-1</sup> , resolution 4 cm <sup>-1</sup>
Morphology	Optical microscopy, scanning electron microscopy
Thermal properties	Thermogravimetry, thermomechanical analysis, differential scanning calorimetry
Viscoelastic properties	Dynamic mechanical analysis (DMA) in compression mode

### 3. SUMMARY OF RESULTS

#### 3.1. Polyols

##### 3.1.1. Chemical Structure of Polyols

In the synthesis of RO/PET polyols, esterification of rapeseed oil with TEA (results in RO/TEA polyol), PET glycolysis, as well as transesterification of the obtained aromatic polyester polyol with RO/TEA polyol took place. Similarly, TO/PET polyols were synthesized by transesterification of aromatic polyester with TO/TEA polyol. Some of the possible reactions are given in Figure 3.1.

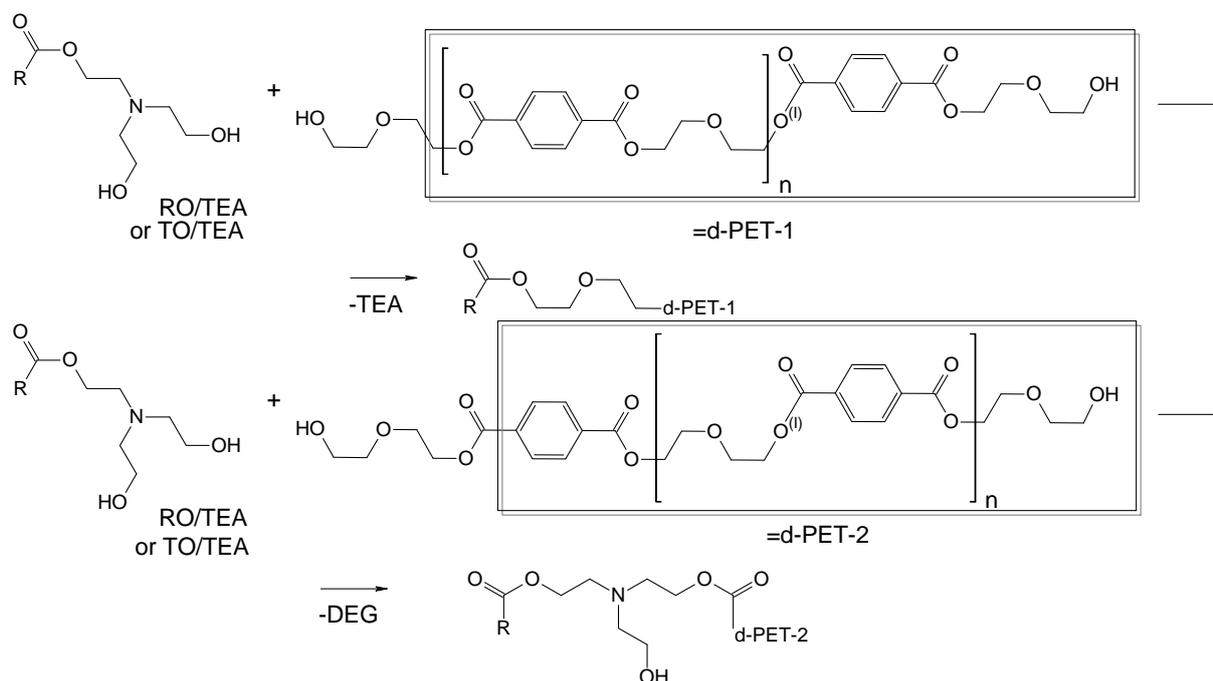


Fig. 3.1. Possible reactions for transesterification of the aromatic polyester polyol with RO/TEA or TO/TEA polyol.

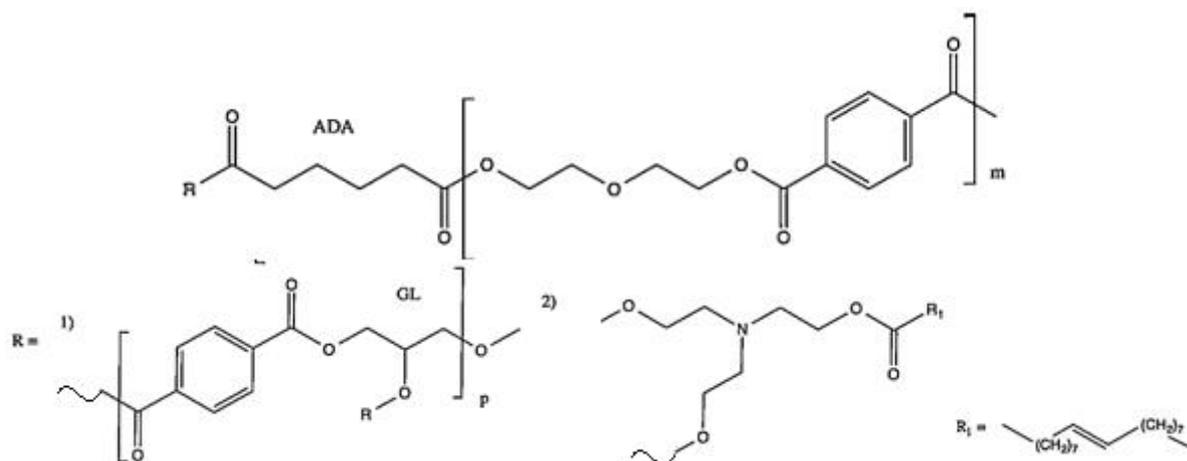


Fig. 3.2. Possible structure of GL/ADA-RO polyols with structure fragments of GL and ADA.

In the synthesis of GL/ADA-RO polyols, fragments of GL and ADA structures were incorporated in the polyol structure (Fig. 3.2). GL serves as a cross-linking reagent and ADA as a chain extender.

FTIR-ATR analysis was performed to characterize the chemical structure of polyols. The results are shown in Figure 3.3. Spectra of RO/TEA and NEO polyol were also added to compare the polyols. 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 Figure 3.3 d.

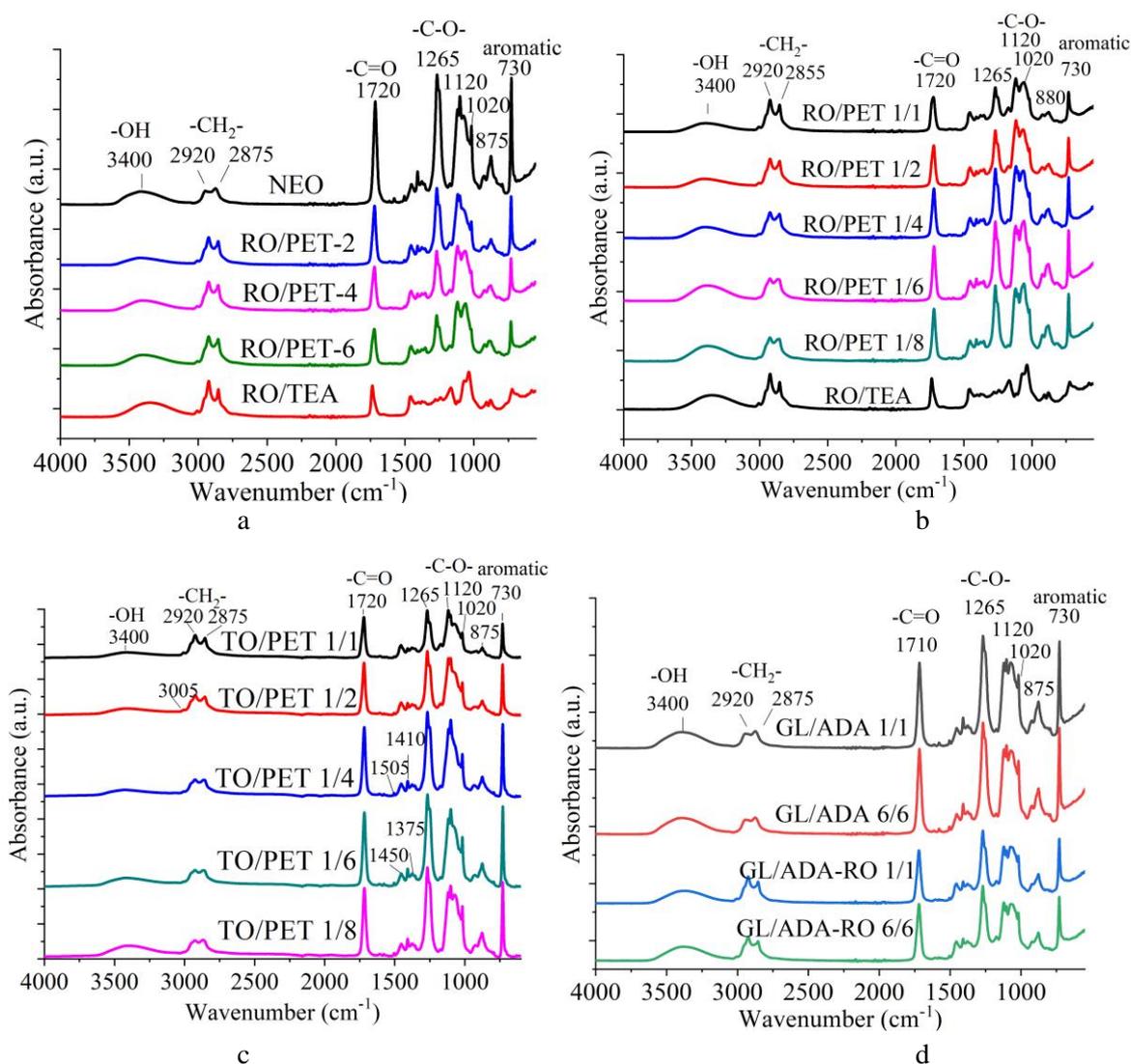


Fig. 3.3. FTIR-ATR spectra of synthesized polyols: a) RO/PET polyols with different PET/DEG ratios; b) polyols with different RO/PET ratios; c) TO/PET polyols; d) GL/ADA and GL/ADA-RO polyols.

For the synthesized polyols, similar relationships are observed in the FTIR-ATR spectra:

1. The band at  $3400\text{ cm}^{-1}$  (valence fluctuations of hydroxyl groups) increases by the increasing amount of PET and correlates with  $OH_v$  (Table 3.1).
2. For TO/PET polyols, a small peak at  $3005\text{ cm}^{-1}$  corresponds to cis-double bond stretching from oleic and linoleic acid in tall oil, therefore this peak increases for polyols with higher tall oil content.
3. Symmetric and asymmetric stretching of  $CH_2$  (two bands at  $2920\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$ ) are more intense for polyols with a higher amount of rapeseed oil. Absorption in this region results from the long fatty acid side chains.
4. A sharp band at  $1720\text{ cm}^{-1}$  corresponds to the carbonyl  $C=O$  bonds in the ester groups. With depolymerized PET more ester bonds are introduced into the structure of polyols. The absorption intensity for GL/ADA-RO polyols is less than for GL/ADA polyols, which is in line with the decrease in the number of ester groups due to the transesterification reaction.
5. The presence of depolymerized PET aromatic structures is confirmed by two small peaks  $-C=C$  stretching vibrations at  $1505\text{ cm}^{-1}$  and  $1410\text{ cm}^{-1}$ , as well as absorption bands of bending and stretching vibrations of aromatic  $C-H$  at  $875\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$ , and the stretching vibration band of the aromatic  $C-O$  carbonyl group at  $1265\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$ .
6. A peak around  $1450\text{ cm}^{-1}$  indicates the presence of methylene groups, while an additional peak at about  $1375\text{ cm}^{-1}$  is caused by a methyl group.
7. A small peak at  $892\text{ cm}^{-1}$  (over-lapped with a peak at  $875\text{ cm}^{-1}$ ) corresponds to the  $-OC_2H_4$  moieties of DEG backbone, and a small peak at  $920\text{ cm}^{-1}$  is due to the vibrations of  $C-O$  in DEG. These two peaks form the basis of DEG detection [45].

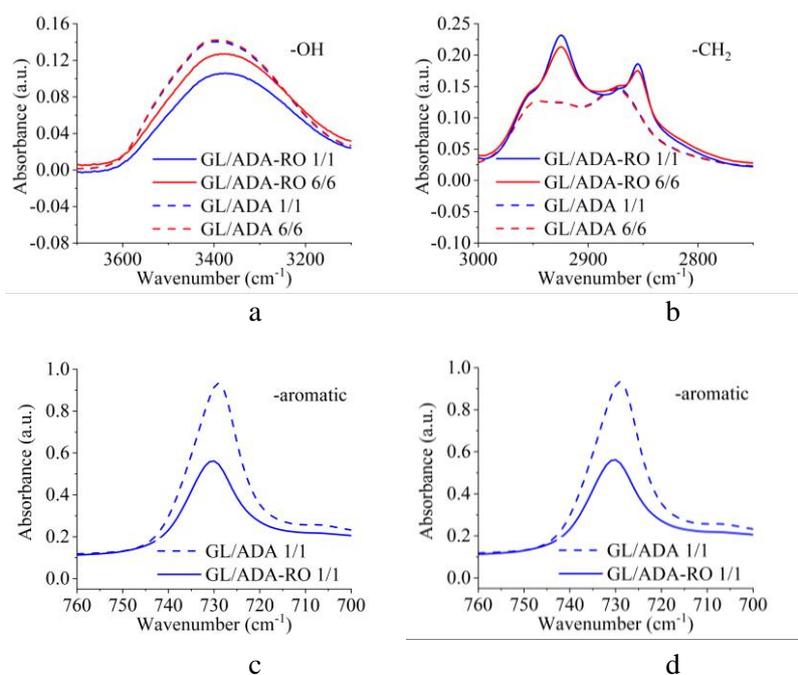


Fig. 3.4. FTIR spectra for GL/ADA and GL/ADA-RO polyols: a)  $-OH$ ; b)  $-CH_2-$ ; c) aromatic group absorption at  $875\text{ cm}^{-1}$ ; d) aromatic group absorption at  $730\text{ cm}^{-1}$ .

For GL/ADA and GL/ADA-RO polyols, the ranges of vibrations of hydroxyl, aliphatic bonds, and aromatic groups, which are important for the information on polyol bonds, are shown in more detail in Figure 3.4. The absolute absorption intensity at  $3400\text{ cm}^{-1}$  is higher for GL/ADA polyols associated with higher  $OH_v$  values compared to the GL/ADA-RO polyol series. The OH groups of GL/ADA polyols are consumed for transesterification with RO/TEA polyol. In the  $3000\text{--}2700\text{ cm}^{-1}$  range, two intense bands at  $2920\text{ cm}^{-1}$  and  $2875\text{ cm}^{-1}$  can be observed, which, as mentioned above, is due to the  $\text{CH}_2$  groups in the polymer chain backbone. These characteristic intensities are more pronounced for GL/ADA-RO polyols than for GL/ADA polyols. Another significant difference is the appearance of an absorption band at  $875\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$  corresponding to the aromatic groups from recycled PET oligomers. These absorption bands intensify for GL/ADA-RO polyols, which is consistent with the overall decrease in the recyclate (aromatic component) content in the GL/ADA-RO polyols.

### 3.1.2. Polyol Suitability in the Production of Rigid PU Foams

The properties of developed polyols are summarized in Table 3.1 along with the properties of reference polyols. Further, the suitability of polyols in the production of rigid PU foams was evaluated. The moisture content in all polyols is in acceptable amounts. The moisture content of polyols used in the specific PU formulation is taken into account, water serves as a foaming agent. It is recommended that the acid number is below 5 (mg KOH)/g. Otherwise, polyol systems formulated with amine-type catalysts are unstable because acid groups react with amine groups, making them ineffective. This criterion is almost met by all polyols, except for TO/PET 1/1 and TO/PET 1/2. TO/PET polyols have a higher acid number than other polyols because tall oil contains 20 % resin acids.

$OH_v$  of the obtained polyols vary in a wide range from 193 (mg KOH)/g (for TO/PET 1/1 polyol) to 520 (mg KOH)/g (for RO/PET 1/8 polyol).  $OH_v$  is higher for polyols that contain more recycled PET. This is due to both the higher  $OH_v$  of aromatic polyester than RO/TEA and TO/TEA polyols and the excess of DEG used in polyol synthesis. Polyols with such  $OH_v$  can be used in the development of rigid PU foams of different densities.

In GL/ADA polyols with increasing concentrations of the functional additives GL and ADA from 0/1 to 6/6,  $OH_v$  increases by 20 % (from 472 (mg KOH)/g to 515 (mg KOH)/g). After the transesterification reaction, GL/ADA-RO polyols  $OH_v$  decrease by ~20 %.

In PET glycolysis oligomeric polyols with high viscosity (for polyol GL/ADA 0/1 polyol  $\mu = 3130\text{ mPa}\cdot\text{s}$ ) were obtained. The addition of a small amount (1–6 %) of GL and/or ADA reduced the viscosity of these polyols by about three times (for GL/ADA 6/6 polyol  $\mu = 1165\text{ mPa}\cdot\text{s}$ ). Low-viscosity polyols have several advantages: more efficient mixing of polyol systems is possible (which affects the homogeneity and quality of the foam) and easiness of processing polyol in the production of rigid PU foam [46]. The viscosity of RO/PET polyols is ~20 times lower than that of the commercially available aromatic polyester polyol NEO, but only three times higher than that of RO/TEA polyol.

Table 3.1

## Polyol Characteristics

Polyol series	Sample	$OH_v$ , (mg KOH)/g	Acid value, (mg KOH)/g	$w_{H_2O}$ , %	Viscosity $\pm$ 30, 20 °C, mPa·s
RO/PET	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
	RO/PET 1/1	312	3.0	0.38	380
	RO/PET 1/2	322	3.5	0.26	410
	RO/PET 1/4	388	2.6	0.20	400
	RO/PET 1/6	514	1.8	0.18	280
	RO/PET 1/8	520	1.5	0.17	260
GL/ADA	GL/ADA 0/1	472	3.0	0.17	3130
	GL/ADA 1/1	466	2.9	0.18	2490
	GL/ADA 1/3	466	2.6	0.22	2060
	GL/ADA 1/6	492	2.7	0.18	1650
	GL/ADA 3/3	531	1.8	0.11	1260
	GL/ADA 3/6	503	3.2	0.11	1170
	GL/ADA 6/6	515	1.3	0.09	1170
GL/ADA-RO	GL/ADA-RO 0/1	405	4.0	0.11	700
	GL/ADA-RO 1/1	408	4.2	0.14	730
	GL/ADA-RO 1/3	417	2.9	0.09	820
	GL/ADA-RO 1/6	399	2.8	0.13	730
	GL/ADA-RO 3/3	449	2.5	0.10	710
	GL/ADA-RO 3/6	440	2.7	0.16	730
	GL/ADA-RO 6/6	400	3.2	0.11	850
TO/PET	TO/PET 1/1	193	6.2	0.23	1170
	TO/PET 1/2	246	5.5	0.11	1500
	TO/PET 1/4	306	3.6	0.08	1850
	TO/PET 1/6	292	3.4	0.07	2300
	TO/PET 1/8	384	3.7	0.22	2750
Reference	RO/TEA	363	2.5	0.12	160
	Neopolyol 380	366	2.9	0.12	9640
	Lupranol 3300	400	–	0.09	370

The obtained polyols were tested for compatibility with physical foaming agent Solkane 365/227. The compatibility of polyol with the foaming agent determines the stability of the polyol system as well as affects the properties of rigid PU foams, such as shrinkage and dimensional stability. It was verified that all RO/PET and TO/PET polyols are compatible with physical foaming agents – Solkane 365/227 and pentane. Compatibility is good because polyol contains long, non-polar, hydrophobic chain sections that are introduced with rapeseed or tall oil. The aromatic ester polyol Neopolyol 380 showed poor compatibility with the foaming agent – phase separation of the foaming agent was observed (Fig. 3.5 a). GL/ADA polyols were also incompatible with Solkane 365/227. The foaming agent delaminates less (Fig. 3.5 b) by increasing the concentration of GL and ADA in polyol because the number of aliphatic fragments in the polyol increases. All GL/ADA-RO polyols were fully compatible with Solkane 365/227, as the polyols contain long, non-polar aliphatic chains that are introduced with the fatty acid residues in the RO/TEA polyol.

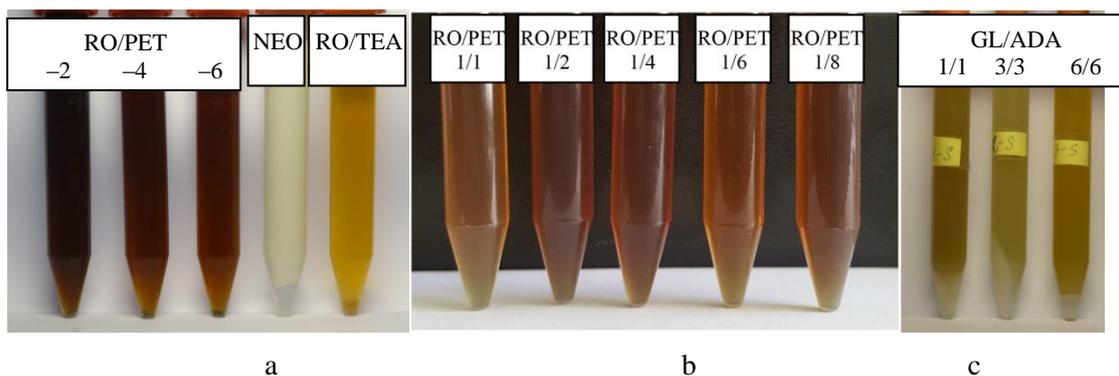


Fig. 3.5. Polyol compatibility with Solkane 365/227: a) RO/PET polyols with different PET/DEG ratio and reference polyols; b) RO/PET polyols 1/1–1/8; c) GL/ADA polyols.

Within half a year, no crystallization was observed for the polyols containing rapeseed or tall oil. The only exceptions were RO/PET 1/8, TO/PET 1/6, and TO/PET 1/8 polyols, which crystallized at room temperature 2 months after synthesis.

### 3.1.3. Sustainable Material Content

The content of renewable and recycled raw materials is shown in Figure 3.6. By increasing the molar ratio of RO/PET from 1/1 to 1/8, the content of sustainable raw materials in RO/PET polyols decreased significantly from 56 % to 39 %. Therefore, a lower RO/PET ratio should be chosen to achieve a higher content of sustainable raw materials. TO/PET polyols have a similar tendency, but the difference between the polyols is smaller: the content of sustainable raw materials varies from 49 % to 55 % depending on the TO/PET ratio. The GL/ADA and GL/ADA-RO series polyols are plotted as series averages, as the difference between the content of renewable and recycled raw materials of polyols of the same series was very minimal (within 5 %). GL/ADA polyols contain on average 45 % of sustainable raw materials (consisting only of recycled materials), while sustainable material content of GL/ADA-RO polyols reached as much as 56 %.

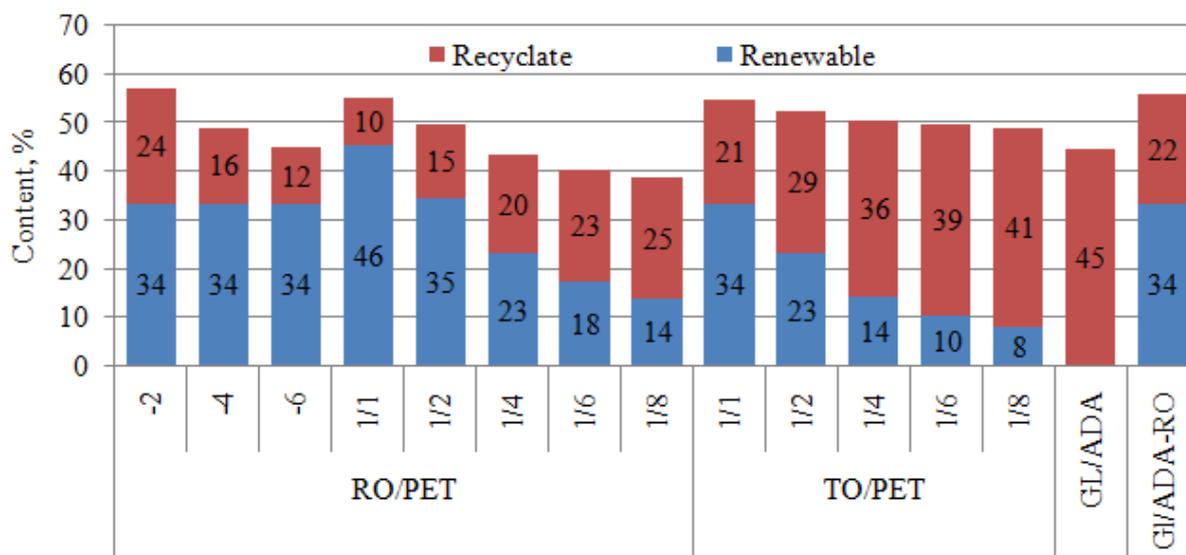


Fig. 3.6. Recycled and renewable raw material content in synthesized polyols.

### 3.2. Rigid PU foams

Rigid PU foams with  $II = 130$  were obtained from all synthesized polyols. As well as rigid PU foam series with  $II = 110; 120; 130; 150; 180$  based on RO/PET 1/4 and reference polyols. The apparent densities of the obtained PU foams are given in Table 3.2, which also shows the results of closed-cell content and water absorption. The aim was to obtain foam with an apparent density of 40–45 kg/m<sup>3</sup>, as high as possible closed-cell content and as low as possible water absorption. The apparent density, closed-cell content >90 vol. %, and the water absorption (maximum 2–5 vol. %) correspond to the typical materials used for thermal insulation [44], [45].

Table 3.2

Apparent Density, Closed-Cell Content and Water Absorption of PU Foams

Series	Sample	Apparent density, kg/m <sup>3</sup>	Closed-cell content $\pm 1$ , vol. %	Water absorption in 7 days $\pm 0.1$ , vol. %
RO/PET (with different PET/DEG ratio)	PUR NEO	42.0 $\pm$ 0.4	96	2.1
	PUR RO/PET-2	42.0 $\pm$ 0.7	95	2.3
	PUR RO/PET-4	45.3 $\pm$ 0.1	95	2.6
	PUR RO/PET-6	42.0 $\pm$ 0.3	96	2.7
	PUR RO/TEA	45.2 $\pm$ 0.4	95	3.4
RO/PET (with different RO/PET ratio) $II = 130$	PUR RO/PET 1/1	44.6 $\pm$ 1.5	97	2.1
	PUR RO/PET 1/2	41.3 $\pm$ 2.0	97	2.0
	PUR-RO/PET 1/4	44.8 $\pm$ 1.5	96	2.0
	PUR RO/PET 1/6	45.8 $\pm$ 1.2	95	2.1
	PUR RO/PET 1/8	48.0 $\pm$ 0.5	92	2.1
RO/PET with different isocyanate indices (based on polyol RO/PET 1/4)	RO/PET $II = 110$	39.1 $\pm$ 0.4	95	2.9
	RO/PET $II = 120$	38.5 $\pm$ 0.1	98	3.1
	RO/PET $II = 130$	44.3 $\pm$ 1.3	98	2.9
	RO/PET $II = 150$	39.1 $\pm$ 0.4	99	2.6
	RO/PET $II = 180$	41.7 $\pm$ 0.1	97	3.1
TO/PET	TO/PET 1/1	47.5 $\pm$ 0.5	– <sup>1</sup>	– <sup>1</sup>
	TO/PET 1/2	43.2 $\pm$ 0.6	– <sup>1</sup>	– <sup>1</sup>
	TO/PET 1/4	43.5 $\pm$ 1.2	92	2.4
	TO/PET 1/6	42.0 $\pm$ 1.2	96	2.3
	TO/PET 1/8	41.4 $\pm$ 0.2	97	2.4
GL/ADA	GL/ADA 0/1	42.6 $\pm$ 1.3	95	2.2
	GL/ADA 1/1	42.5 $\pm$ 0.7	96	2.2
	GL/ADA 1/3	42.8 $\pm$ 0.6	93	2.5
	GL/ADA 1/6	43.1 $\pm$ 0.6	97	2.8
	GL/ADA 3/3	45.9 $\pm$ 0.8	90	1.9
	GL/ADA 3/6	45.1 $\pm$ 0.7	91	2.2
	GL/ADA 6/6	45.9 $\pm$ 0.9	98	2.3
GL/ADA-RO	GL/ADA-RO 0/1	38.3 $\pm$ 1.3	96	3.3
	GL/ADA-RO 1/1	37.7 $\pm$ 1.5	95	3.2
	GL/ADA-RO 1/3	38.8 $\pm$ 1.1	94	3.2
	GL/ADA-RO 1/6	47.2 $\pm$ 0.9	94	3.1
	GL/ADA-RO 3/3	44.7 $\pm$ 0.5	93	1.9
	GL/ADA-RO 3/6	46.4 $\pm$ 0.3	97	3.3
	GL/ADA-RO 6/6	52.5 $\pm$ 0.4	93	2.3

<sup>1</sup> not measured because of the material shrinkage.

### 3.2.1. Rigid PU Foams Based on Polyols With Different PET/DEG Ratios

From RO/PET polyols with different PET/DEG molar ratios (1/2 M, 1/4 M, 1/6 M) PU foams with  $II = 130$  were obtained (respectively named RO/PET-2, RO/PET-4, RO/PET-6) to select the optimal PET/DEG ratio for further syntheses. The compressive strength and thermal conductivity of the obtained rigid PU foams were compared with the reference foams NEO (based on Neopolyol 380) and RO/TEA (based on RO/TEA polyol). The results of compression strength parallel and perpendicular to the direction of foaming are shown in Figure 3.7. The calculated anisotropy was in the range of 1.2 to 1.7, which is typical for free-rise foams. RO/PET-2 and RO/PET-4 showed the same compression strength as NEO ( $0.28 \text{ MPa} \pm 0.04 \text{ MPa}$ ) within the margin of experimental error.

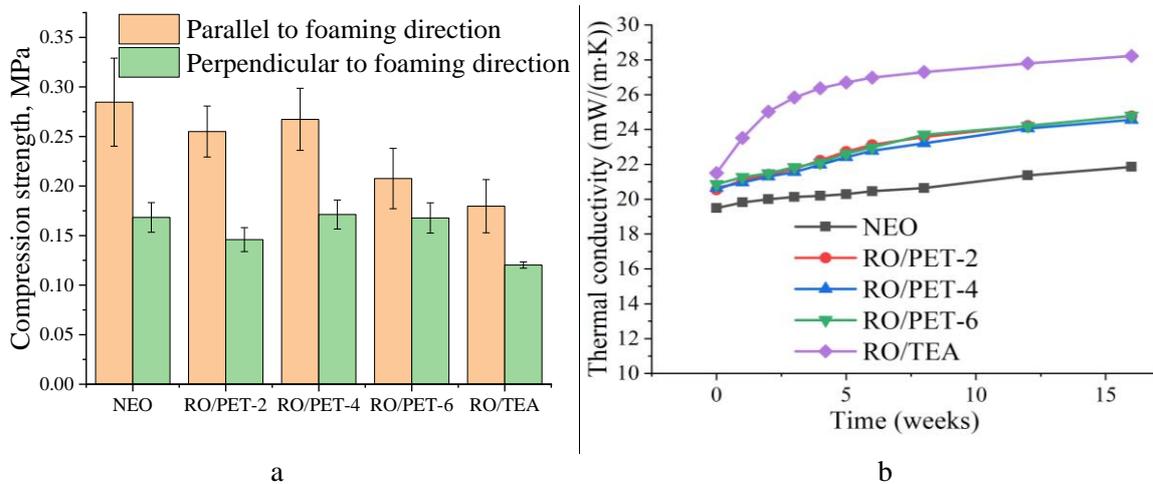


Fig. 3.7. Characteristics of rigid PU foams: a) compression strength; b) thermal conductivity.

The thermal conductivity of the prepared rigid PU foams is one of the most important properties to evaluate suitability of materials for this appliance. In general, thermal conductivity of rigid PU foams depends on the foam density, cell size, closed-cell content, and the thermal conductivity of the gases trapped in the foam cells [49]. Since the foaming agent with low thermal conductivity becomes diluted with air as it diffuses into the foam over time, thermal insulating properties of PU foams worsen (thermal conductivity increases) [50]. The thermal conductivity of Solkane 365/227,  $\text{CO}_2$ , and air are  $10.9 \text{ mW}/(\text{m}\cdot\text{K})$  [51],  $15.3 \text{ mW}/(\text{m}\cdot\text{K})$ , and  $24.9 \text{ mW}/(\text{m}\cdot\text{K})$  [52]. As rigid PU foams as an insulation material are intended for long-term use, the retention of the thermal conductivity value is also an important property for PU foams.

No difference was found in either the initial or the long-term thermal conductivity between PU foams from the synthesized RO/PET polyols with different PET/DEG ratio. In comparison to reference foams, RO/PET foams had lower thermal conductivity by  $\sim 1.1 \text{ mW}/(\text{m}\cdot\text{K})$  than RO/TEA foams, but higher by  $\sim 0.6 \text{ mW}/(\text{m}\cdot\text{K})$  than NEO foams. These both differences more than doubled, reaching a significant difference of  $\sim 10 \%$  within 16 weeks. It was decided to use PET/DEG 1/2 and 1/4 molar ratios for further polyol syntheses.

### 3.2.2. Rigid PU Foams Based on Polyols With Different RO/PET and TO/PET Ratios

Five polyols with a PET/DEG ratio of 1/4 M and RO/PET ratios ranging from 1/1 M to 1/8 M were synthesized from rapeseed oil and PET. Also, five polyols with PET/DEG ratio of 1/2 M and TO/PET ratios ranging from 1/1 M to 1/8 M were synthesized from tall oil and PET. A series of PU foams with  $II = 130$  was obtained from these polyols. Rigid PU foams from TO/PET 1/1 and TO/PET 2/2 polyols showed significant shrinkage, therefore they were not used for further tests. The shrinkage of these rigid PU foams could be explained by the low  $OH_v$  of polyols as well as increased acid values (Table 3.1). To use TO/PET 1/1 and TO/PET 2/2 polyols in PU foams that have acceptable dimensional stability, the formulations could be adjusted as follows: polyol with higher  $OH_v$  should be added and/or isocyanate index should be increased. For other TO/PET foams and RO/PET foams, the effect of TO/PET or RO/PET ratio on compression strength (Fig. 3.8) and thermal conductivity (over 24 weeks, Fig. 3.9) was evaluated.

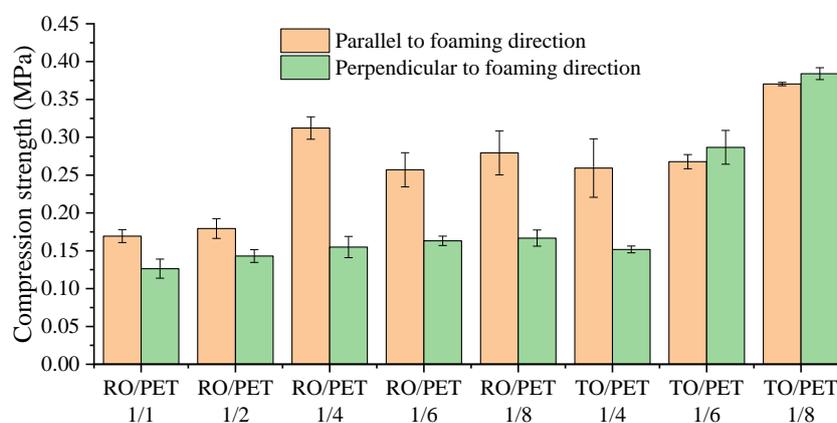


Fig. 3.8. Compression strength of RO/PET un TO/PET rigid PU foams.

The obtained rigid PU foams showed the anisotropy (1.3 to 2.0) typical for free-rised foam. RO/PET 1/4–1/8 foams showed ~2 times higher compression strength than RO/PET 1/1–1/2. The highest compression strength (0.31 MPa  $\pm$  0.01 MPa) was shown by RO/PET 1/4 where the optimal ratio of aromatic groups and fatty acids side chains was reached (Figure 3.8). The compression strength of rigid PU foams increased with the use of polyols with a higher TO/PET ratio. This is consistent with the investigations of Cabulis *et al.* and Van Haveren *et al.* that the incorporation of the aromatic structure into the PU polymer matrix improves mechanical properties of foams [48], [49]. Overall, the showed compression strength meets the requirements for thermal insulation materials for use in construction industry [55].

The initial thermal conductivity of RO/PET foams ranged from 19.7 mW/(m·K) (for RO/PET 1/8 sample) to 21.6 mW/(m·K) (for RO/PET 1/1 sample). Over 24 weeks, the thermal conductivity of all RO/PET samples increases, but still is according to the typical thermal conductivity of PU insulation materials, which is around 18.0 mW/(m·K) to 28.0 mW/(m·K); that is, twice lower than polystyrene, which is an alternative thermal insulation material [1], [5]. Rigid PU foams from RO/PET 1/8 polyol showed the best retention of thermal conductivity. The change in thermal conductivity for this sample was

only 15 % in 24 weeks while for RO/PET 1/1 retention changed by 26 %. Over time, the thermal conductivity increased more slowly for foams with higher PET content.

The initial thermal conductivity of TO/PET rigid PU foams was similar (18.3–19.3 mW/(m·K)) and increased to 22.2–23.1 mW/(m·K) within 10 weeks (Fig. 3.9). TO/PET 1/6 sample showed the lowest thermal conductivity, but in general, the thermal conductivity of all TO/PET foams was equivalent and appropriate for the application as thermal insulation material [1,5]. Although the initial thermal conductivity of TO/PET foams was lower than that of RO/PET foams, their thermal conductivity increased faster over time and within 3 weeks TO/PET 1/6 reached the same thermal conductivity as RO/PET 1/8. Aromatic groups in the polyol structure improve the long-term thermal conductivity of the material.

RO/PET 1/4 polyol was chosen for further studies on the effect of the isocyanate index on the properties of rigid PU foams.

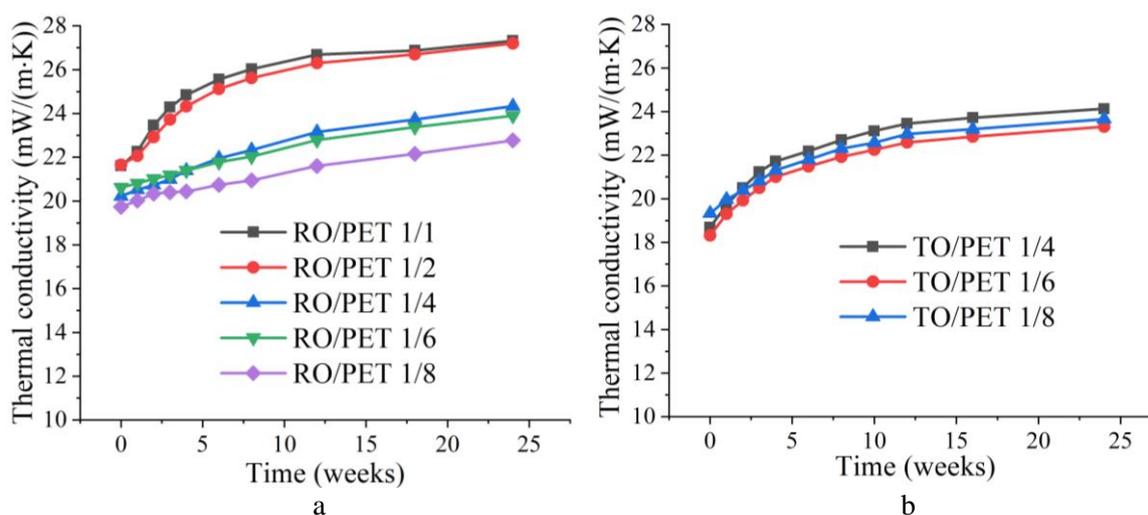


Fig. 3.9. Long term retention of thermal conductivity: a) RO/PET foams; b) TO/PET foams.

### 3.2.3. Rigid PU Foams With Different Isocyanate Indices

It is known that using a higher isocyanate index results in more isocyanurate rings in PU foam as well as in an increase in the amount of non-renewable materials in the final product. The amount of isocyanurate rings in the polymer matrix affects the properties of PU foams – increases the glass transition temperature ( $T_g$ ) and improves dimensional stability as well as thermal insulation properties [15], [39].

To study the effect of the isocyanate index on the properties of rigid PU foams and to discuss the optimal isocyanate index, a series of rigid PU foams with different isocyanate indices ( $II = 110; 120; 130; 150; \text{ and } 180$ ) were obtained from RO/PET 1/4 polyol, as well as several reference foam series – LUPR, NEO, and RO/TEA – based on Lupranol 3300, Neopolyol 380, and RO/TEA polyols, respectively.

It is expected that the crosslinking density will increase at a higher isocyanate index. Two effects contribute to this: 1) the functionality of PMDI is 2.7 and its molecular mass is relatively small (381 g/mol), so it will work as a crosslinking reagent by itself; 2) when isocyanate is added in excess, allophanates, biurets and isocyanurates may be formed via side reactions. That will add additional crosslinking points in the PU polymer matrix.

Additionally, the increase in  $T_g$  is expected for higher crosslinking [46]. FTIR-ATR analysis was carried out for RO/PET series to judge the amount of isocyanurate formation. Since the peak of the isocyanurate group is at  $1410\text{ cm}^{-1}$ , in FTIR curves over the area  $1460\text{--}1340\text{ cm}^{-1}$  are shown. The peak intensities are very similar for foams with  $II = 110\text{--}130$ . KAc, which acts as a trimerization catalyst, was not added to the formulations of these foams. Therefore, both the intensities of the isocyanurate peak and the glass transition temperatures  $T_g$  are similar, which were determined from the damping factor  $\tan\delta$  curves, see Figure 3.10 b. The  $T_g$  RO/PET for  $II = 120$  and  $II = 130$  foams are similar:  $121\text{ }^\circ\text{C}$  and  $129\text{ }^\circ\text{C}$ , respectively. A larger increase in  $T_g$  was observed by increasing the isocyanate index to 150 and 180, then the  $T_g$  reached  $172\text{ }^\circ\text{C}$  for RO/PET  $II = 180$  sample. The results of FTIR and DMA show that the formation of isocyanurates increased the crosslinking density.

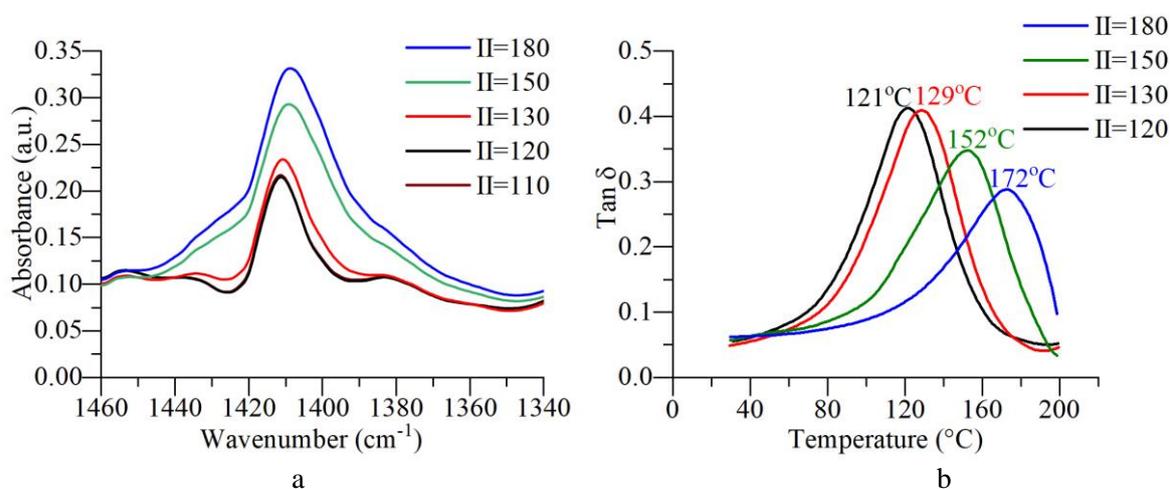


Fig. 3.10. FTIR and DMA results of RO/PET series rigid PU foams: a) isocyanurate band at  $1410\text{ cm}^{-1}$ ; b)  $\tan\delta$  curves with detected  $T_g$  values.

### Compression strength

Both an increase and a decrease in the compression strength of PU foams depending on the isocyanate index have been reported in literature. This is due to differences in the polymer matrix structure and the bulk density of PU foam. In the study of Kuranska *et al.*, two types of polyols were synthesized from rapeseed oil:

- 1) by epoxidation and opening of oxirane rings;
- 2) by transesterification with TEA or transamidation with diethanolamine.

For PU foams from the first type of polyols, the compressive strength decreased with increasing isocyanate index, but the compressive strength increased for PU foams from the second type [57]. In the investigation of Javni *et al.*, the soy polyol based PU foam with the lowest index ( $II = 110$ ) showed the highest compression strength due to the higher apparent density [58]. Similarly, Kim *et al.* showed a decrease in the compression strength by increasing the isocyanate value (from 90 to 130), but also in this case the apparent density of PU foams had a greater effect than the structure of the polymer matrix [41]. In the present study, the results of the compression strength and elastic modulus were normalized to the same apparent density –  $45\text{ kg/m}^3$ .

The compression strength of RO/PET PU foams slightly increased with an increase in the isocyanate index. It raised from  $0.30\text{ MPa}$  (for the sample RO/PET  $II = 110$ ) to  $0.37\text{ MPa}$  (for

the sample RO/PET  $II = 180$ ). The same trend was observed for elastic modulus too, which raised from 6.35 MPa to 7.61 MPa (Fig. 3.11).

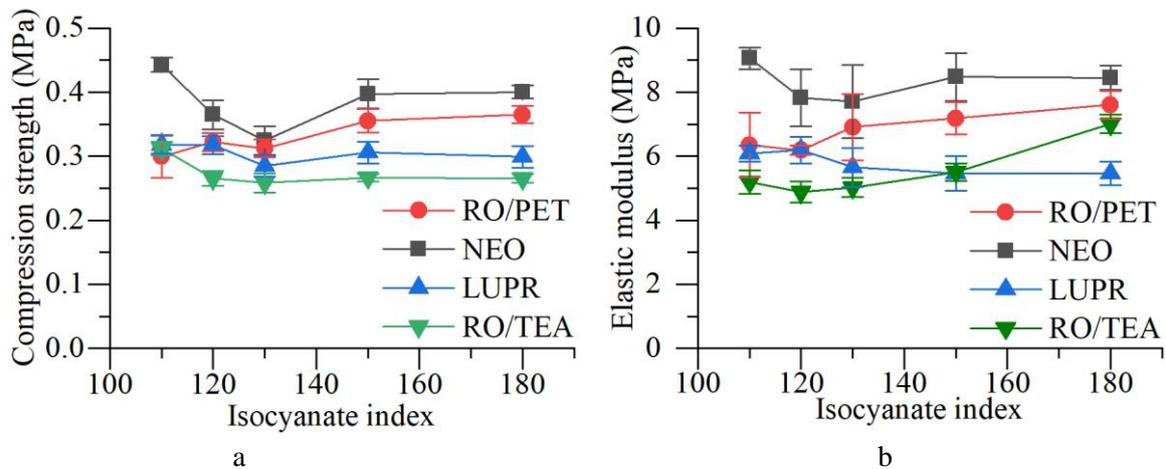


Fig. 3.11. Physical-mechanical properties of PU foams with different isocyanate indices: a) compression strength; b) elastic modulus.

Due to the higher elasticity of the foam, the anisotropy coefficient for RO/PET  $II = 180$  was lower (the anisotropy coefficient was 1.79) than for the samples with a lower isocyanate index (the anisotropy coefficient is 1.85–2.16). The RO/PET foam series had a higher compression strength than the LUPR and RO/TEA series, but slightly lower than the NEO series. For reference foams, the compression strength and modulus of elasticity decreased for samples with an isocyanate index from 110 to 130. This could be due to the lack of a trimerization catalyst – the isocyanate does not trimerize, no additional crosslinking points are formed and unreacted isocyanate remains in the foam. Nevertheless, the compression strength of all samples corresponded to a typical industrially produced rigid PU foam (0.15–0.25 MPa) [58].

### Dimensional stability

The increase of the isocyanate index improves dimensional stability due to the incorporation of the isocyanurate ring into the PU foam matrix [59]. The results of dimensional stability for the RO/PET series and reference foams are presented in Figure 3.12.

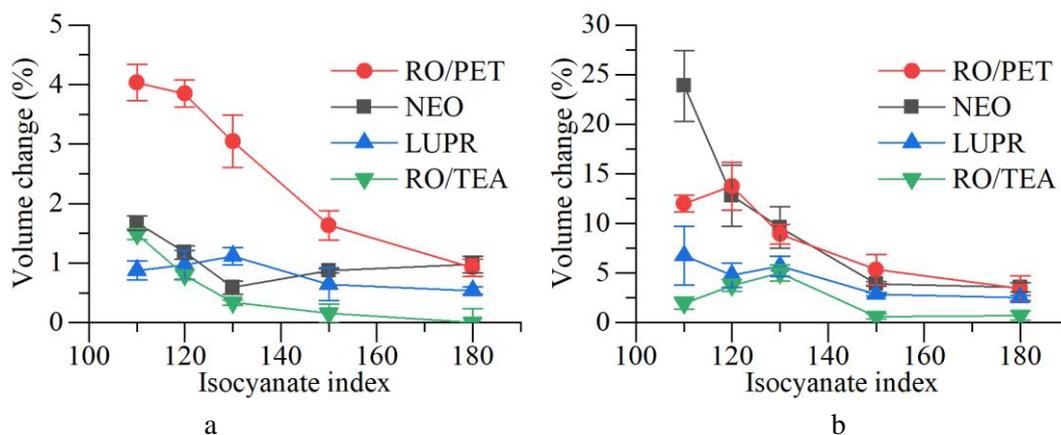


Fig. 3.12. Dimensional stability – relative volume change under 2 test conditions: a) 28 days at 70 °C, dry conditions; b) 28 days at 70 °C,  $R.H. = 97\%$ .

Relative change of volume decreased from 4.0 % to 1.0 % with increasing isocyanate index after 28 days at 70°C, ambient *R.H.* At mode where *R.H.* = 97 %, volume change for RO/PET series was below 15 % and reached the minimum 3.4 % when *II* = 180. Although RO/PET polyols show better compatibility with blowing agents, which could improve dimensional stability, it was not observed in the results of the present study. Overall, starting from *II* = 130 and up, dimensional stability is considered to be acceptable.

### Thermal conductivity

The initial thermal conductivity of rigid PU foams was measured, and the increase of thermal conductivity in the aging process of the material was evaluated. The initial thermal conductivity is given in Figure 3.13 a, which shows that rigid PU foams from RO/PET polyol showed as good thermal insulation properties (series average  $\lambda_{\text{RO/PET}} = (20.7 \pm 0.7) \text{ mW}/(\text{m}\cdot\text{K})$ ) as NEO and LUPR foams from commercially used polyols (series average  $\lambda_{\text{NEO}} = (21.2 \pm 0.7) \text{ mW}/(\text{m}\cdot\text{K})$  and  $\lambda_{\text{LUPR}} = (21.9 \pm 0.2) \text{ mW}/(\text{m}\cdot\text{K})$ ). Rigid PU foam from RO/TEA polyol showed slightly higher thermal conductivity (average  $\lambda_{\text{RO/TEA}} = (22.9 \pm 1.2) \text{ mW}/(\text{m}\cdot\text{K})$ ). The graph also shows that the isocyanate index does not affect the initial thermal conductivity of PU foams significantly.

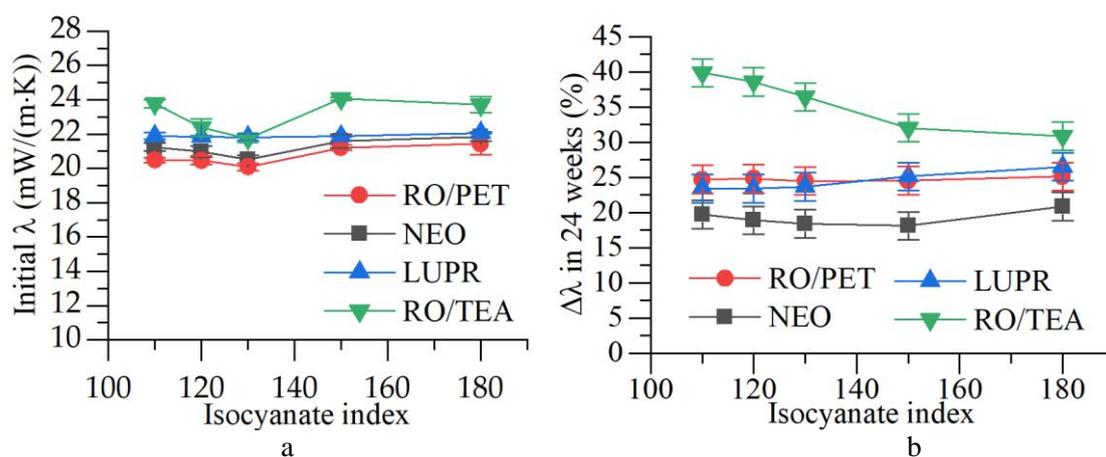


Fig. 3.13. Thermal conductivity of PU foams: a) initial thermal conductivity; b) relative change of thermal conductivity in 24 weeks.

To evaluate the retention of thermal conductivity in the long term, Figure 3.13 b is presented with results of relative change of thermal conductivity in 24 weeks. The best retention of thermal conductivity was shown by the PU foams of NEO series from PET-based aromatic polyester polyol. The retention of thermal conductivity depends on the gas diffusion rate of the blowing agent through rigid PU foam material. This is related to the crosslink density of PU polymer matrix, cohesion energy, and ability of macromolecular conformation of PU 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 the 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 and inward flow of air, thus enhancing long-term thermal conductivity retention.

### 3.2.4. Rigid PU Foams From Polyols With Functional Additives

Rigid PU foams with an apparent density of  $\sim 43 \text{ kg/m}^3$  were obtained from GL/ADA and GL/ADA-RO polyols. The structure, branching, and functionality of the polyol chain can be changed by changing the amount of ADA, GL, and rapeseed oil. The incorporation of fatty oil-based aliphatic fragments from rapeseed oil decreased the viscosity of the polyol and increased the overall flexibility of the molecular chain [60]. As a result of that, PU foams from GL/ADA-RO polyols were with larger and more regular cells than from GL/ADA polyols. The average cell size of the GL/ADA PU foams was about  $330 \text{ }\mu\text{m}$ . Whereas the GL/ADA-RO foams had an average cell size of  $420 \text{ }\mu\text{m}$ , approximately 30 % larger than of GL/ADA foams. Altering the GL/ADA content in the polyol had little effect on the resulting cell size.

#### Compression strength and elastic modulus

The mechanical properties of the PU rigid foams directly depend on the chemical structure of polyols used in their production [61], on the density and developed cell anisotropy [62]. Elasticity (Fig. 3.14) and compression strength (Fig. 3.15) in parallel to the foam rise direction (index  $z$ ) are larger than in the perpendicular to foam rise direction (index  $x$ ) for all compositions, which is indicative of high anisotropy of the cell structure of the foams. Elastic modulus and compression strength increased significantly as greater amounts of functional additives were introduced into the polyols. Increasing the GL content of polyols results in a branched-chain structure with additional hydroxyl groups in the middle of the chains [63]. Consequently, the reaction with the isocyanate results in the formation of a dense PU polymer structure with a higher crosslinking density. The addition of ADA produces extra alkyl soft segments in the PU polymer network [60]. These short soft segments in the PU macromolecular chain are favorable for the conformational mobility and development of the dense networks of hydrogen bonds [46]. The influence of hydrogen bonding on the mechanical properties of rapeseed oil-based PU foams has also been demonstrated previously [60], [61]. Possible reasons for hydrogen bond formation in PUs include ester–urethane, urethane–urethane, and urethane–amide hydrogen bonding. The following examples of improvement in mechanical properties by adding functional additives may be mentioned:  $E_z$  of PU foam GL/ADA 3/3 ( $E_z = 11,5 \text{ MPa}$ ) is almost 3-times higher than for PU foam GL/ADA 0/1 ( $E_z = 3,5 \text{ MPa}$ ); For GL/ADA 0/1  $\sigma_z$  it is  $0,18 \text{ MPa}$ , but for GL/ADA 6/6 almost 2-times higher –  $0,35 \text{ MPa}$ .

The PU rigid foams prepared from GL/ADA polyols had a slightly higher compression strength and elasticity modulus than foams prepared from GL/ADA-RO polyols. It seems likely that the long flexible aliphatic chains (fatty acid chains  $\text{C}_{16}\text{--}\text{C}_{18}$ ), which are present in the PU macromolecular network of the GL/ADA-RO foams, have a plasticizing effect, resulting in improved viscoelasticity of the foams [66]. The distance between the crosslinking points in the PU network was larger 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 [46]. Thus, it can be assumed that a more efficient and stronger hydrogen bonding network

occurs between the functional groups in the PU GL/ADA polymer than in the PU GL/ADA-RO polymer [67].

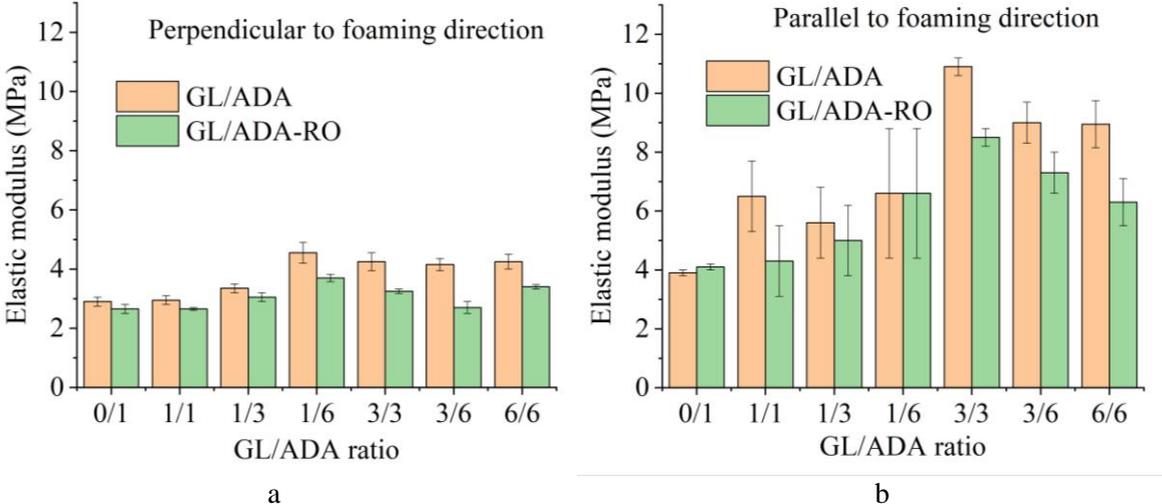


Fig. 3.14. Elastic modulus of GL/ADA and GL/ADA-RO PU foams: a) perpendicular to foaming direction; b) parallel to foaming. direction.

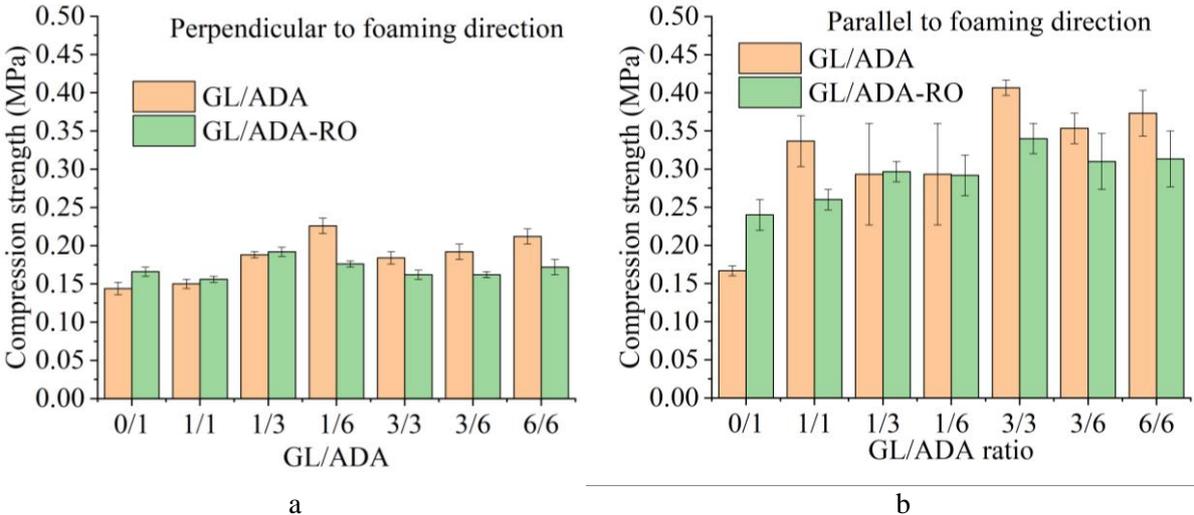


Fig. 3.15. Compression strength of GL/ADA and GL/ADA-RO PU foams: a) perpendicular to foaming direction; b) parallel to foaming direction.

**Storage, loss modulus, and glass transition temperature**

The DMA of PU foams was recorded versus the temperature at the heating operation mode (Fig. 3.16). Viscoelasticity of polymer material improves and rigidity drops, while the operation temperature increases due to the dominance of viscous flow of the macromolecular chain. The loss modulus of PU foams GL/ADA-RO 1/1, GL/ADA-RO 1/3, and GL/ADA-RO 1/6 had 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 [68]. 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  $E'$ . Peak height intensity of  $\tan\delta$  decreased 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 [69]. This drop in effectivity of energy dissipation after the incorporation of soft dangling segments also greatly confirmed the enhancements of the material's viscoelastic characteristics due to the following factors:

- 1) restrained conformation mobility of the chain segments between the entanglement sites [70];
- 2) strong interactions between the soft-hard segments of the developed chain network [71];
- 3) dense packing density of the soft segments [72].

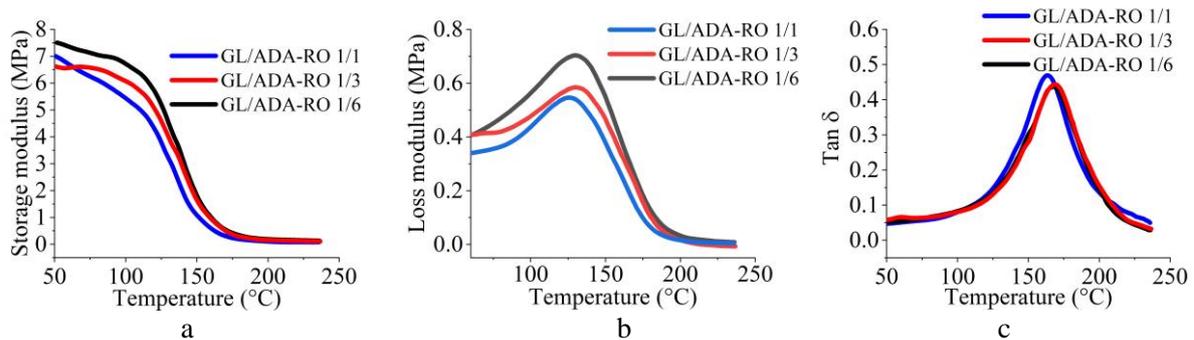


Fig. 3.16. DMA spectra: a) storage modulus  $E'$ ; b) loss modulus  $E''$ ; c)  $\tan \delta$ .

### Thermal conductivity

The time-dependent thermal conductivity of the prepared PU foams is shown in Figure 3.17. The thermal conductivity of foams decreased by 10 % when ADA content increased in the formulations, and this decrease is significant for thermal insulation materials. The obtained cellular structure of the PU foams was very regular, the average cell size was about 110  $\mu\text{m}$ . Altering the ADA content in the polyol did not affect 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 of the chain segments between the entanglement sites in the crosslinked polymer chain network and possible development of additional hydrogen bonding, thereby substantially limiting the diffusion of foaming agent Solkane 365/227 out of cells. Overall, GL/ADA-RO PU rigid foams have sufficient properties to be used for different thermal insulation applications.

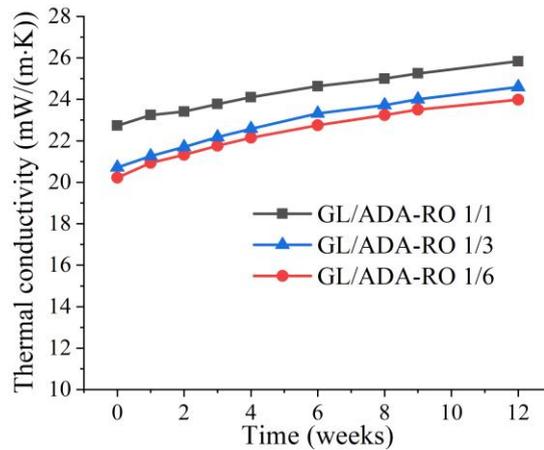


Fig. 3.17. Thermal conductivity of GL/ADA-RO and GL/ADA PU foams.

### 3.2.5. The Most Promising Rigid PU Foams

From all rigid PU foam series, the most promising samples were selected (Table 3.3). The criteria were the thermal insulation and physical-mechanical properties of PU foams, as well as the amount of sustainable raw materials (sum of renewable + recycled raw materials) in the material.

Table 3.3

Characteristics of Most Promising Rigid PU Foams

Sample	Apparent density, kg/m <sup>3</sup>	$\lambda$ , mW/(m·K)	$\lambda_{12weeks}$ , mW/(m·K)	$\sigma_z$ , MPa	Renewable materials, %	Recycled materials, %	Sustainable materials, %
RO/PET-4	45.3 ± 0.1	20.7	24.1	0.27	11.3	3.9	15.2
RO/PET 1/4	44.8 ± 1.5	20.2	23.2	0.31	8.4	4.9	13.3
TO/PET 1/4	43.5 ± 1.2	18.7	23.5	0.26	6.6	10.4	17.1
RO/PET II = 150	39.1 ± 0.4	21.2	25.5	0.36	7.5	4.4	12.0
GL/ADA-RO 1/6	47.2 ± 0.9	20.7	24.6	0.23	10.8	5.4	16.2
GL/ADA-RO 3/3	44.7 ± 0.5	20.2	24.0	0.26	10.5	5.2	15.7

The closed-cell content, thermal conductivity, and compression strength values of rigid PU foams shown in the table are typical of PU thermal insulation material. The highest content of sustainable raw materials (17.1%) is for TO/PET 1/4 PU foam, this foam also showed the lowest initial thermal conductivity. For PU foam derived from rapeseed oil, the maximal content of sustainable raw materials (16.2 %) is for GL/ADA-RO 1/6 PU sample. For all PU foams mentioned in the table, water absorption and dimensional stability are appropriate for the application of thermal insulation material. The base polyols of these PU foams are compatible with the foaming agent Solkane 365/227. Base polyols are stable during long-term storage – they do not crystallize. Their viscosity is from 540 mP·s to 1850 mP·s (which is more than 5 times lower than NEO polyol). The results show that selected polyols and polyol system formulated using these polyols are suitable for the production of rigid PU foams that can be applied as thermal insulation material.

## CONCLUSIONS

1. Characterization of RO/PET and TO/PET polyols, their suitability for obtaining rigid PU foams.
  - a. The viscosity of RO/PET and TO/PET polyols is several times lower than that of aromatic polyester polyols. The lower viscosity improves applicability of polyols in the production of rigid PU foam (no heating required, the polyol system and the reaction mixture including the isocyanate component can be mixed more efficiently, thus obtaining a higher quality material).
  - b. All synthesized RO/PET and TO/PET polyols are compatible with physical foaming agent Solkane 365/227, which is used in the production of rigid PU foams.
  - c. Polyols with an RO/PET ratio of 1/1 M to 1/6 M and a TO/PET ratio of 1/1 M to 1/4 M are stable in long-term storage and no crystallization is observed. Crystallization of polyols is undesirable in the production of rigid PU foams.
  - d.  $OH_v$  varies over a wide range, from 193 mg KOH/g (for TO/PET 1/1 polyol) to 520 (mg KOH)/g (for RO/PET 1/8 polyol).  $OH_v$  is higher for polyols that contain more PET. This is due to both, aromatic polyester's higher  $OH_v$  than RO/TEA and TO/TEA polyols, and with the excess of DEG used in polyol synthesis.
  - e. the moisture content of all synthesized polyols is appropriate for obtaining rigid PU foams.
  - f. the content of sustainable raw materials in polyols reaches up to ~55 %.
  
2. By using functional additives such as GL and ADA in the synthesis of polyols, it is possible to vary and improve the properties of obtained rigid PU foams.
  - a. Glycolysis of PET without the addition of rapeseed oil gives oligomeric polyols with high viscosity (for polyol GL/ADA 0/1  $\mu = 3130$  mPa·s). The addition of a small amount (1–6 wt. %) of GL and/or ADA reduces the viscosity of these polyols by about three times, increases the hydroxyl number, and improves compatibility with foaming agent Solkane 365/227.
  - b. Transesterification of GL/ADA polyols with rapeseed oil polyol gives lower viscosity polyols that are compatible with foaming reagent Solkane 365/227 and are stable during long-term storage.
  - c. Physical-mechanical properties of rigid PU foams are improved when functional additives are added in the synthesis of base polyols.
  - d. Increasing the amount of ADA in the formulation reduces the thermal conductivity of PU foams by 10 %.

3. Influence of aromatic groups on the properties of rigid PU foams.
  - a. Using recycled PET in the synthesis of polyols, aromatic groups are introduced into the structure of polyols. This makes it possible to obtain rigid PU foams with improved properties compared to the PU foams obtained from rapeseed and tall oil polyols without PET.
  - b. As the amount of PET in rigid PU foams increases, the physical-mechanical properties (compression strength) and long-term retention of thermal insulation properties improve.
  
4. The most promising rigid PU foam formulations.
  - a. the optimal TO/PET ratio in polyol is 1/4 M. The acid value for polyols with lower TO/PET ratios is too high ( $>5$  mg KOH/ g) and the resulting rigid PU foams have insufficient dimensional stability. In turn, polyols with higher TO/PET ratios crystallize during storage (in 2 months).
  - b. The optimal RO/PET ratio is from 1/4 M to 1/6 M. For the series with different isocyanate indices, the most promising RO/PET 1/4 polyol was chosen.
  - c. RO/PET 1/4 polyol contains ~44 % of sustainable raw materials, but the most promising polyol TO/PET 1/4 in the TO/PET series – 50 % of sustainable materials.
  - d. Recommended isocyanate index for rigid PU foam from RO/PET 1/4 polyol is  $II = 150$ , which ensures excellent dimensional stability of the foam. The content of sustainable raw materials for such material is 12 %.
  - e. GL/ADA-RO 1/6 and 3/3 polyols have been selected as optimal GL/ADA-RO polyols. Rigid PU foams obtained from them contain ~16 % of sustainable raw materials.

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