European Polymer Journal 123 (2020) 109422

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

# Effect of bio-based components on the chemical structure, thermal stability and mechanical properties of green thermoplastic polyurethane elastomers

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ARTICLE INFO

*Keywords:*
Bio-based thermoplastic polyurethane elastomer
Fully bio-based linear polyester polyol
Chemical structure
Thermal analysis
Mechanical properties

ABSTRACT

It seems to be obvious that conditions changes during polyols synthesis have impact on the polyols properties. Even the chemical formula is the same or similar, physicochemical properties and also molecular weight of polyols might be different and are significant in term of future polyurethanes properties and processing. In this work, fully bio-based poly(propylene succinate)s synthesized at different temperature conditions were used as a polyol in thermoplastic polyurethane elastomers (TPU) synthesis. Novel bio-based TPUs were synthesized with the use of mentioned bio-based linear polyester polyols, poly(propylene succinate)s and also 4,4-diphenylmethane diisocyanate (MDI) and a chain extender 1,4-butanediol (BDO) or 1,3-propanediol (PDO), both with the natural origin. Influence of synthesized bio-based polyols on thermoplastic polyurethane elastomers characteristic was determined based on investigation of chemical structure, thermal, thermomechanical, mechanical and physical properties of synthesized bio-based TPU. Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance ($^1$H NMR) were applied to the chemical formula determination. Thermogravimetry was supportive in thermal analysis, dynamic mechanical analysis (DMA), tensile test and hardness were used to determine thermomechanical behavior and mechanical properties at static and dynamic condition. The density of the obtained materials was also measured. It was established that using obtained fully bio-based polyester polyols the thermoplastic polyurethane elastomers can be synthesis without catalyst usage. Based on the results demonstrated greater influence of type of chain extender on bio-based TPU properties than condition of bio-based polyester synthesis. Each sample was characterized by glass temperature ($T_g$) ca. 0–5 °C and similar thermal stability ca. 320 °C. The tensile strength of prepared bio-based TPUs reach even 30 MPa with an elongation at break ca. 550%.

## 1. Introduction

Nowadays, the huge amount of recent research focused on the bio-based polyurethanes (bio-based PUs), their properties, and application. These activities have a great influence on the environment and the developing of the polyurethane industry. The most apparent effects include the reduction of energy consumption during bio-based monomers and then polymers production, the decrease at the greenhouse gases emission and $CO_2$ emission. Moreover for example application of polyester polyols might lead to the biodegradability improvement. Commonly polyester polyols are used in polyurethane synthesis as one of two major components next to diisocyanates. Crosslinking agents, chains extenders and catalyst are used as well to the polyurethane preparation. Currently, all of these ingredients are commonly available as chemicals with the natural origin [1].

Currently, polyurethanes belong to the crucial class of polymeric materials which are used almost in every branch of industry. After relevant preparation can be used as thermoplastic materials, elastomers, coatings, adhesives or foams. The worldwide demand for polyurethanes including thermoplastic polyurethanes is constantly growing. Zion Market Research estimated that over the years 2016–2022, the value of the global market will increase from 1.93 to 2.84 billion dollars with a CAGR (Compound Annual Growth Rate) of 6.7%. Asia-Pacific has the largest market share, while Europe ranks second. The world's largest leaders are API Plastics, BASF SE, Bayer Material Science Ag, COIM, Headway Polyurethane Co. Ltd., Hexpol AB, Huntsman Corporation, Lubrizol Corporation, Miracll Chemical Co. Ltd., Polyone Corporation, Taiwan Sheen Soon and Wanhua Chemical Group Co. Ltd [2].

The properties of polyurethanes strongly depend on the utilized components, including their chemical structure, type and amount of catalyst, and finally of the molar ratio of isocyanates to hydroxyl groups [NCO]/[OH]. Catalyst addition can significantly increase in the

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https://doi.org/10.1016/j.eurpolymj.2019.109422
Received 8 October 2019; Received in revised form 10 December 2019; Accepted 12 December 2019
Available online 13 December 2019

chemical reaction rate, reduce the gel time and curing time, improve the phase separation in segmented polyurethanes, and consequently, mechanical properties and thermal stability of the materials. The effect of catalyst type and its concentration on the structure and mechanical and thermal properties of synthesized polyurethanes were investigated in [3–7].

Taking into account the mentioned catalyst issue, well known is the impact of catalyst usage during polyurethane synthesis on resulted materials properties. Certain researchers [8–10] indicated that the residual catalysts at PUR structure can lead to adverse side reactions which detract selected properties of the material. For instance, the residual metal catalyst can react during exploitation with other materials and provide to toxic compounds. It is huge disadvantages especially when the material is dedicated to the biomedical application.

In the case of the impact of isocyanates to hydroxyl groups molar ratio ([NCO]/[OH]) there is plenty of research which indicates its indisputable effect on polyurethanes properties [11]. [NCO]/[OH] is controlled by main ingredients and their content: isocyanates, polyols, and chain extender or crosslinking agent. Polyurethanes with different [NCO]/[OH] ratio usually are synthesized by changing chain extender amount under the constant content of other components [12]. Study of structure-property relationships in segmented polyurethanes has acquired importance due to the broad range of applications of polyurethanes (PUs) [13]. The NCO/OH ratio strongly influences the tendency to phase separation between polyurethanes hard and soft segments closely correlated with their properties [14,15].

Considering the influence of components on the polyurethanes properties special attention was given polyols which constitute predominant components in term of weight % of every single polyurethane composition. Depends on the chemical structure (polyester, polyether, hybrid polyols), topology (linear or branched), average molecular mass and functionality, different kinds of polyols can be used for obtaining various type of PU. Nowadays, it is necessary to design the bio-based polyols characterized by selected properties suitable for PU synthesis. Our research group is focused on bio-based linear polyester polyols, which are dedicated especially for elastomeric and thermoplastic polyurethanes. The series of syntheses were conducted with the use of succinic acid (SA) and 1.3-propanediol (PDO), both with natural origin. The extensive analysis of various investigations of our products was described in previously published works [16–18].

Huge benefit resultant of application of bio-based polyols instead petrochemical polyols constitute increasing green carbon content in polyurethane materials. The strong development in the bio-based polyols synthesis such ester-based polyols lead to the new fresh look on polyurethanes properties, even that the chemical composition of this bio-based polyols is identical that the petrochemical analogs. The traditional ester-based polyurethanes and the effect of [NCO]/[OH] ratio on their gelation process, network structure, micro-phase separation, morphology, rheological, thermal, and mechanical properties were investigated by Suzuki et al. [14] and Gogoi et al. [15]. Ester-based polyols usually are characterized by the major viscosity, which is strongly depended on the molecular mass of the polyol [19]. This aspect can play an important role in the processing of polyurethanes and, next to the hydroxyl and acid number of polyol, on their properties. There are many works available at the literature describing selected properties of the bio-based thermoplastic polyurethanes obtained with using bio-based polyester polyol and examples were described below.

Petrovic at al. [20] investigated novel fast-responding shape memory bio-based thermoplastic polyurethanes. These materials were synthesized with the use of bio-based polyester polyol which was methyl ester of hydroxynonanoic acid. The researchers found that these unique properties are related to the high crystallization rate of the soft segment. Moreover, they proclaimed a high degree of elastic elongations and good mechanical strength of these materials. The values of tensile strengths ranged from 10 to 18 MPa, while the elongation at break ranged from 70 to 480%.

Eceiza, Angeles Corcuera and co-workers [21] also investigated thermoplastic polyurethane materials with the use of bio-based components. The vegetable-oil based polyesters were used as polyols. The conducted measurements verified that the chemical structure and average molecular weight of the used polyols have a great impact on the resulted properties of the segmented thermoplastic polyurethanes. They confirmed that with an increasing molecular weight of the used polyol, the degree of soft segment crystallinity and microphase separation also increase, which improved mechanical properties and thermal stability of the obtained products. The mechanical properties of these materials revealed tensile strengths between 13 and 30 MPa, while the elongation at break ranged from 18 to 900%. The researchers confirmed that the use of bio-based component makes it possible to obtain the bio-based polyurethane materials characterized by good mechanical properties similar to petrochemical-based counterparts.

The main aim of this study was concentrated on fully bio-based linear polyester polyols (poly(propylene succinate)s), their synthesis, characteristics and application in bio-based thermoplastic polyurethane elastomers synthesis. The novelty of this work is related with a determination of influence of condition changes during polyols synthesis on the chemical structure, mechanical, thermal and thermomechanical properties of the obtained bio-based thermoplastic polyurethane elastomers. Moreover the usage of different chain extenders on obtained thermoplastic polyurethane elastomers were investigated. The synthesis of bio-based TPU materials were prepared without catalyst usage for confirmation of possibility to obtain the bio-based TPUs characterized by good mechanical properties.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Materials used in bio-based polyester polyols synthesis

In synthesis of bio-based polyols as main substrates were used bio-based succinic acid, SA (Biosuccinium, Reverdia - Netherlands), bio-based 1,3-propanediol, PDO (Susterra, DuPont - USA) and catalyst as tetraisopropyl orthotitanate, Ti(O-i-Pr)$_4$, TPT (TCI Chemicals - India).

#### 2.1.2. Materials used in bio-based thermoplastic polyurethane elastomers synthesis

For the synthesis of bio-based thermoplastic polyurethane elastomers, the above-mentioned fully bio-based polyester polyols were employed. All polyurethane materials were synthesized with the use of aromatic diisocyanate, 4,4′-diphenylmethane diisocyanate, MDI (BorsodChem - Hungary). Two chain extenders, as low molecular weight bio-based glycols were used, earlier mentioned 1,3-propanediol, PDO (Susterra, DuPont - USA) and 1,4-butanediol, BDO (BASF - Germany).

### 2.2. Sample preparation

#### 2.2.1. Procedure of preparation of bio-based polyester polyols

Linear and fully bio-based polyester polyols were prepared with the use of succinic acid SA and 1,3-propanediol PDO. Catalyst, tetraisopropyl orthotitanate TPT, was used as a glycol equivalent in the amount of 0.25 wt%. The catalyst content was determined according to our previous work [19]. All bio-based poly(propylene succinate)s were synthesized by two-step polycondensation method according to the method described in reference [19]. To determine the effect of polycondensation condition of polyols on selected properties of thermoplastic polyurethane elastomers, fully bio-based polyols were synthesized at different temperature conditions under the first and second step of the reaction. In the first step of polycondenstaion, the bio-based components mixtures were reacted at 140 °C. The temperatures of the second step amounted to 160, 190 and 200 °C according to the first step. The acidic number was measured to track the reaction progress

**Table 1**

Primary properties of bio-based polyols used for thermoplastic polyurethane elastomers preparation.

| POLYOL (temperatures of I step/II step) | *ACID NUMBER [mg KOH/g] | *HYDROXYL NUMBER [mg KOH/g] | *VISCOSITY [Pas, 80 °C] | *$M_n$ [g/mol] | *PD [-] |
|---|---|---|---|---|---|
| A1 (140/160) | 0.8 | 51.5 | 3.43 | 2578 | 1.801 |
| A2 (140/190) | 1.0 | 58.5 | 4.66 | 2534 | 2.039 |
| A3 (140/200) | 1.0 | 77.4 | 2.76 | 2048 | 1.718 |

* Features measured in accordance with methods described in our previous work [19].

and after achieving the value of the acidic number ca. or preferably below 1 mg KOH/g, the polycondensation was stopped. Table 1 shown the primary properties of the prepared polyols.

Polyols dedicated for thermoplastic polyurethane elastomers preparation should be characterized by acid number value approximately or even lower than 1 mg KOH/g and hydroxyl number which should not exceed 100 mg KOH/g. All synthesized bio-based polyester polyols revealed established values of these both parameters. The lowest value of acid number disclosed polyol coded A1 (140/160). The same polyol characterized also the lowest value of hydroxyl number. Another important parameter for TPU production processing constitutes viscosity of all compounds. The lower viscosity of polyols at the temperature of the TPU synthesis can lead to the better dispersity of all compounds in the reaction mixture, better phase separation of obtained TPU materials and the lowest energy consumption. The lowest value of viscosity characterized A3 polyol. The same polyol revealed an average molecular weight closest to established ca. 2000 g/mol and the lowest value of polydispersity.

### 2.2.2. Procedure of preparation of bio-based thermoplastic polyurethane elastomers

Bio-based thermoplastic polyurethane elastomers were synthesized with the use of described bio-based poly(propylene succinate)s via a two-step method (Fig. 1). Each bio-polyol was vacuum dried for 2 h at 95 °C before being used. Firstly, urethane prepolymer was synthesized with bio-based polyol and MDI at 85 °C and during 3 h. At the end of the prepolymerization reaction, the content of free NCO groups in urethane prepolymers were determined by the titration method (in accordance with ISO 14,896 standard) and equaled approximately from 8.5 to 9.0 wt%. The excepted theoretical content of NCO group was 8 wt%. In the second step, each urethane prepolymers were extended by using one of the two bio-based glycols, PDO or BDO and carried out for $[NCO]_{prepolymer}/[OH]_{glycol}$ molar ratios equaled to 1.0. Mixing and degassing times of polyurethane system was revealed approximately 30 s. This step of bio-based TPU synthesis was conducted without catalyst addition. Molded thermoplastic polyurethane elastomers were cured at 100 °C for 24 h in a laboratory oven, which permitted to complete the reaction. Based on the known amount of all of the reagents the bio-carbon content at the prepared polyurethane elastomers were determined. Moreover, the hard segment content was calculated according to the following equation (1):

$$HS = [n * M_{MDI} + (n-1) * M_{PDO\backslash;or\backslash;BDO}] / [n * M_{MDI} + M_{POLYOL} + (n-1) * M_{PDO\backslash;or\backslash;BDO}] * 100\% \quad (1)$$

where: HS – hard segment [%]; n - amount of moles of reagent [mol]; M – molar mass of reagent [g/mol].

## 2.3. Measurements

### 2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy was used to obtain the spectra of the synthesized bio-based polyester polyols, prepolymers, and bio-based thermoplastic polyurethane elastomers in order to indicate the characteristic functional groups for these materials. The measurements were carried out using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, USA) with the use of the ATR technique. Sixty-four scans in the wavenumber range from 4500 to 500 $cm^{-1}$ were taken with the resolution 4 $cm^{-1}$ under room temperature. Each bio-based TPU samples were degreased with acetone prior to FTIR analysis. The results allowed to determine the degree of phase separation (DPS) and the degree of phase mixing (DPM). It could be calculated based on the amounts of free carbonyl bonded and H-bonded −C=O in amorphous and ordered regions. After the deconvolution of spectrum in the

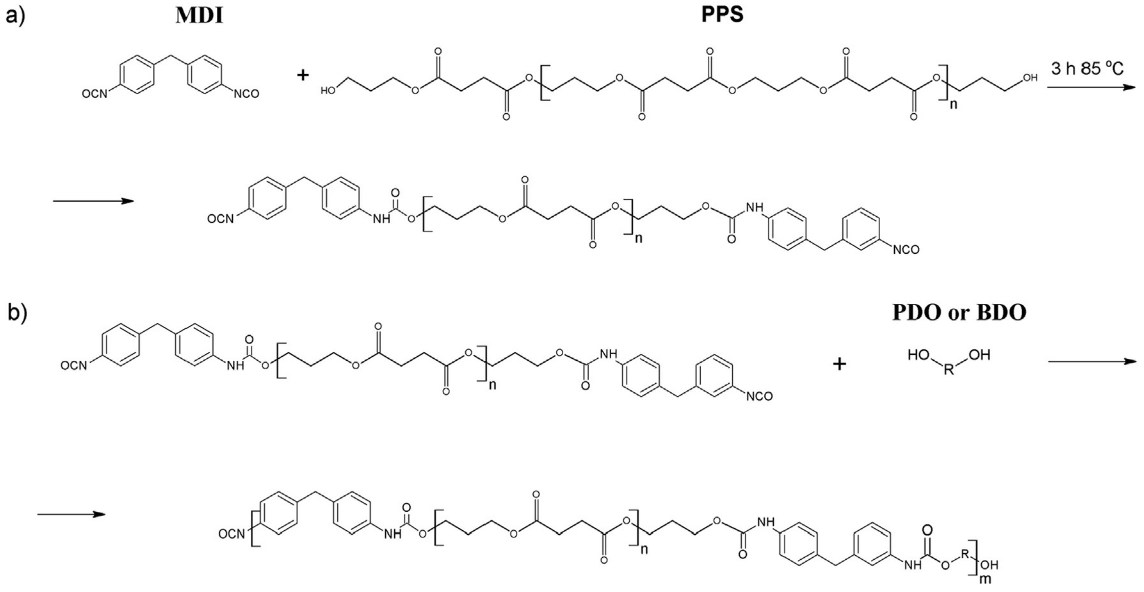

**Fig. 1.** Two-step method of bio-based thermoplastic polyurethane elastomer synthesis.

carbonyl region, the following equations [22] were used:

$$R= A_{1703}/A_{1730} \tag{2}$$

$$DPS = R/(R+1) \tag{3}$$

$$DPM = 1 - DPS \tag{4}$$

where: R – the ratio of the absorbance intensity of the peaks at wavenumber ca. 1703 and 1730 $cm^{-1}$, respectively; $A_{1703}$, $A_{1730}$ – the absorbance intensity of the peaks at wavenumber ca. 1703 (absorption intensity of hydrogen-bonded carbonyl) and 1730 (absorption intensity of free carbonyl) $cm^{-1}$, respectively; DPS – degree of phase separation; DPM – degree of phase mixing.

### 2.3.2. Proton nuclear magnetic resonance ($^1H$ NMR)

Proton nuclear magnetic resonance ($^1H$ NMR) spectra of the two prepared bio-based TPUs were obtained with the use of Bruker spectrometer. Samples A1_MDI_PDO and A1_MDI_BDO were chosen due to their opportunity to solubility at the used solvent. The operating frequency was 400 MHz for protons. The ca. 10% w/v solutions of the PUR samples were prepared in a DMSO-$d_6$ solvent at ambient temperature. The simulation and iteration of spectra were carried out using Bruker software. The results allowed verifying the chemical shifts appropriate for both samples.

### 2.3.3. Thermogravimetry (TG)

Thermogravimetric analysis was performed by using Perkin Elmer apparatus (Pyris 1 TGA) towards to get to know the thermal behavior of obtained bio-based thermoplastic polyurethane elastomers. Measurements were taken at a temperature range from 30 °C to 650 °C with ramp heating rate equaled 20 °C/min in the presence of nitrogen atmosphere. The weight of each sample was ca. 5 mg. Based on results the weight loss of 5%, 50% and also maximum degradation rate and ash residue at 600 °C were registered.

### 2.3.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical tests were carried out with the use of a DMA Q 800 analyzer (TA Instruments). The specimens with dimensions 40 × 10 × 2 mm were analyzed at a heating rate of 4 °C/min for the temperature range from −100 to 100 °C. The tests were performed in air, with a frequency of 10 Hz. The single torsion mode was used as mechanical stress during measurements. The bio-based TPUs obtained with using polyester polyols were tested. Determination of storage and loss modulus, tangent delta (damping factor) and glass temperature of bio-based PU soft segments (based on tan δ curves) and verification of the influence of the used polyester polyol type and chain extender on the thermomechanical properties have been performed.

Moreover, the results of the DMA measurements can be used to calculate the average molecular weight between crosslinks, Mc (g/mol), which was determined by using the high flexibility theory [23] according to the following equation (5):

$$M_C = (3 \times \delta \times R \times T)/E_T \tag{5}$$

where: ρ [$g/cm^3$] means the density of the measured bio-based polyurethanes; R – gas constant [8.314 ($m^{3x}$ Pa)/(mol × K)]; T – temperature in the area of inflection of the log dependence curve of the storage modulus (E’) at the transition to the plateau state in which the sample reached the viscoelastic state [K]; $E_T$ – value of the storage modulus (E’) at the temperature T [Pa].

### 2.3.5. Tensile properties

The tensile properties, such as tensile strength, elongation at break, and permanent set after the break, were determined with the use of a Zwick/Roell Z020 universal testing machine. The tests were performed in accordance with ISO 527, with the crosshead speed set to 100 mm/min and the 20 kN load cell. The dumbbell-shaped specimens of all materials were tested. The obtained results are reported as average values calculated from three samples.

### 2.3.6. Hardness

The hardness measurements were performed with a Shore type D Durometer (Zwick/Roell). The specimens were tested in accordance with the standard ISO 868. The presented results are the mean values of hardness based on ten independent measurements.

### 2.3.7. Physical properties

The density of the prepared materials was determined by using a RADWAG electronic analytical balance equipped with a kit for measuring the density of solids. All measurements were performed at a temperature of 23 °C in accordance with ISO 2781. During the measurements as an immersion liquid methanol was used. The presented results are the mean values calculated from five independent measurements.

## 3. Results and discussion

### 3.1. Chemical structure characterization

The fully bio-based polyester polyol, prepared prepolymer, and synthesized bio-based thermoplastic polyurethane elastomers were subjected the Fourier Transform Infrared Spectroscopy (FTIR) in order to chemical structure analysis. The main characteristic of functional groups for each sample was recognized. Fig. 2 shown the obtained spectra of the selected to the analysis polyol coded A1. In the case of fully bio-based polyester polyol, the characteristic peak of absorption for ester groups were indicated at 1725 $cm^{-1}$ and 1150 $cm^{-1}$. In the spectra of prepolymer, except for peaks related to ester groups from polyol, there is visible also intensive peak at 2268 $cm^{-1}$ which is related with the stretching vibration of the −NCO groups from MDI isocyanate.

In the case of the spectra of polyurethanes are expected mainly signals derived from urethane groups, and decline signal of free −NCO group. The first characteristic region which should be visible on FTIR spectra for polyurethane materials is in the range of wavenumbers from 3400 to 3200 $cm^{-1}$, assigned to the stretching vibration of −NH bonds from urethane groups. In this region two distinct bands can be observed, namely, the free −NH bonds at 3400 $cm^{-1}$ and hydrogen-bonded −NH at 3300–3275 $cm^{-1}$, respectively. The biggest peak intensity for the wavenumbers was observed around 3300 $cm^{-1}$, what proclaims for that the majority of N-H groups were hydrogen bonded [11]. Next appearing double peak at higher value of wavenumber ca.3000–2850 $cm^{-1}$ was assigned to the methylene groups which appeared for all materials. The first maximum of this peak is presented by the asymmetric stretching vibration of −CH and was observed at 2965 $cm^{-1}$ and second maximum for the symmetric stretching vibration of −CH was observed at 2875 $cm^{-1}$. The lack of peak at ca. 2268 $cm^{-1}$ related with −NCO groups on bio-based TPU spectra confirm completed reaction of free isocyanate groups and the hydroxyl groups present in the structures of chain extender. The double peak observed in the region from 1750 to 1690 $cm^{-1}$ was attributed to the characteristic stretching vibration of the −C=O carbonyl groups. The peak maximum connected to the hydrogen bonded carbonyl groups in the amorphous regions manifested itself by the absorbance band at 1740 $cm^{-1}$, while the hydrogen-bonded carbonyl groups in ordered crystalline regions could be observed at 1720 $cm^{-1}$. The maximum at 1730 $cm^{-1}$ is assigned to −C=O groups stretching vibration related to the free carbonyl groups of the urethane bond [24]. The band assigned at 1596 $cm^{-1}$ was attributable to the out-of-plane bending vibration of −NH groups [25]. The stretching vibration of −CN groups was registered at 1529 $cm^{-1}$. The multiple absorption peak at the range 1100–1200 $cm^{-1}$ is related to the C(O)−O−C stretching vibration from the ester groups derived from the used polyols.

Table 2 contains the codes assigned to the produced materials with

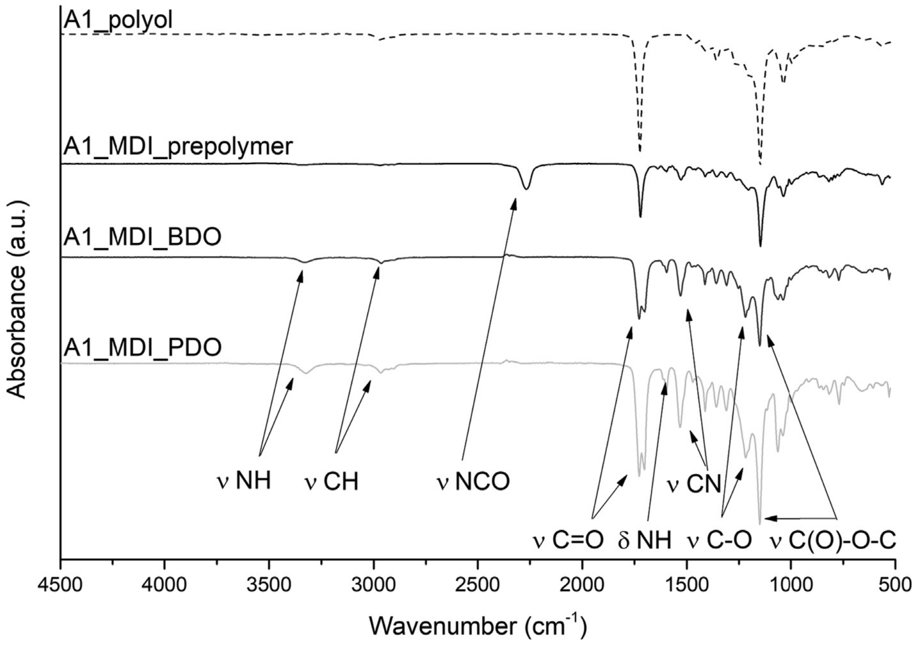

**Fig. 2.** Fourier Transform Infrared Spectroscopy spectra of the selected bio-based thermoplastic polyurethane elastomers, pure polyol, and prepolymer.

**Table 2**
The values of bio-carbon content, hard segment content (HS), the degree of phase separation (DPS) and phase mixing (DPM) of the bio-based thermoplastic polyurethane elastomers.

| Bio-based TPU | | Bio-carbon content [wt. %] | HS [%] | DPS [-] | DPM [-] |
|---|---|---|---|---|---|
| A1 (140/160) | BDO | 70.4 | 36.8 | 0.470 | 0.530 |
| _MDI | PDO | 70.0 | 36.2 | 0.484 | 0.516 |
| A2 (140/190) | BDO | 69.6 | 37.1 | 0.424 | 0.576 |
| _MDI | PDO | 69.2 | 36.6 | 0.387 | 0.613 |
| A3 (140/200) | BDO | 67.3 | 39.2 | 0.468 | 0.532 |
| _MDI | PDO | 66.9 | 38.7 | 0.513 | 0.487 |

values of the bio-carbon content, the hard segment calculation results, the degree of phase separation (DPS) and the degree of phase mixing (DPM). The results of the bio-based carbon content calculation confirmed high bio-based carbon footprint at ca. 70% of the prepared bio-based thermoplastic polyurethane elastomers. The residual part constitutes carbons from petrochemical-based diisocyanate used during polyurethane synthesis.

Based on the FTIR spectra and with the correlation with the intensity of the two peaks related to $-C{=}O$ carbonyl groups, it was calculated that in the most cases the degree of phase separation revealed lower values than the degree of phase mixing. The most of the non-hydrogen bonded carbonyl groups are usually assigned to polyester soft segments [26]. The formation of hydrogen bonds leads to the creation of rigid domains and, in the sequel, conduce to the process of micro-phase separation. Therefore, the fraction of hydrogen-bonded hard segments is a relative measure of the degree of phase separation in PUs [27]. DPS slightly increased for bio-based thermoplastic polyurethane elastomer obtained with the PDO as a chain extender. The results can be in correlation with the increasing hard segment content. According to the literature, materials with a higher content of the hard segments possess more urethane groups [11]. These groups are able to associate with the ester groups from polyols, increasing the interactions between HS and SS and prompting the phase mixing.

$^1$H NMR measurements were used to analyze the macromolecular structure of the selected polyurethane materials prepared based on the bio-based poly(propylene succinate)s. The obtained spectra of A1_MDI_BDO and A1_MDI_PDO samples are shown in Figs. 3 and 4, respectively.

Based on the spectra the chemical shifts of the protons were investigated. The characteristic single peak at 9.50 ppm is attributed to protons ‘1′ derived from the urethane groups $-\underline{\mathbf{NH}}-(C{=}O)-O-$ [28]. Peaks marked ‘2′ and ‘3′ at 7.10 and 7.30 ppm, respectively, are connected with doublets corresponding to methylene protons $-CH-\underline{\mathbf{CH}}$-C- from aromatic rings of the methylene diphenyl diisocyanate. The little single peak named ‘4′ at ca. 3.80 ppm is assigned to methylene protons $-C-\underline{\mathbf{CH_2}}-C-$ also from MDI molecules. At the sample spectra are also visible other peaks in lower intensity which can indicate the end groups of bio-based TPU macromolecules. The peak at 4.20 ppm named ‘8′ is attributed to the triple peak corresponding to methylene protons $-\underline{\mathbf{CH_2}}-O-$ from glycol terminated ends group. The little triple peak at 1.90 ppm named ‘9′ attributed to methylene protons from hydroxyl-terminated ends $-\underline{\mathbf{CH_2}}-OH$ of polymer macromolecules. Peaks marked ‘5′ and ‘6′ at 4.10 and 1.80 ppm, respectively, are connected with a triple and multiple peaks, respectively. These peaks are corresponding to methylene protons $-O-\underline{\mathbf{CH_2}}-CH_2-$ and $-CH_2-\underline{\mathbf{CH_2}}-CH_2-$ from glycol molecules embedded in the polyol structure used in bio-based thermoplastic polyurethane elastomer synthesis. The intensive triple peak named ‘7′ at 2.50 ppm, is attributed to methylene protons $-C(O)-\underline{\mathbf{CH_2}}-CH_2-$ from succinic acid molecules also embedded in the used polyol structure.

### 3.2. Thermal analysis

Thermal properties of thermoplastic polyurethane elastomers strongly depend on applied substrates and provide many important information about materials which determine their future application. Based on thermogravimetric measurements TG and DTG curves versus temperature were plotted and presented in Figs. 5 and 6, respectively.

Generally, thermal decomposition of polyurethanes is complex process because of creating many gaseous products [29]. Taking into account segmented structure of this polymer degradation will be connected with hard and soft segments including its part in PU. Well separated peaks on DTG curve will provide additional information about phase separation of obtained bio-based TPU materials. Each thermoplastic polyurethane elastomers decomposed in two steps and it is common for these polymers and confirm the segmented structure of

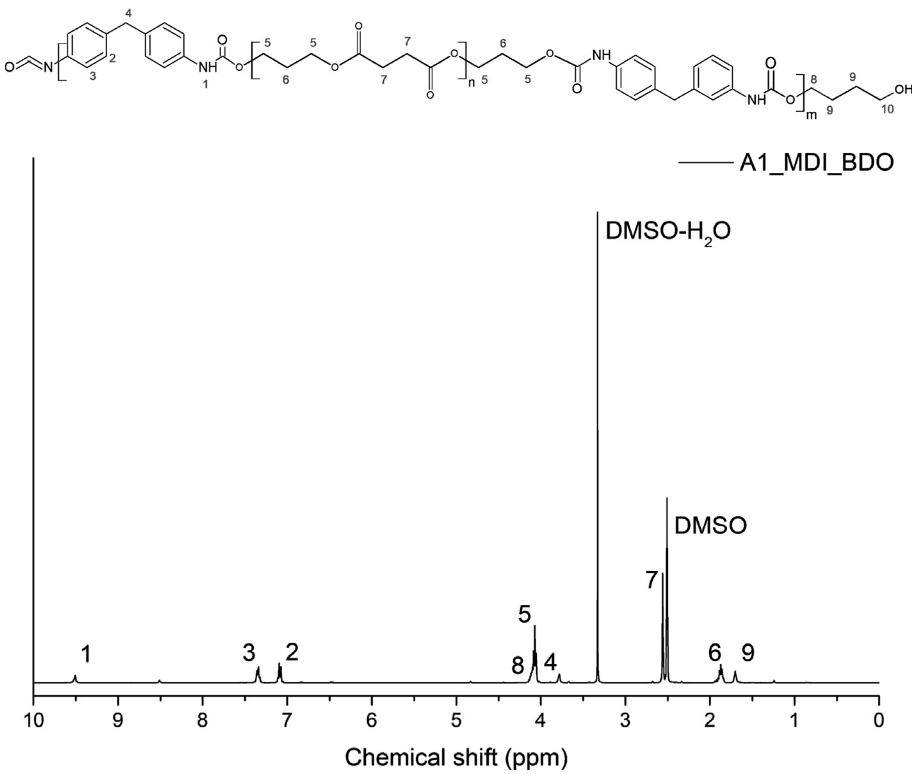

**Fig. 3.** $^1$H NMR spectrum of the A1_MDI_BDO sample.

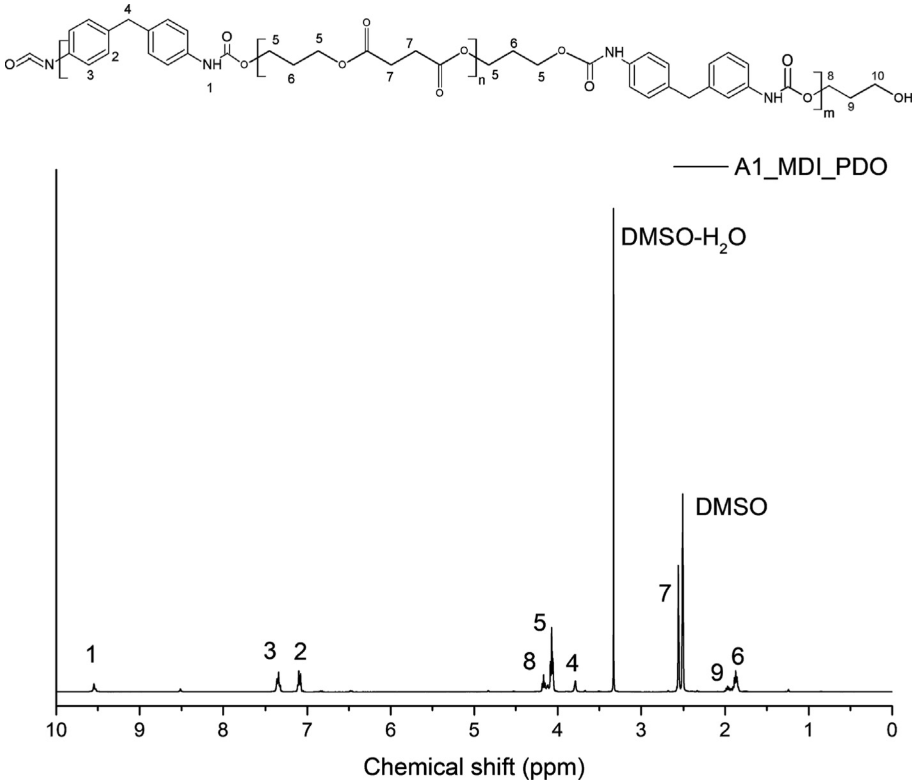

**Fig. 4.** $^1$H NMR spectra of the A1_MDI_PDO sample.

obtained materials (Fig. 6). Despite the thermal condition of bio-based polyester polyols synthesis and the type of chain extender the number of decomposition steps is persistent. At the first step decomposed hard segments built from diisocyanates and chain extenders, while during the second step decomposed soft segments consist of polyols. According to literature, decomposition of urethane group leads to formation of isocyanate and alcohol, primary or secondary amine and olefin, and carbon dioxide [29]. Based on DTG curves (Fig. 6) and partially separated peaks of decomposition steps, measured bio-based TPUs are characterized by significant degree of phase mixing what was also

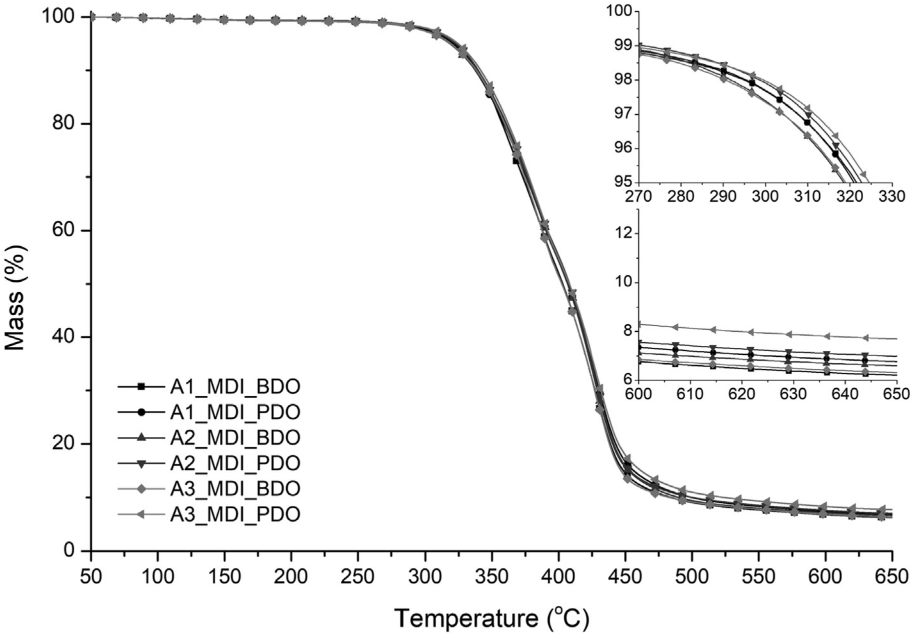

**Fig. 5.** Dependence of TG in the function of temperature for the obtained bio-based TPUs.

confirmed by FTIR analysis and calculated DPM and DPS values (Table 2). It is result of strong interaction between ester groups and urethane groups present in the structure of the obtained bio-based TPU. This interaction leads to creation of hydrogen bonding between ester and urethane groups.

Bio-based TPUs obtained with using A3 polyester polyol, which was characterized by a low value of PD, viscosity molecular mass ca. 2000 g/mol and the same good processing properties beginning degrade at higher temperature in comparison to materials based on polyols A1 and A2 (Fig. 5).

The differences between all samples are resulted in chain extender application and result in the changes of the rate of thermal decomposition. On TG curve (Fig. 5) it is noticeable that bio-based thermoplastic polyurethane elastomers obtained with BDO are characterized by the lower value of the maximum decomposition rate of I step of thermal decomposition. The most organized structure exhibit bio-based TPU series A3.

Table 3 presents thermal degradation characteristics for all measured bio-based thermoplastic polyurethane elastomers.

All samples characterized the temperature of 5% mass loss at ca. 320 °C. This temperature is known as a temperature of the beginning of thermal decomposition. In both cases, $T_{5\%}$ and $T_{50\%}$ there are visible higher values of temperatures for bio-based TPUs prepared with using bio-based PDO as a chain extender, except for value $T_{5\%}$ of A1_MDI_PDO sample. Samples A3_MDI_BDO disclosed the lowest values of the $T_{5\%}$, $T_{50\%}$ and temperatures of the maximum rate of mass loss at the first and second stages. The results of thermogravimetric analysis allowed also demonstrate that higher amount of ash at 600 °C disclosed bio-based TPUs prepared with the use of PDO as a chain extender.

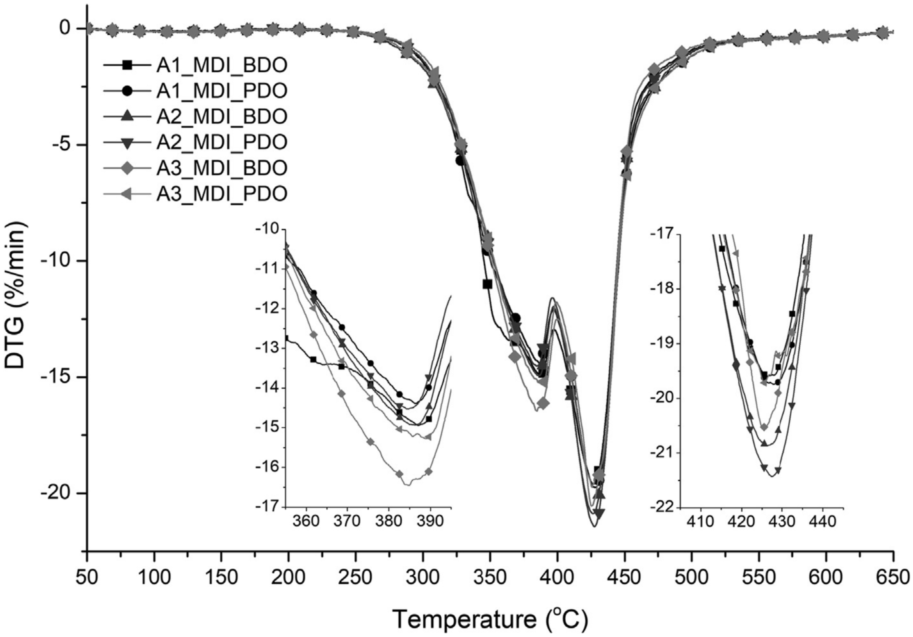

**Fig. 6.** Dependence of DTG in the function of temperature for the obtained bio-based TPUs.

**Table 3**
The thermal decomposition characteristics of the obtained bio-based TPUs.

| Bio-based TPU | | Thermal decomposition characteristics | | | |
|---|---|---|---|---|---|
| | | $T_{5\%}$ [°C] | $T_{50\%}$ [°C] | $T_{max}$ [°C] [Istep/II step] | Residue at 600 °C [%] |
| A1 (140/160)_MDI | BDO | 321.5 | 402.9 | 387.1/426.5 | 6.7 |
| | PDO | 320.9 | 406.8 | 386.4/427.7 | 7.3 |
| A2 (140/190)_MDI | BDO | 318.6 | 406.6 | 386.6/426.3 | 7.1 |
| | PDO | 322.7 | 408.0 | 384.7/427.3 | 7.5 |
| A3 (140/200)_MDI | BDO | 319.0 | 402.4 | 384.9/425.7 | 6.8 |
| | PDO | 324.6 | 407.9 | 389.0/425.2 | 8.3 |

Where: $T_{5\%}$ is a temperature of 5% mass loss, $T_{50\%}$ is a temperature of 50% mass loss and $T_{max}$ is a temperature of the maximum rate of mass loss.

### 3.3. Dynamic-mechanical properties analysis

For a comprehensive investigation of the soft and hard segments dynamic mechanical analysis, DMA, which is one of the most sensitive methods for following the changes in the viscoelastic properties, was carried out. Measurements were conducted for all prepared bio-based TPUs. Based on DMA measurements there are noticed influence of polyols type in term of the temperature conditions during polyol synthesis on storage modulus (logE'), loss modulus (E'') and tangent delta (tanδ). Fig. 7 a, b and c presents the obtained results.

Analyzing the logE' dependence in the function of temperature (Fig. 7a) for all bio-based thermoplastic polyurethane elastomers below the temperature about −10 °C bio-based TPU exhibit glassy state and registered storage modulus is the highest. After achieving the temperature of ca. − 10 °C, a sharp decreasing trend was observed in the curve. It is assigned as the alpha transition temperature of the soft phase of bio-based thermoplastic polyurethane elastomers. In this temperature range occurs the relaxation of the long chain sequences of bio-based polyols embedded in the bio-based TPU structure. The midpoint of the decreasing curve at the temperature range from ca. −10 to ca. 15 °C indicates the position of the alpha transition of the soft segments domains. Glass transition of hard segments is assigned at the width range of temperature above about 60 °C and dependence of bio-based polyester polyol type. Nevertheless, the width range of temperature, there is not possible to clearly determined the glass transition temperature of the hard segments. At the highest temperatures, above 110 °C, especially for bio-based TPUs obtained with using A1 and A3 polyols the thermoplastic behavior is visible, what is correlated with melting of hard segments (Fig. 7a).

Taking into account polyester polyol type, an increase of the temperature condition during second step of polycondensation of fully bio-based polyester polyol lead to obtaining the thermoplastic polyurethane elastomers characterized by higher E' and thereby, higher stiffness at the whole range of temperature. The highest stiffness characterized especially bio-based TPU obtained using A3 polyol and PDO as a chain extender. The decline in the temperature conditions during the synthesis of bio-based polyester polyols consequently caused decreasing in storage modulus and also in the melting temperature of hard segments what can be noted based on E'' curve. The loss modulus E'' curves shown a weak, broad absorption at the range from −75 to −40 °C. These little peaks are assigned to the β-transition of methylene groups of polyols and correspond to their local motions [30].

The storage modulus is clearly correlated with the degree of elasticity, which is also proportional to the crosslink density. Based on the results of the dynamic mechanical analysis of the samples, it can be described that the lowest stiffness and the highest ability to the damping capacity at the temperature 100 °C (temperature of the plateau state in which the sample reached the viscoelastic state) characterized samples based on A1 polyol.

Considering the applied type of chain extender and its effect on thermomechanical characteristic of obtained bio-based TPU it can be statement that bio-based 1,3-propanediol compounded their thermoplastic behavior. What is more, depend on the type of chain extender the glass temperature of the soft segments ($T_{gSS}$) is changed. Bio-based TPUs prepared with bio-based 1,3-propanediol have higher $T_{gSS}$ (determined based on tanδ curves), irregardless to polyols synthesis condition $T_{gSS}$ is ca. 0 °C. Insignificant impact of chain extender type on damping properties expressed by tanδ was observed (Fig. 7c). The glass transition temperatures of the soft segments of the measured materials are gathered in Table 4. Eceiza et al. [31] affirmed that the tan δ peak shifts to a higher temperature as SS content increases. Moreover, the value of tan δ is correlated with the degree of crosslinking density of the macromolecular chains. The decreasing trend at the $T_{gSS}$ suggested the decline in the crosslinking in the prepared materials. This fact also confirmed the highest crosslink density value for sample A3_MDI_PDO (at 100 °C) (Table 4). The highest values of the $M_c$ revealed bio-based TPUs obtained with the use of A1 and A2 polyols. After reaching 20 °C the materials go to the rubbery state with the long-range rubbery plateau at high deformation temperature which indicates particularly desirable properties. Elastomers often show the decrease at the rubbery modulus with the growing temperature which verifies the partial melting of the HS domains or incomplete phase separation [30].

Slight increasing in HS content (about 3%) in the case of bio-based TPU coded as A3, regardless of the type of chain extender caused increasing in the $T_{gSS}$ what is consistent with literature [23].

### 3.4. Mechanical properties analysis

The tensile properties such as tensile strength, elongation at break, permanent set after break and hardness, were measured for all of the prepared thermoplastic polyurethane elastomers. Table 5 shows the obtained results. The highest values of the tensile strengths, at 30.8 and 31.8 MPa revealed samples A2_MDI_BDO and A3_MDI_BDO, respectively. The same samples revealed values of elongations at break at 578 and 591%, respectively. Differences at the elongation at break are related to the decrease in the chain mobility, for these samples it was confirmed by shifting glass transition temperature to higher values. The lowest mechanical properties are characterized for samples based on the A1 polyol and it is also confirmed by the lowest value of glass transition temperatures.

The permanent set after the break characterized the possibility of macromolecular chains to return to the state before the test. The low value of this parameter is characteristic for elastomers when higher permanent set after the break characterized thermoplastic materials. According to the issue, sample A3_MDI_BDO is characterized by the highest value of the permanent set after the break. Hardness is closely connected with the crosslink density. The hardness decreases for materials which the molecular chain mobility is hindered and also when crosslink density decreases. This resulted in the reduced elasticity of the samples which led to more rigid materials. The highest hardness revealed samples prepared based on the polyol A3 which values equaled ca. 44 to 48 °Sh D. This results can indicate that these both bio-based

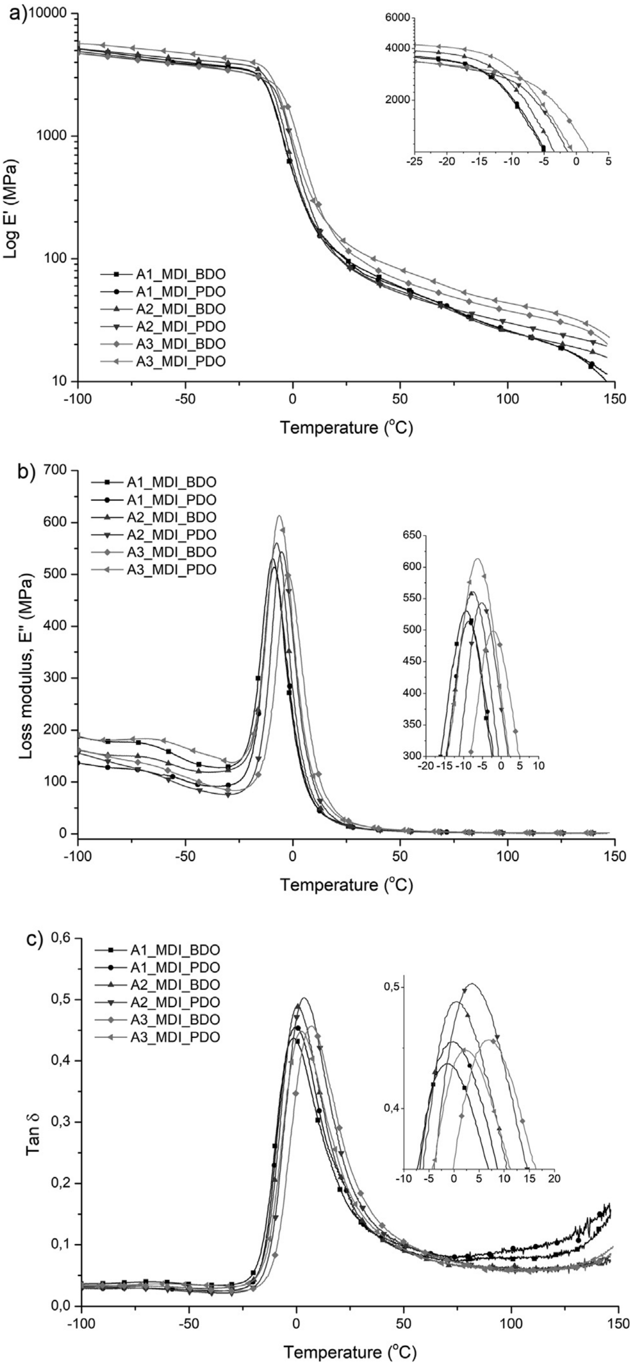

**Fig. 7.** DMA results, where: a) storage modulus (E'), b) loss modulus (E''), c) loss factor (tan δ) versus temperature were presented for the obtained bio-based TPUs.

**Table 4**
The results of the glass transition temperature of the soft segments and the molecular weight of the sections between the crosslinks of the measured bio-based TPUs.

| Bio-based TPU | | $T_{gSS}$ [°C] | ρ [g/cm$^3$] | $E'_T$ [Pa] | T [K] | $M_c$ [g/mol] |
|---|---|---|---|---|---|---|
| A1_MDI | BDO | −2 | 1.272 ± 0.002 | 25,9 | 373.15 | 457 |
| | PDO | 0 | 1.280 ± 0.001 | 25,9 | | 459 |
| A2_MDI | BDO | 1 | 1.247 ± 0.002 | 25,4 | | 456 |
| | PDO | 4 | 1.277 ± 0.001 | 30,1 | | 395 |
| A3_MDI | BDO | 7 | 1.270 ± 0.003 | 37,6 | | 314 |
| | PDO | 2 | 1.277 ± 0.001 | 43,6 | | 273 |

TPUs characterized the lowest crosslink density from measured materials. With increasing crosslink density, the stiffness of the materials also increases. The value of the HS content is also responsible for the results of the tensile strength when the SS content is connected with the elongation at the break values. The elongation at break is also related to the decrease in the chain mobility when the permanent set after the break characterized the possibility of macromolecular chains to returning to the state before the test.

## 4. Conclusion

In this work, the extensive and knowledgeable investigation of the type of the bio-based poly(propylene succinate) employment as a polyol for bio-based thermoplastic polyurethane elastomers synthesis were described. Based on conducted experiments, it was proved that using prepared bio-based poly(propylene succinate) synthesis of bio-based TPU could be carried out without using catalysts. The chemical structure analysis by FTIR confirmed present characteristic groups for bio-based polyester polyols, urethane prepolymers, and bio-based TPU. Moreover, the differences at the chemical structure of the final bio-based polyurethane materials based on different chain extender were also confirmed by $^1$H NMR measurements. It was affirmed, that the low variation of the molar mass of soft segment and the difference of methylene group on the diol used for the hard segment do not vary significantly the properties of the obtained TPUs. The most important for prospects are thermal, mechanical and dynamic mechanical properties of the obtained materials. The results of DMA showed that using bio-based polyols led to bio-based thermoplastic polyurethane elastomers with the glass transition temperature at the range of ca. 0–5 °C. Moreover, it was verified that measured samples characterized by low stiffness and good ability to the damping capacity. Furthermore, prepared bio-based polyurethanes have good mechanical properties. They feature value of the hardness ca. 40°Sh D and tensile strength even 30 MPa with ca. 550% elongation at break. The obtained investigation allowed confirming capability of bio-based thermoplastic polyurethane elastomers employment at the production of the utility goods as toys, seals, watchbands, mats, rubbers, etc..

## CRediT authorship contribution statement

**Paulina Parcheta:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration. **Ewa Głowińska:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. **Janusz Datta:** Visualization, Project administration.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

Authors acknowledged the DuPont Tate&Lyle BioProducts (Loudon, Tennessee, USA) for supplying the bio-based PDO glycol (1.3-propanediol) and the BASF (Germany) for providing the bio-based BDO sample used in this study.

## Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

**Table 5**
The results of tensile strength and hardness measurements of the obtained bio-based thermoplastic polyurethane elastomers.

| Bio-based TPU | | Tensile strength [MPa] | Elongation at break [%] | Permanent elongation after break [%] | Hardness [°Sh D] |
|---|---|---|---|---|---|
| A1 (140/160)_MDI | BDO | 17.4 ± 1.3 | 438 ± 17 | 64 ± 5 | 39.7 ± 3.3 |
| | PDO | 21.4 ± 3.2 | 521 ± 57 | 84 ± 4 | 39.2 ± 1.7 |
| A2 (140/190)_MDI | BDO | 30.8 ± 1.9 | 578 ± 24 | 77 ± 9 | 39.9 ± 2.3 |
| | PDO | 29.4 ± 2.0 | 550 ± 19 | 75 ± 5 | 41.5 ± 0.6 |
| A3 (140/200)_MDI | BDO | 31.8 ± 2.3 | 591 ± 42 | 89 ± 9 | 44.6 ± 0.3 |
| | PDO | 23.9 ± 1.5 | 490 ± 15 | 77 ± 8 | 48.1 ± 1.8 |

## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2019.109422.

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