

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]. It's 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

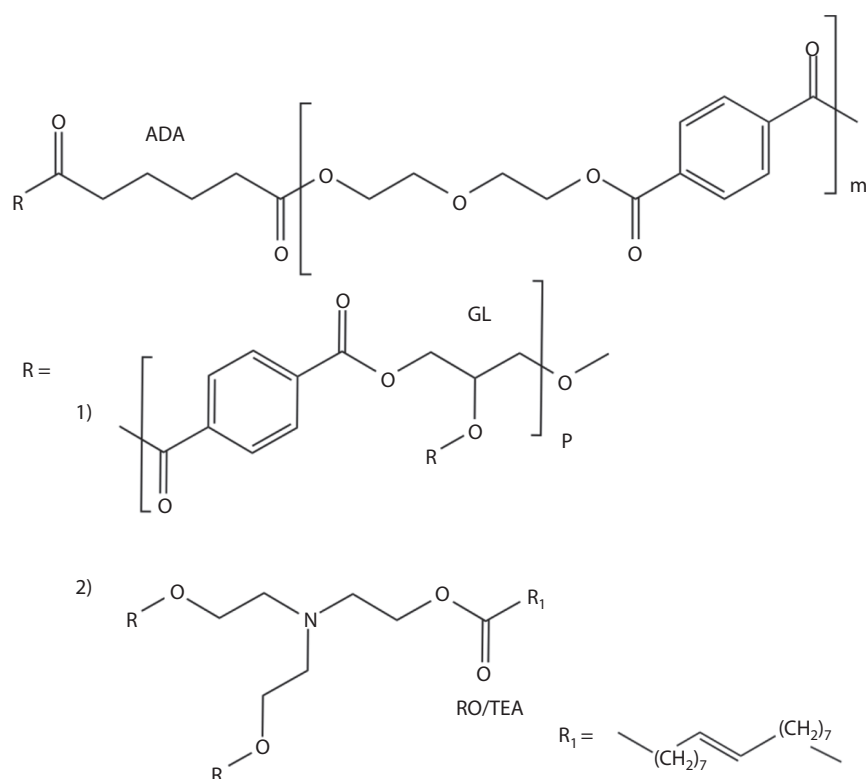
PET flakes of clear grade were obtained from PET Baltija, Latvia. RO (Iodine number = 117 mg/100 g) was supplied by Iecavnieks & Co, Latvia. Triethanolamine (TEA) (99.5%) was supplied by BASF, Germany; zinc

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.

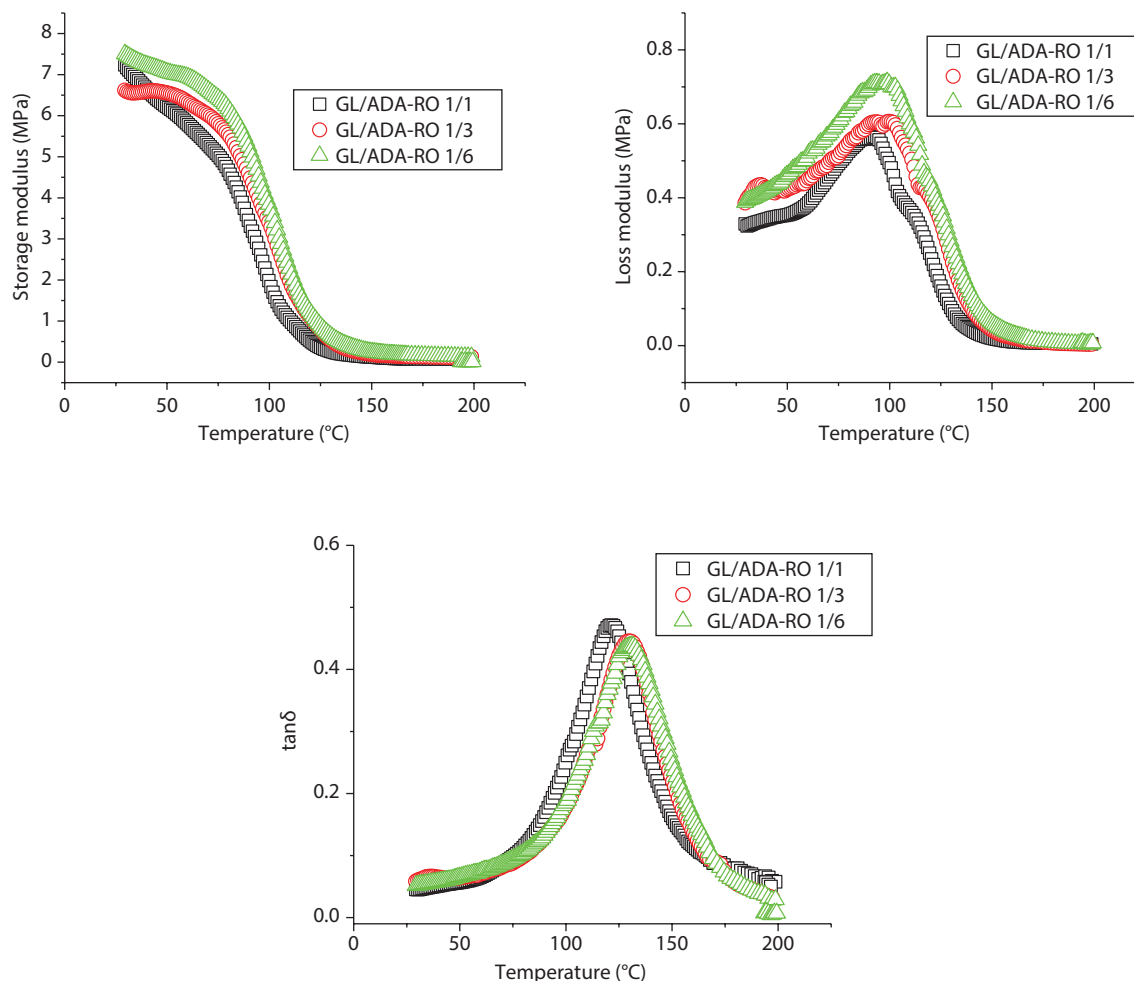
The thermal conductivity of the rigid PUR foams was measured periodically for 8 weeks after the foam's preparation. These tests were carried out based on the ISO 8301 standard using a Linseis Heat Flow Meter 200. The temperature range was 10–30 °C and dimensions of samples were 20 × 20 × 3 cm.

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

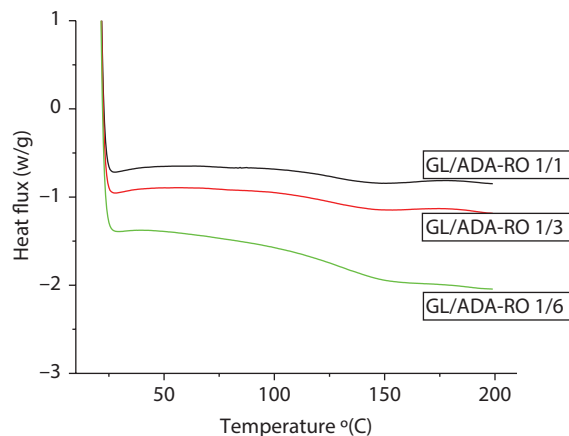
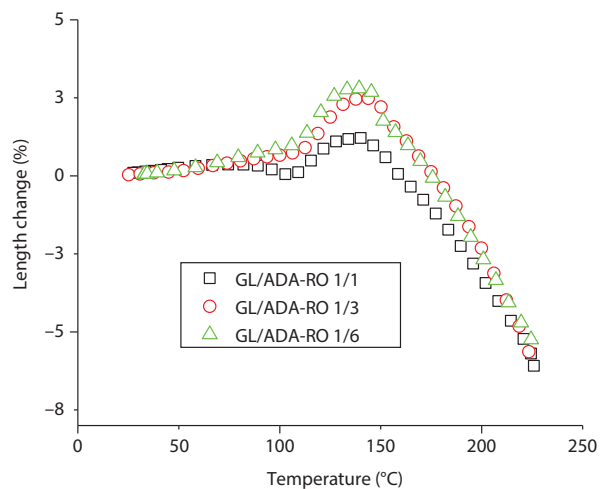
Table 2 Storage modulus, loss modulus and loss factor of PU foams.

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 °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

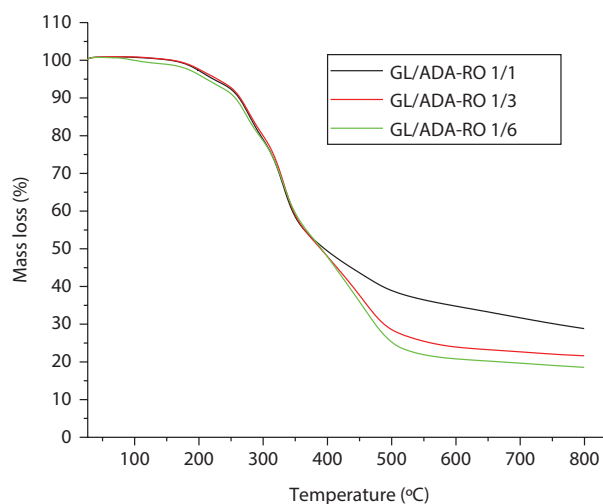


Figure 4 TGA curves of PU foams.

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 (°C)		T_{soft} (°C)	T_{deg} (°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

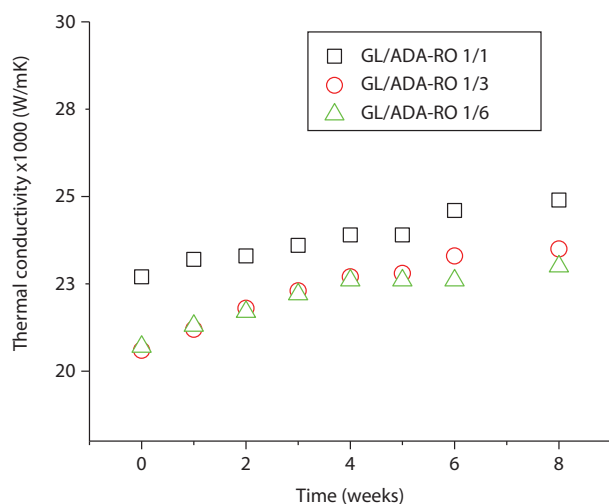


Figure 5 Time-dependent thermal conductivity of PU foams.

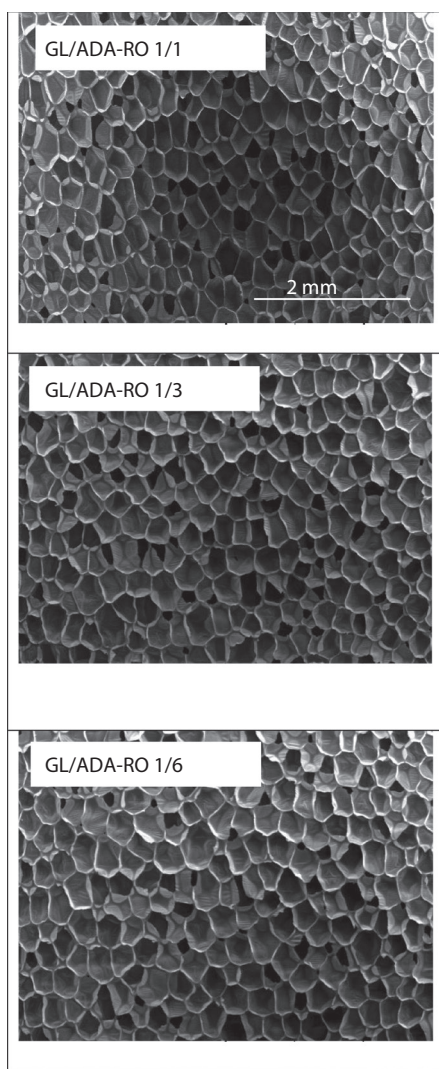


Figure 6 SEM images of PU foams.

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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