



Structure versus hydrolytic and thermal stability of bio-based thermoplastic polyurethane elastomers composed of hard and soft building blocks with high content of green carbon

Ewa Głowińska¹ · Joanna Smorawska¹ · Joanna Niesiobędzka¹ · Janusz Datta¹

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Abstract

Nowadays, sustainability plays a key role in the design and synthesis of new materials. One of the methods for the preparation of green materials is incorporation into their structure the monomers with a high content of green carbon. Therefore, the aim of this work was to investigate the influence of the type and molecular mass of two bio-based polyester polyols and bio-glycol on the properties of aliphatic partially bio-based thermoplastic polyurethane elastomers (bio-TPU). Two series of bio-TPUs materials composed of hard and soft building blocks with high green carbon content were prepared via the two-step method (prepolymer method). Two amorphous bio-based polyester polyols with the molecular mass ~2000 (P1) and ~3000 (P2) were used. Bio-TPUs were prepared at three different molar ratio of [NCO]/[OH]: 0.9, 0.95, and 1.0. In order to determine the influence of bio-based polyols and the content of hard segments on the properties of bio-TPU, relevant test methods were used. The Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetry (TG) revealed hydrolytic and thermal stability of bio-TPUs. Viscoelastic behavior, mechanical and physical properties were examined in terms of dynamic mechanical thermal analysis (DMTA), tensile test, hardness, and density. Analysis of the measurement results confirmed the significant influence of the molecular mass of the bio-based polyols and the molar ratio of [NCO]/[OH] on the bio-TPUs properties. Due to good mechanical properties, low density, and thermal stability up to 300 °C, the obtained materials can find many useful applications. This issue is essential in terms of sustainable development and reduction in the CO₂ emissions to the atmosphere.

Keywords Bio-based polyurethanes · Bio-based polyols · Environmentally friendly materials · Hydrolytic stability · Thermal stability

Introduction

The growing popularity of environmentally friendly solutions for the plastics industry has led to a great interest in the preparation of polyurethanes using bio-based components, especially those derived from plants [1–3]. Bio-based components used in polyurethane industry might comprise polyols, chain extenders, crosslinkers and di/polyisocyanates. The main class of bio-based components are bio-based polyols, which are obtained by chemical conversion of natural

compounds. The suitable selection of raw materials has a major influence on the nature and properties of the PUs. In general, polyols are one of the two main components used in the synthesis of PUs and constitute more than half mass% of the resulting polymer. Polyols with molecular mass of 1000–2000 g mol⁻¹ are widely used in the TPU industry. The type of polyol, including the chemical structure, chain morphology, as well as molecular mass affects the flexible segments of the polyurethane. Higher polyol mass affects the flexibility of the chains, while lower mass affects stiffness and hardness. An increase in mass can also affect the increased phase separation of PU and its mechanical strength. In the literature, there are plenty of examples of the use of vegetable oil-based polyols for polyurethane synthesis. Plant oils such as soybean oil, palm oil, tung oil, canola oil, linseed oil, palm oil, kernel oil, castor oil and flaxseed oil are commonly used for bio-based polyols preparation via

✉ Ewa Głowińska
ewa.glowinska@pg.edu.pl

¹ Faculty of Chemistry, Department of Polymers Technology, Gdansk University of Technology, 11/12 Gabriela Narutowicza Street, 80-233 Gdansk, Poland

hydroformylation and reduction in aldehyde groups, epoxidation and ring opening, ozonolysis or transesterification [4–8]. Bio-based polyols can be obtained from the polycondensation reaction of bio-glycols and bio-based carboxylic acids [9–12].

Polyurethanes depend on the chemical structure of the starting monomers, cross-linking density, and morphology might exhibit different mechanical properties, thermal stability, and chemical resistance. Overall, polyester-urethanes are more susceptible to hydrolysis, while polyether-urethanes are more susceptible to oxidation. Overall, the hydrolytic stability and acid and alkali resistance of the ester linkage are generally poor [13]. Therefore, hydrolytic degradation begins with the breaking of the ester linkage and then ether linkage [14]. The degradation of polyester-urethanes can take place by surface erosion or by bulk degradation [13]. Nevertheless, if the polyester polyols contain hydrophobic branches among the main chains, the resistance of bio-TPUs to hydrolysis can be improved. Moreover, in the case of polyester-urethanes, degradation depends on the environment in which the process takes place. Haryńska et al. conducted a short degradation test of PCL-based polyurethane in acidic and alkaline conditions. They found that the PUs were more susceptible to degradation in acidic conditions compared to alkaline ones. The authors observed that the erosion of the material surface depends on the molar ratio of [NCO]/[OH] [15].

Oh et al. [16] used bio-based polyester polyols with number average molecular mass (M_n) of 1000 and 2000 g mol⁻¹ and reacted with 4,4'-methylene diphenyl diisocyanate for polyurethane synthesis. The mentioned polyols were synthesized from 1,3-propanediol and sebacic acid raw material. The authors described the relationship between the molecular mass of the polyols and the resulting molecular mass of the polyurethanes they produced. TPUs based on bio-based polyester polyol with $M_n \sim 1000$ g mol⁻¹ have a higher average molecular mass than TPUs based on polyols with $M_n \sim 2000$ g mol⁻¹. It is worth noting that TPUs synthesized with a low molecular mass polyol had a higher hard segment (HS) content of 35.9% compared to TPUs with polyol 2000 g mol⁻¹, which had a hard segment content of 22.1%. Moreover, HS content above approx. 25% leads to a physical cross-linking effect through crystallization, and thus, TPUs show the desired properties of a thermoplastic elastomer [17]. In other work, Oh et al. synthesized TPU using succinic acid (CA)-based polyester bio-polyesters with $M_n \sim 1000$ and 2000 g mol⁻¹ [18]. Compared to these samples, the sebacic acid-based samples have a higher bio content as well as a higher average molecular mass.

Chon et al. [19] studied a high-performance citric acid-based polyester elastomer (poly(1,4-cyclohexanedimethanol succinate/citrate, PCSCs)) obtained via a hot pressing technique. Depending on the citric acid (CA) content in

the polyol structure, the modulus and toughness could be modified. It was found that as the CA content increased, Young's modulus increased significantly, and the elongation at break decreased. In general, changes in properties can be designed based on the ratio of citric acid: succinic acid and 1,4-cyclohexanedimethanol (CHDM). When the ratio was 0.5:0.5:1.25, PUs exhibited the highest hardness, with significantly higher modulus and tensile strength than materials containing with higher CHDM and SA contents. The elastomers were found to stiffen with increasing CA content, indicating increased cross-linking. With an increase in cross-linking density, the Young's modulus increased proportionally, while the elongation at break decreased.

Bio-based TPUs were also investigated by Bueno-Ferrero et al. [20] and synthesized from a bifunctional dimeric polyol based on fatty acid, diphenylmethane 4,4'-diisocyanate (MDI) and 1,4-butanediol (BDO) at different hard segment contents and with an NCO/OH ratio of 1.0. It was found that the properties of the bio-based polyol derived from rapeseed oil influenced the structure and properties of the polyurethanes. The total molar mass of the polyol (3000 g mol⁻¹) was higher than that used in standard petroleum-based TPUs. The effect of HS content was studied. The results of this study suggest that as the HS content increases, the average molecular mass decreases. This could be attributed to the higher concentration of BDOs, which are short diols, present in TPUs with higher amounts of HS. It was revealed that TPUs with 20% and 40% HS content have spherulitic-like textures with higher phase segregation, indicating that HS content affects the properties of TPUs.

Parcheta-Szwindowska et al. [21] also undertook research on the properties of bio-based thermoplastic polyurethane elastomers. For this purpose, novel bio-based poly(propylene succinate)s were obtained via polycondensation of succinic acid and 1,3-propanediol, both with a bio-based origin. The synthesized polyols were used with 4,4-diphenylmethane diisocyanate and 1,4-butanediol or 1,3-propanediol for the synthesis of novel bio-TPU. The application of two types of chain extenders caused obtaining bio-TPUs to differentiate properties. It is worth mentioning, that bio-TPUs based on poly(propylene succinate)s exhibit great mechanical properties (tensile strength ca. 30 MPa, elongation at break ca. 550%) and thermal stability up to 320 °C. It is evident that bio-based polyurethanes can exhibit diverse properties that make these materials useful and common in industrial applications.

Previous years were full of research studies related to bio-based monomers. This led to a rapid development in the use of renewable raw materials in the synthesis of plastics, including PUs. The key aspect has been to reduce the negative impact of plastics on the environment. The use of plant-derived components results in a significant reduction in CO₂ emissions into the atmosphere and a lower carbon footprint.

This paper focuses on the influence of the type and molecular mass of bio-polyols and the presence of a bio-based chain extender on the chemical structure, thermal and hydrolytic stability, and mechanical properties of thermoplastic bio-based polyurethane elastomers. The scope of the work is important due to the growing demand for environmentally safe plastics. The properties of such materials are as good as those of polyurethanes synthesized from petrochemical-derived monomers.

Materials and measurements

Materials and synthesis of bio-TPU

The synthesis of the bio-TPU materials was conducted via two-step method, the 'prepolymer method'. In the first step, pre-polymerization was carried out. For the synthesis, two amorphous bio-based polyester polyols with the branched structure and based on dimer technology were used. The first polyol coded as P1 was Priplast 3238 (Croda, United Kingdom) with a molecular mass of $\sim 2000 \text{ g mol}^{-1}$ and the second polyol, P2, Priplast 3196 (Croda, United Kingdom) with a molecular mass of $\sim 3000 \text{ g mol}^{-1}$, respectively. Hexamethylene diisocyanate (HDI) (Vecnorex, France) was used as the diisocyanate component. The reaction between the bio-based polyester polyol and the diisocyanate was carried out at a temperature of approx. $80 \text{ }^\circ\text{C}$, under vacuum, and for 2 h. After the pre-polymerization process, the free NCO content was determined by titration method according to ASTM D 2572-97. The free NCO was 7.7 and 9.4% for pre-polymers based on polyol P1 and P2, respectively. In the second step of the bio-TPU synthesis, the prepolymer was extended by using bio-based 1,3-propanediol with the trade name Susterra[®] (DuPont, USA). The reaction in the second step was catalyzed by dibutyltin dilaurate, DBTDL (Sigma Aldrich, Poland). The bio-TPUs were cured at $100 \text{ }^\circ\text{C}$ for 24 h in laboratory oven. Two sets of bio-TPU materials with molar ratio of $[\text{NCO}]/[\text{OH}]$ of 0.9, 0.95, and 1.0 were obtained (see Table 1). Figure 1 shows the procedure of the

bio-TPUs synthesis by prepolymer method: reaction between polyol and diisocyanate, and prepolymer chain extension.

Measurements

Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy was performed using a Nicolet FTIR 8700 spectrophotometer (Thermo Electron Corporation, USA). Spectra were registered at the room temperature and wavenumber range from 500 to 4500 cm^{-1} . The resolution of the apparatus was equalled 4 cm^{-1} . Each spectrum was acquired with 64 scans. The measurements were performed for bio-TPUs synthesized at the $[\text{NCO}]/[\text{OH}]$ equal to 1.0. Based on FTIR spectra carbonyl index, the degree of phase separation and mixing was calculated using the following Eqs. (1)–(3):

$$R = \frac{A_{\text{bonded}}}{A_{\text{free}}} \quad (1)$$

$$\text{DPS} = \frac{R}{R + 1} \quad (2)$$

$$\text{DPM} = 1 - \text{DPS} \quad (3)$$

where R carbonyl hydrogen bonding index; A_{bonded} absorption intensity of hydrogen-bonded carbonyl; A_{free} absorption intensity of free carbonyl, DPS degree of phase separation, DPM degree of phase mixing. Prior calculation, all spectra were normalized, and next carbonyl peak was decomposed into three and four peaks.

Short-term degradation test

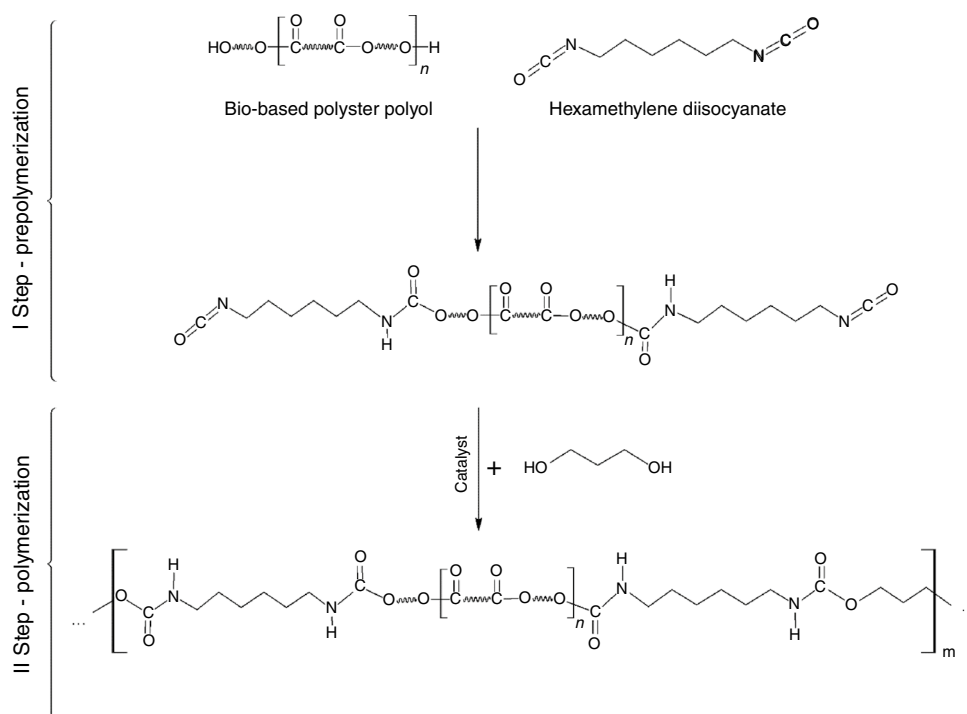
Short-term degradation tests were determined as hydrolytic stability in 2 M HCl and 5 M NaOH. Prior test, rectangular samples ($10 \times 10 \times 2 \text{ mm}$) were dried to a constant mass for 4 h at $60 \text{ }^\circ\text{C}$ in the laboratory oven. Next, the samples were placed in 5 mL of the 2 M HCl, or 5 M NaOH solution and placed in a laboratory oven for 28 days at $37 \text{ }^\circ\text{C}$. After 7,

Table 1 Codes, molar ratio and hard segments content of obtained bio-TPUs

Cod of material	Bio-based polyols	Molar ratio of $[\text{NCO}]/[\text{OH}]$	HS* content/%	Bio content/%
P1_0.9	Priplast 3238	0.9	28.6	78.9
P1_0.95		0.95	28.2	78.8
P1_1.0		1.0	28.0	78.7
P2_0.9	Priplast 3196	0.9	30.5	78.1
P2_0.95		0.95	30.2	78.0
P2_1.0		1.0	29.9	77.9

HS*: hard segments content was calculated according to equation: $\text{HS} = \frac{(m_{\text{HDI}} + m_{\text{PDO}})}{(m_{\text{HDI}} + m_{\text{PDO}} + m_{\text{polyol}})} \cdot 100\%$

Fig. 1 Scheme of bio-TPUs synthesis based on prepolymer method



14, 21, and 28 days, the mass of the samples was measured by using analytical balance RADWAG AS 310.R2. Three samples were taken for each of the tests.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was carried out by using the DSC 204 F1 Phoenix® calorimeter (NETZSCH, Selb, Germany). Each sample with a mass of ca. 10 mg was placed in a closed aluminum pan and heated twice from $-80\text{ }^{\circ}\text{C}$ to $240\text{ }^{\circ}\text{C}$ at a scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and cooled once from 240 to $-80\text{ }^{\circ}\text{C}$ at a scanning rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Measurements were performed with nitrogen as the purge gas (20 mL min^{-1}). DSC analysis was conducted on the bio-TPU samples obtained with a molar ratio of NCO to OH groups equal to 1.0. Enthalpy values of melting and crystallization peaks were indicated with the use of baseline type sigmoidal.

Thermogravimetry (TG)

Thermogravimetric analysis (TGA) was performed using a TG 209F3 (NETZSCH, Germany) instrument. The measurements were performed under a nitrogen atmosphere, at a heating rate of 10 K min^{-1} , and a temperature range from 35 to $800\text{ }^{\circ}\text{C}$. The mass of samples was ca. 10 mg.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis of bio-TPU was performed using a DMA Q800 Analyzer (TA Instruments, USA) in a nitrogen atmosphere. Measurements were carried out according to ASTM D4065:2012. The measurements were made at temperatures range from -100 to $150\text{ }^{\circ}\text{C}$ at an operating frequency of 10 Hz with a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$.

Tensile test

The tensile test was performed using a universal testing machine Zwick/Roell Z020 (Zwick Roell Group, Germany). Measurements were carried out according to PN-EN ISO 527-1 and PN-EN ISO 527-2 ISO 37. The crosshead speed was 100 mm min^{-1} , and measurements were performed at room temperature. Four dumbbell specimens, type 1, were used. Tensile strength (TS_b), the elongation at break (ϵ_{break}) and permanent elongation (ϵ) were determined.

Hardness

Hardness was determined by using a Shore type D Durometer (Zwick Roell Group, Germany). Measurements were made at room temperature, and according to ISO 868 standard. The presented results are averages calculated from ten points per one type of sample.

Density

Density was measured with an analytical balance (RAD-WAG AS 310.R2, Poland) by a hydrostatic method. The measurements were carried out in accordance with the ISO 2781 standard, and at room temperature. Five measurements were taken for each sample.

Results and discussion

Effect of alkali and acidic treatment on the chemical structure of bio-TPUs in the short-term degradation test

The chemical structure of the obtained bio-TPUs (before and after alkali and acidic treatment) was analyzed by Fourier transform infrared spectroscopy. It is worth to mention that all analyzed bio-TPUs in term of FTIR technique were synthesized at the molar ratio of isocyanate to hydroxyl groups equaled 1.0. Considering the spectra of reference materials, coded P1_1.0 and P2_1.0 (see Fig. 2) characteristic absorption bands for functional groups present in the structure of aliphatic polyester-urethane materials were observed. Among them, urethane, ester and methylene groups were identified. Above all, FTIR analysis confirmed the formation of urethanes groups via fully reacted hydroxyl and isocyanate groups. Based on the analysis of the spectra presented in Fig. 2, it can be seen the absence of peaks at wavenumbers from 2270 to 2250 cm^{-1} related to NCO groups [22]. The formation of the urethane group (NHC(O)O) is confirmed by the presence of the characteristic absorption band. The stretching vibration of the -NH bond of the urethane group was noticed at 3319 cm^{-1} . Then, the band corresponding to the stretching vibration of the -CN was revealed at 1539 cm^{-1} , while the C=O group (multiple bands) was identified in the range of wavenumber from 1684 to 1734 cm^{-1} . In general, the C=O multiple peaks can be divided into two main vibrations. The first one, at lower wavenumber (1684 cm^{-1}) corresponds to the hydrogen-bonded carbonyl group and the second one, at 1734 cm^{-1} , is related to the free urethane carbonyl group and the ester carbonyl. Next to the characteristic band of carbonyl, distinctive bands due to the nature of the polyester polyol used in the synthesis were registered as a double absorption peak related to the symmetric and asymmetric C-O vibration was revealed at 1140 and 1151 cm^{-1} , and a peak at 1260 cm^{-1} . Stretching vibrations of the methylene group (CH_2), present in the form of symmetric and asymmetric vibrations can be observed at a wave number of 2850 cm^{-1} and 2920 cm^{-1} [23–26].

The following FTIR spectra allowed the identification of the chemical structure of the synthesized bio-TPU subjected to short degradation test as a hydrolytic stability

under selected pH conditions (acidic, 2 M HCl and alkaline, 5 M NaOH). Bio-TPUs materials conducted alkali and acidic treatment were coded: P1_1.0_NaOH, P2_1.0_NaOH, P1_1.0_HCl, P2_1.0_HCl. Taking into account the presence of long fatty acid chain in the structure, the enhancement of the hydrolytic stability of bio-TPUs should be noted. Based on the literature (27), saponification of ester bonds was suspected, resulting in an increase in the depolymerization rate of polyester-urethanes.

Figure 2a presents FTIR spectra registered for bio-TPUs obtained using P1 (polyol with the molecular mass $\sim 2000 \text{ g mol}^{-1}$). As can be seen in Fig. 2a, there are slight changes in the chemical structure of the bio-TPUs regardless of the pH of the solution. Characteristic urethane and ester groups were detected during short-term degradation tests, similar to the reference materials. Changes in vibration intensity of free C=O, C(O)O, and C-O-C were observed due to changes in solution pH. In the case of materials immersed in NaOH solution, the band intensity of free C=O band decreased, suggesting that the content of hydrogen bonds and/or hydrolysis of ester groups might take place. Similar findings were observed also by Haryńska et al. [15] and explained by initial erosion by breaking of ester bonds in soft segments and the degradation of hydrogen-bonded urethane groups.

In the case of bio-TPUs based on P2 polyol (polyol with the molecular mass 3000) noticeable decreasing in the absorbance of carbonyl groups for bio-TPUs immersed in NaOH solution can be observed (Fig. 2b). Similar to the hydrolytic stability against alkali environment of P1-based bio-TPUs, the hydrolysis of ester bonds in the case of P2-based TPUs also occurred. Looking at Fig. 2b, there was a visible decrease in the absorbance of free carbonyl (1684–1734 cm^{-1}) and an increase in the absorbance of NH bonds (3319 cm^{-1}). Considering the influence of acidic solution on P2-based bio-TPU (reference and immersed samples), decrease in absorbance of vibration of NH bonds at 3319 cm^{-1} can be seen. It can be a reason for hydrolysis not only of ester bonds, but also of urethane bonds.

In Fig. 3, normalized and decomposed carbonyl peaks of bio-TPUs before and after hydrolytic stability testing in alkaline and acidic solution were presented. In each cases, the *R*-square equaled ca. 0.99, and low value of reduced Chi square indicated on high level of matching. Analyzing bio-TPUs prior short degradation test, the first (peak I), and the second peak (peak II) correspond to hydrogen-bonded urethane carbonyl constituting ordered and disordered hard phase, respectively [28]. The position of these peaks, ca. 1684 and 1696 cm^{-1} , indicated on H-bonded carbonyl groups between hard segments [29]. Peaks III and IV are related to free urethane carbonyl group in the ordered phase and urethane and ester carbonyl in the disordered phase. After a short-term degradation test, the carbonyl bonds of

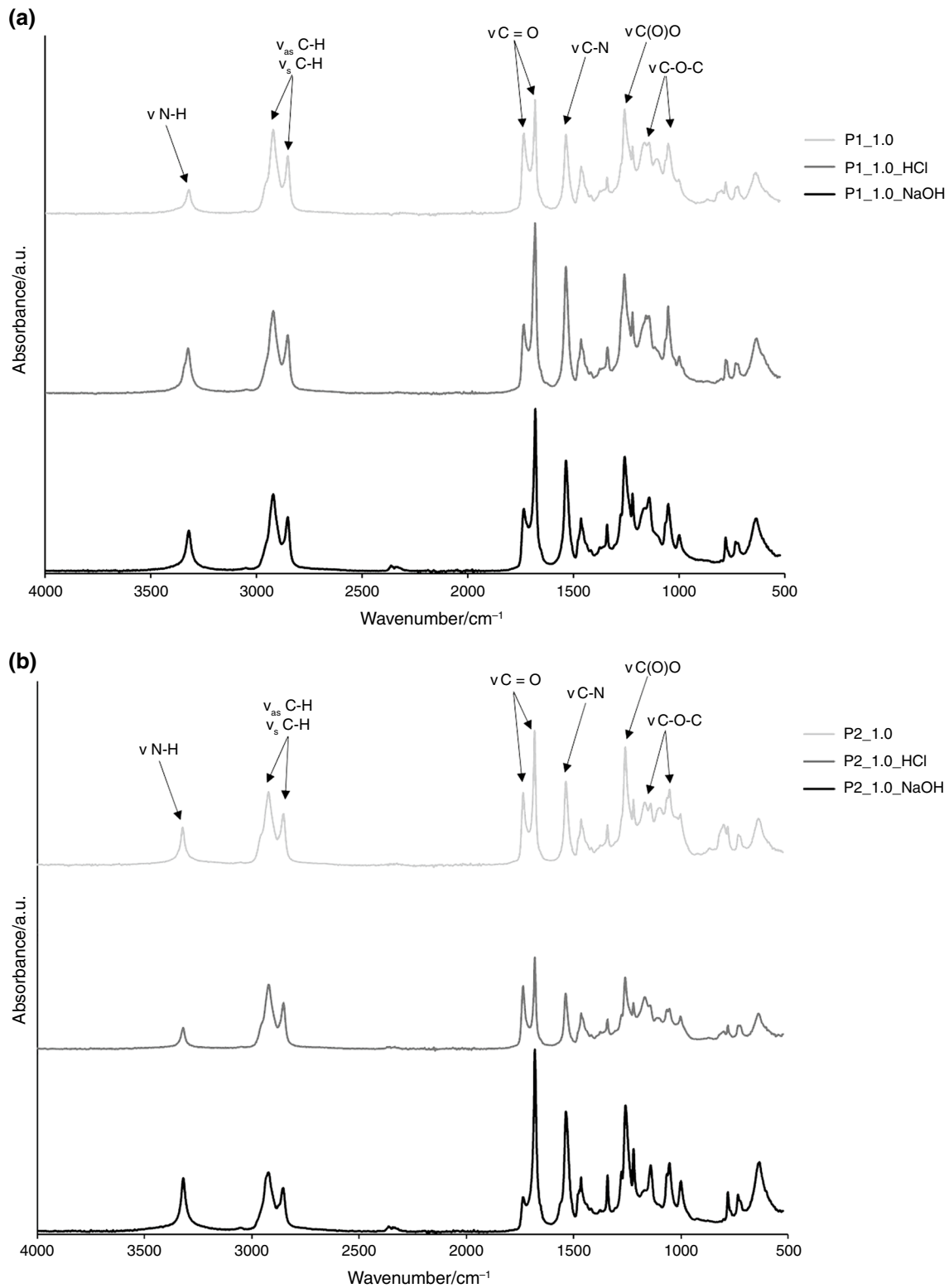


Fig. 2 FTIR spectra of bio-TPU coded **a** P1_1.0, and **b** P2_1.0 after hydrolytic stability test in alkaline and acidic condition

bio-TPUs were divided into three main peaks. The positions of these peaks indicate the presence of hydrogen-bonded C=O in both the ordered (peak I) and disordered (peak II)

phases, as well as free carbonyl in the ordered phase (peak III). It can be concluded that the ester linkage is hydrolyzed

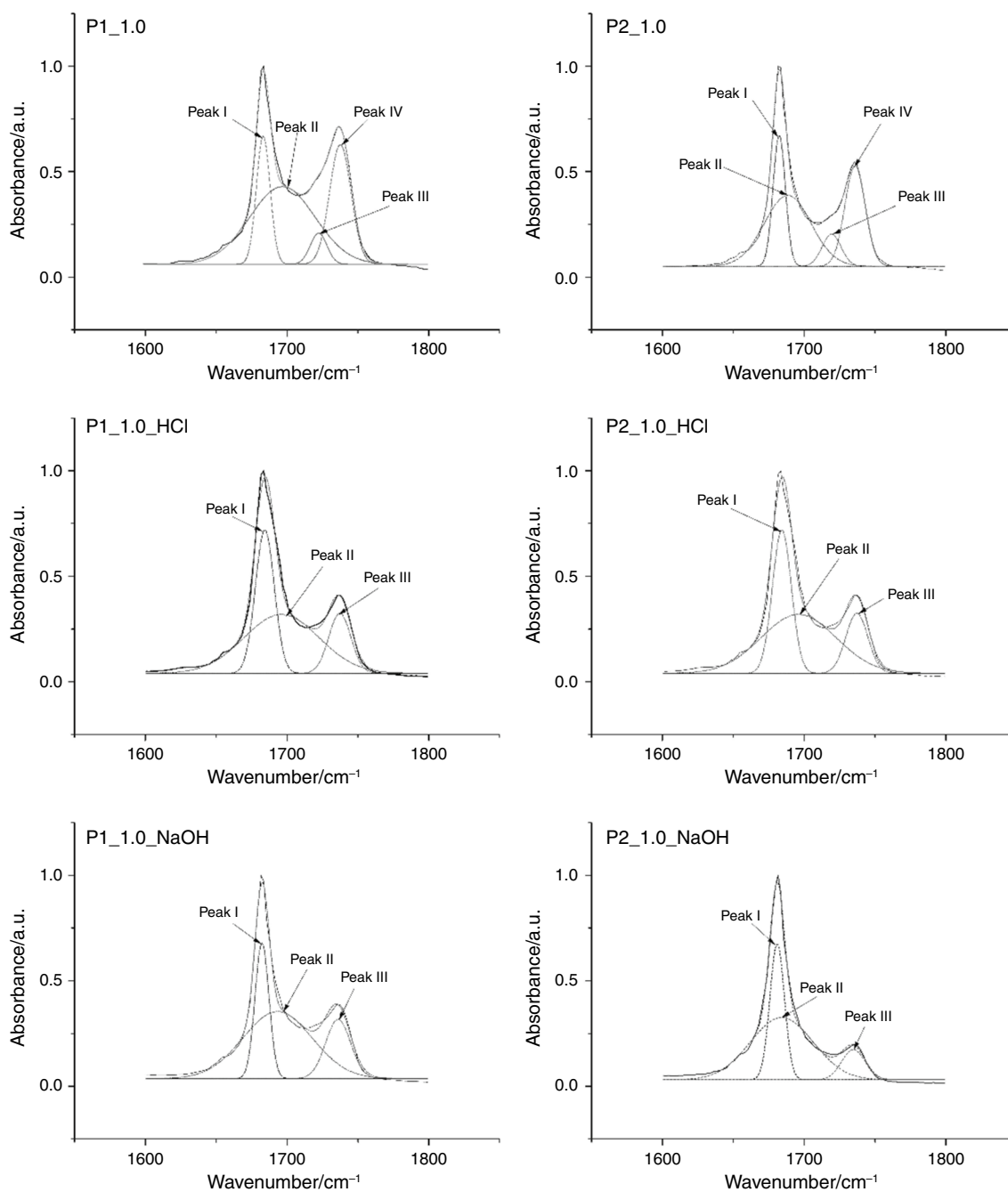


Fig. 3 Decomposed carbonyl multiple bands of bio-TPUs before and after hydrolytic stability test in alkaline and acidic condition

firstly in the disordered phase and then at the ordered phase, regardless of the type of polyol and pH test conditions.

In Table 2, the location (wavenumber) and peak absorbance (high), carbonyl index (R), degree of phase separation (DPS) and phase mixing (DPM) of bio-TPU before and after alkali and acid treatment were presented. In general, the higher the R -value, the higher the hydrogen bonding degree

in the structure [30]. Considering mentioned parameters it can be noticed that alkali and acid treatment have an influence on phase separation and hydrogen bonding of the prepared bio-TPUs. Regardless of pH of the solution and the molecular mass of the soft segments, the degree of phase separation increases. This can be explained by removing of amorphous phase from the hard and soft segments as well

Table 2 Carbonyl index, degree of phase separation and phase mixing for bio-TPU before and after alkali and acidic treatment

Sample	Wavenumber/cm ⁻¹	High/a.u	R	DPS	DPM	R-square	Reduced Chi-square
P1_1.0	1683	0.606	2.08	0.675	0.325	0.996	2.71•10 ⁻⁴
	1696	0.367					
	1722	0.147					
	1737	0.627					
P1_1.0_HCl	1684	0.279	2.80	0.737	0.263	0.992	4.12•10 ⁻⁴
	1696	0.678					
	1737	0.285					
P1_1.0_NaOH	1682	0.641	3.25	0.765	0.235	0.993	3.10•10 ⁻⁴
	1693	0.318					
	1737	0.281					
P2_1.0	1682	0.397	2.34	0.700	0.300	0.996	1.70•10 ⁻⁴
	1688	0.807					
	1719	0.619					
	1736	0.335					
P2_1.0_HCl	1684	0.678	3.19	0.762	0.238	0.994	3.44•10 ⁻⁴
	1696	0.279					
	1737	0.285					
P2_1.0_NaOH	1680	0.642	5.73	0.851	0.149	0.994	2.58•10 ⁻⁴
	1684	0.144					
	1734	0.296					

as the change in the hydrogen bonding proportion of the soft segments. If we look closer at the area of each peaks of absorption (Table 2), we can confirm our assumption.

One of the most common methods of degradation monitoring is the determination of mass change of material. In Fig. 4a, the comparison of mass changes of bio-TPU based on polyols P1 and P2 upon the immersion time in 5 M NaOH solution was shown. In the first week of the degradation test, there was a slight increase in mass. This was due to the absorption of the NaOH solution on the surface of the samples. After 28 days of samples incubation in alkaline solution slight decrease in bio-TPU mass was observed, which suggests that hydrolysis of ester bonds might occurred. The decrease in hydrolytic stability might be also the effect of poorer interactions between chains [22]. Analyzing Fig. 4b the mass changes are not noticeable. In general, it can be concluded that synthesized bio-TPUs are stable in acidic solution. After the first week of samples immersion in HCl solution, a slight increase in mass was observed. As previously, it was a result of solution absorption by the materials.

During the short degradation test, the visual observation was also performed in order to evaluate surface changes of bio-TPUs materials. The visual changes in the color of the materials after the material tests were observed. The bio-TPUs that were immersed in the HCl solution were visibly yellowed. There was no change in color of material of the HCl and NaOH solutions.

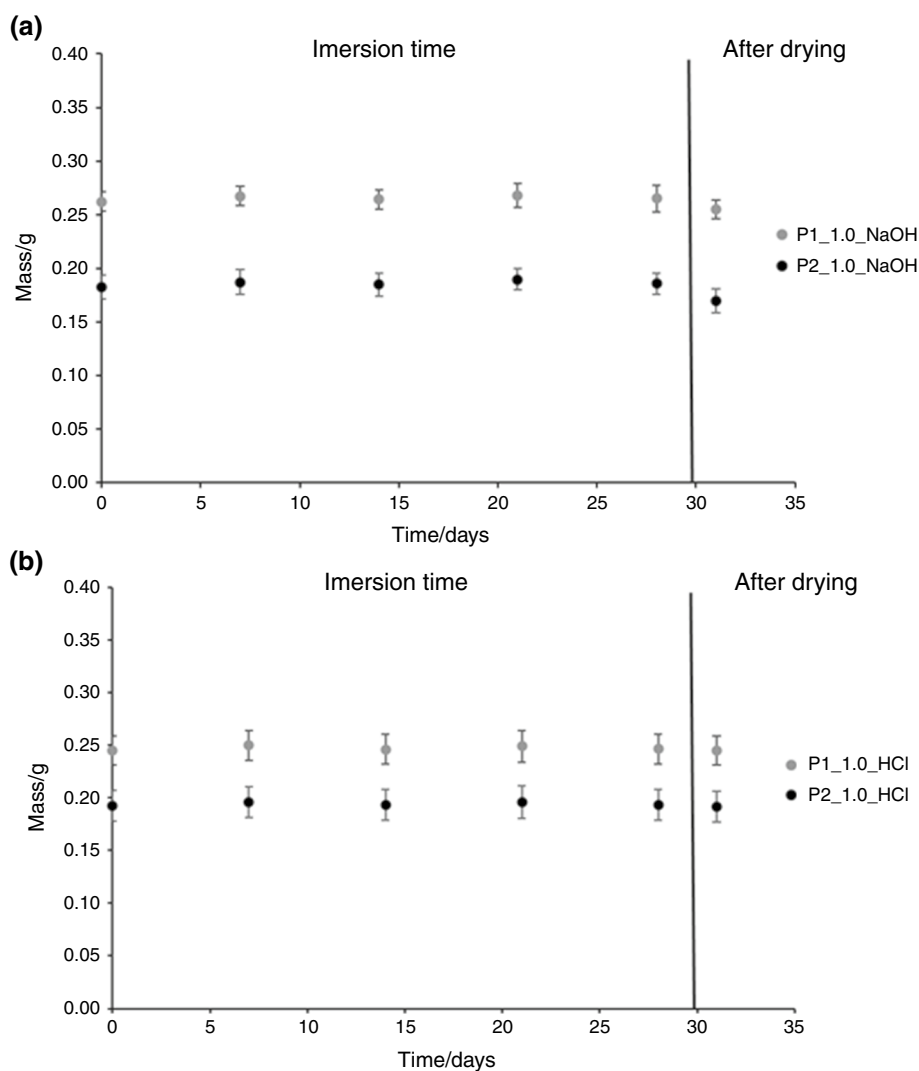
Thermal properties and stability of bio-TPUs

Melting and crystallization behavior of bio-TPU after alkali and acidic treatment—differential scanning calorimetry

Differential scanning calorimetry was used to explain the changes that occurred as a result of a short degradation test accelerated by acid and alkali treatment. Figure 5a and c shows the endothermic peaks for P1- and P2-based TPUs before and after acid and alkali treatment, the first and second run, respectively. Thermal effects such as glass transition temperature of soft and hard segments (T_{gSS} and T_{gHS}), and melting temperature (T_m) and enthalpy (ΔH_m) of hard segments were determined. Based on the exothermic curve shown in Fig. 5b, the crystallization temperature (T_{cHS}), and crystallization enthalpy (ΔH_{cHS}) of hard segments were studied.

Analyzing bio-TPUs, before incubation in alkali and acidic solutions, the differences in thermal behavior between P1-based and P2-based TPUs can be observed. Depends on the polyol molecular mass, the glass transition temperature of soft segments was ranging from -51.1 to -46.9 °C and is higher for bio-TPUs based on polyol with lower molecular mass, what is related to lower mobility of soft segments chains. In the case of T_{gSS} bio-TPUs immersed in alkali or acidic solution insignificant effect was observed (decrease in T_{gSS} ca. 1 °C).

Fig. 4 Mass changes of bio-TPUs immersed in (a) alkali solution (5 M NaOH) and (b) in acid solution (2 M HCl) after 7, 14, 21, and 28 days of immersion and after drying in 3 days



The influence of molecular mass of polyols was revealed in the melting behavior of hard segments. In Fig. 5a and c, multiple melting endotherm signals for P2-based TPUs were noticed for both heating runs, regardless the pH solution in short degradation test. This may be due to the presence of hard segment domains that differ in size and content. On the other hand, this phenomenon might be caused by the presence of single HS phase and a mixed phase which consists of both hard and soft segments. It can be seen that in the case of bio-TPUs based on polyol type P2 (with higher molecular mass), the melting temperature of hard segments decreases (Table 3), what can confirm the foregoing assumption. In the case of bio-TPUs based on P1 polyol, the melting of hard segments occurred at higher temperature in comparison with P2-based bio-TPU indicate the higher ordering in hard phase. Bio-TPUs immersed in acidic solution exhibit a slight decrease in melting temperature of hard segments.

The glass transition of hard segments (T_{gHS}) is weak, and hardly visible in the range of temperature from ca. 30–53 °C.

The lower values were noticed for bio-TPUs based on polyol P2 type. Similar findings were observed in [31]. If we examine the melting and crystallization enthalpy (ΔH_{mHS} and ΔH_{cHS}), we can observe an increase in both cases for TPUs based on polyol with higher molecular mass (P2), regardless of materials were immersed in acidic or alkali solutions. These results confirm our assumption about ‘accelerated’ ordering in the hard segments by acid and alkali treatment by removing the less stable amorphous phase. Considering reference TPUs (prior short degradation test), a lower melting enthalpy was observed. This may indicate the presence of amorphous structures in the hard segments.

Influence of molar ratio of [NCO]/[OH] and polyol type of bio-TPUs on thermal stability–thermogravimetry

The thermal stability of the synthesized bio-TPUs was determined by thermogravimetry. The effect of the molecular mass of the polyester bio-polyols and hard segment

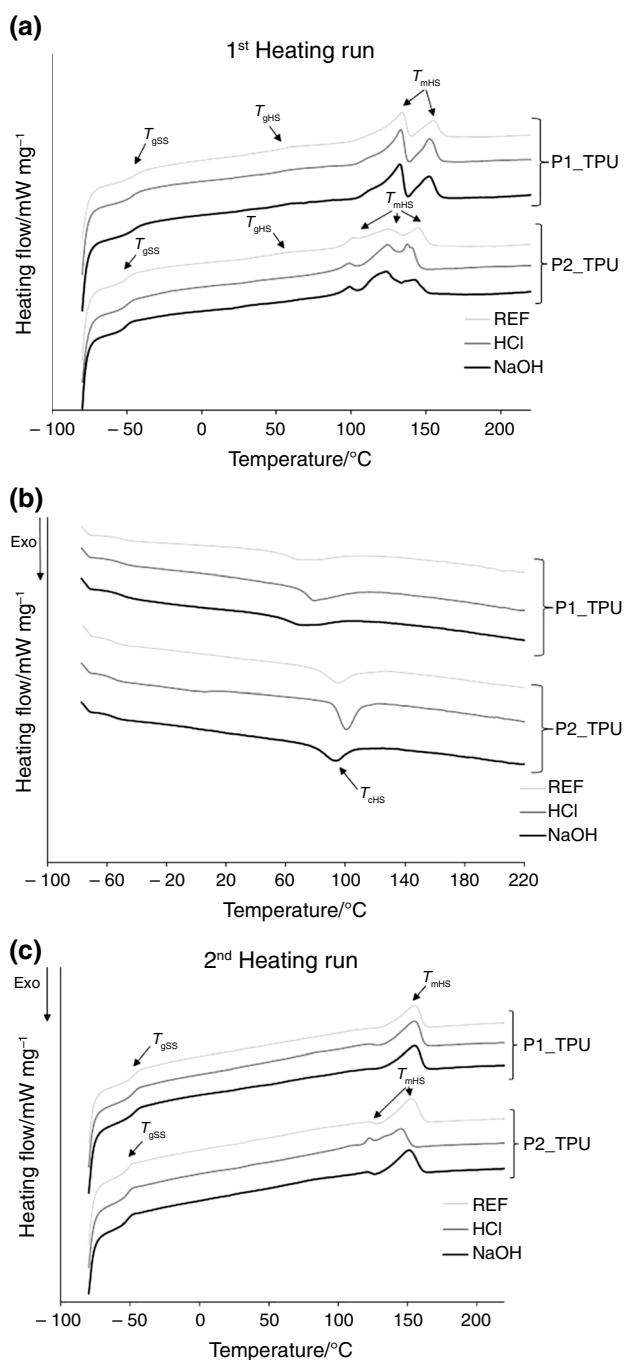


Fig. 5 DSC curves of bio-TPUs before (light gray) and after hydrolytic stability test in acidic (dark gray curves) and alkaline (black curves) condition, **a** first heating run, **b** cooling run, and **c** second heating run

content were taken into account during the analysis. The results are presented in Fig. 6 and Table 4. The purpose of the conducted measurement was to determine, e.g., temperature of 5%, 10%, and 50% of the mass loss, the rate of thermal decomposition at each degradation step

Table 3 Thermal properties of bio-TPUs before and after hydrolytic stability test determined by DSC technique (2nd heating run and cooling run)

	$T_{gSS}/^{\circ}\text{C}$	$T_{mHS}/^{\circ}\text{C}$	$\Delta H_{mHS}/\text{J g}^{-1}$	$T_{chS}/^{\circ}\text{C}$	$\Delta H_{chS}/\text{J g}^{-1}$
P1_1.0	-46.9	155.3	12.91	67.4	-9.77
P1_1.0_HCl	-46.6	154.9	13.61	78.5	-15.11
P1_1.0_NaOH	-47.5	155.1	13.02	68.8	-9.26
P2_1.0	-51.2	152.5	13.81	93.6	-12.96
P2_1.0_HCl	-50.6	122.5 145.6	12.04	100.3	-18.79
P2_1.0_NaOH	-51.5	150.9	13.43	92.5	-15.86

and amount of ash residue. It is important to take into account that the thermal degradation of polyurethanes is a complex process, and its mechanism depends on structure and amount of the monomers used for TPU preparation, or atmosphere of the measurements. According to the literature, the temperature of beginning of degradation $T_{5\%}$ (temperature of 5-percent of mass loss) mainly depends on the hard segments and thereby, chemical structure and length of isocyanate and chain extender used for PUs synthesis. Content of HS also plays a key role. In addition, the products of thermal decomposition of the hard segments could affect the thermal stability of the soft segments [29].

Analyzing the derivative thermogravimetric curves (Fig. 6), the two-step thermal decomposition of bio-based TPUs was observed. This pattern is characteristic for materials with a segmented structure and confirms the sufficient phase separation between hard and soft segments. The first step of degradation occurring at a lower temperature is due to the degradation of the hard segments, which consist of diisocyanate and chain extender. At the second step, soft segments decomposed [31, 32]. In general, $T_{5\%}$ increases with increasing of $[\text{NCO}]/[\text{OH}]$ molar ratio, regardless of the polyol type (Table 4).

Considering the effect of the $[\text{NCO}]/[\text{OH}]$ molar ratio on the thermal stability of bio-TPUs, the relationship between the maximum temperatures of each degradation stage and the DTG values can be observed. In the case of the first peak, both the temperatures at the peak maximum and the rate of degradation depend on the $[\text{NCO}]/[\text{OH}]$ molar ratio, and the type of polyol. As the $[\text{NCO}]/[\text{OH}]$ molar ratio increases, the rate of degradation increases for materials based on polyol P2. On one hand, it is due to the higher content of hard segments, and on the other hand, it can be related to the amorphous structure of polyols which affected the hard segments thermal stability. If we took into account the second peak and registered maxima, slightly higher thermal stability exhibited bio-TPUs based on polyol P2. No predominant

Fig. 6 Dependence of derivative mass loss as a function of temperature for obtained bio-TPUs

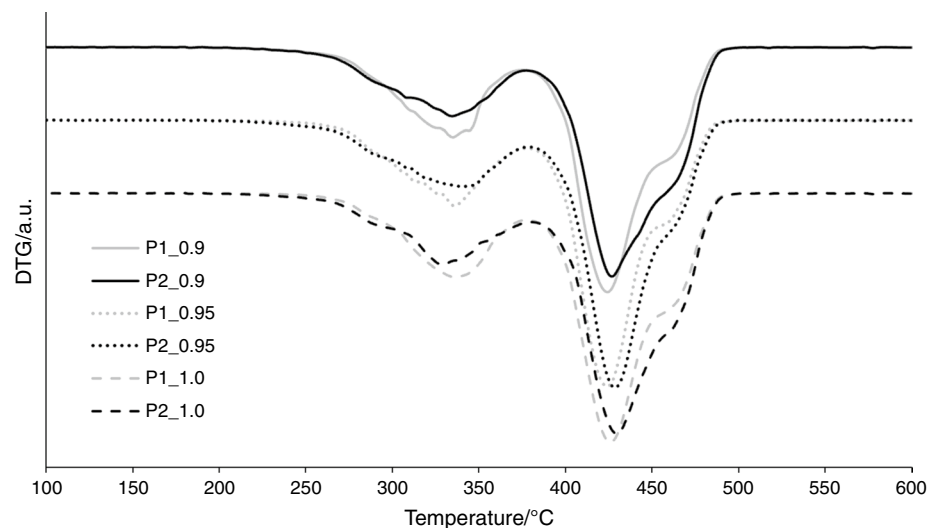


Table 4 Thermal characteristic of bio-based thermoplastic polyurethane elastomers based on polyols P1 and P2

Sample	$T_{5\%}/^{\circ}\text{C}$	$T_{10\%}/^{\circ}\text{C}$	$T_{50\%}/^{\circ}\text{C}$	$T_{\text{DTG1}}/^{\circ}\text{C}$	$\text{DTG}_1/\% \text{min}^{-1}$	$T_{\text{DTG2}}/^{\circ}\text{C}$	$\text{DTG}_2/\% \text{min}^{-1}$	Mass at $800^{\circ}\text{C}/\%$
P1_0.9	303.4	319.5	418.2	335.8	-4.66	424.5	-14.55	1.90
P1_0.95	300.9	316.4	418.4	335.0	-4.90	423.3	-13.99	1.93
P1_1.0	308.7	323.6	420.9	336.1	-4.57	425.9	-13.64	2.33
P2_0.9	297.5	317.6	423.0	340.5	-3.62	428.6	-14.63	2.52
P2_0.95	298.5	317.8	425.0	334.6	-3.75	426.8	-12.54	3.26
P2_1.0	301.7	321.6	425.4	328.6	-3.88	429.6	-13.15	2.75

effect of [NCO]/[OH] molar ratio on thermal stability of soft segments was observed. The rate of each step of degradation (see Table 4) was determined by the type of polyol used for bio-TPUs preparation.

Based on the results presented in Table 4, general conclusions can be formulated about the correlation between both the type of polyol used for the synthesis of bio-TPU, as well as the [NCO]/[OH] molar ratio. The thermal stability of the obtained materials mainly depends on the [NCO]/[OH] molar ratio. With increasing of [NCO]/[OH] molar ratio, the thermal stability increases, which is consistent with theoretical assumptions [21]. The nature of the polyol can be observed in the $T_{50\%}$ values, which are slightly higher for P2 polyol-based bio-TPU. This is due to the higher molecular mass and longer chain of this polyol. Therefore, there is a higher solid residue at 800°C .

Thermomechanical properties

The thermomechanical and damping properties of bio-TPUs were investigated by dynamic mechanical analysis. Based on this measurement viscoelastic properties of the bio-TPUs in term of storage modulus (E'), loss modulus (E'') and glass

transition temperature of the soft segments (T_{gSS}) were determined and shown in Fig. 7a-c.

Figure 7a shows the characteristic changes in storage modulus as a function of temperature for segmented thermoplastic polyurethane elastomers. The first temperature ranges from -100 to -60°C is the area where materials P1 and P2 are in the glassy state. The glass transition of the soft segments takes place in the temperature range from about -60 to $+50^{\circ}\text{C}$ with a maximum at T_{gSS} of -27°C and -32°C for samples P1_1.0 and P2_1.0, respectively. The literature claims that the glass transition of the hard segments occurs in the temperature ranges from 50 to 110°C . Above 110°C , the material starts to flow. Considering the sudden drop in the behavioral modulus, this indicates the presence of an organized phase in the structure of bio-TPUs, specifically in the hard segments. Especially in the case of P2 series of materials. At room temperature (25°C), the P1 polyol-based material shows a higher storage modulus. It follows that this material should be characterized by a higher stiffness. Considering the course of the $\log E'$ curves, it can also be assumed that P2 polyol-based materials can be processed at lower temperatures and due to the lower values of the storage modulus, thereby under lower pressure conditions.

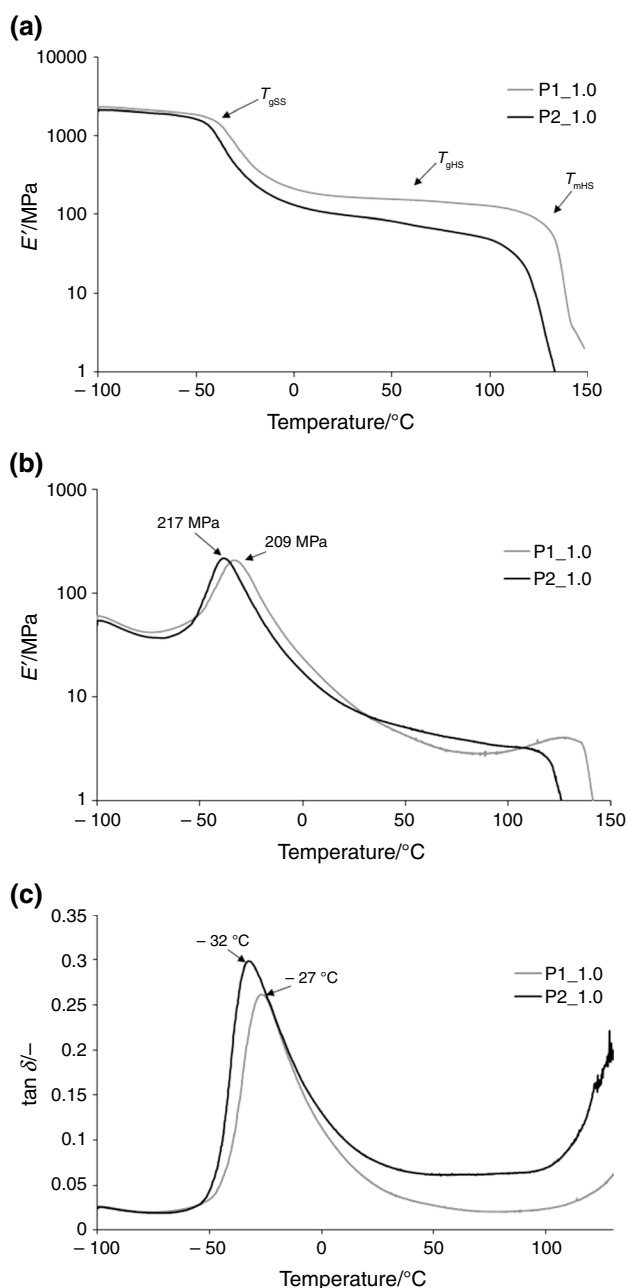


Fig. 7 Comparison of **a** the storage modulus (E'), **b** the loss modulus (E''), and **c** loss factor ($\tan \delta$) curves of thermoplastic polyurethane elastomers exemplified by P1_1.0 and P2_1.0

Analyzing Fig. 7b, which shows the logarithm of the loss modulus as a function of temperature, it can be concluded that the two materials differ slightly in terms of energy loss. Insignificantly higher values of loss modulus were registered for bio-TPU, which is based on a higher molecular mass of polyol. The higher the molecular mass of SS, the greater E'' . This material also has a higher damping coefficient (see Fig. 7c). The glass transition temperatures of the soft segments recorded from the maximum of $\tan \delta$ curve are -32 and -27 $^{\circ}\text{C}$ for P2_1.0 and P1_1.0 materials, respectively. The lower glass transition temperature for the P2 polyol-based material was expected, and it is due to the higher molecular mass of the polyol.

Mechanical and physical properties of bio-TPUs— influence of molar ratio of [NCO]/[OH] and polyol type

In order to predict the possibility of applying synthesized bio-TPUs, mechanical and physical properties were determined based on tensile test, hardness and density measurements and presented in Table 5. It is well known that the mechanical properties of polyurethanes depend and can be controlled by using components of different chemical structures at appropriate molar ratios [13]. For example, the segment flexibility, cross-linking, chain entanglement, segment orientation or hydrogen bonding should be considered when designing the PU structure and characterizing the results from mechanical measurements.

Analyzing obtained results (Table 5), it can be observed that depending on molar ratio and polyols molecular mass, bio-TPUs vary in the values of the strength parameters (tensile strength, the elongation at break and permanent elongation). For both for P1 and P2, the tensile strength and elongation at break increase with increasing isocyanate ratio. According to the literature, increase in molar ratio of isocyanate to hydroxyl groups enhances physical cross-linking by hydrogen bonds, affects the above-mentioned specificity of bio-TPU. On the other hand increasing in molar ratio of [NCO]/[OH] also leads to an increase in molecular mass of polymer and thereby improvement in tensile properties [33].

Considering P1 samples, the increase in tensile strength is more noticeable than in the case of samples series P2.

Table 5 Tensile properties, hardness and density

Sample	TS_b/MPa	$\epsilon_{\text{break}}/\%$	$\epsilon/\%$	H/ShD	$d/\text{g cm}^{-3}$
P1_0.9	3.94 ± 0.19	11 ± 1	0.39 ± 0.21	24.3 ± 1.3	1.004 ± 0.006
P1_0.95	6.85 ± 0.27	30 ± 2	1.84 ± 1.06	37.3 ± 0.1	1.004 ± 0.003
P1_1.0	9.31 ± 0.61	131 ± 16	27.95 ± 4.93	38.2 ± 0.7	1.003 ± 0.004
P2_0.9	2.55 ± 0.42	13 ± 2	1.23 ± 0.85	21.5 ± 0.5	1.019 ± 0.006
P2_0.95	3.03 ± 0.42	18 ± 1	3.38 ± 0.51	21.8 ± 0.6	1.021 ± 0.002
P2_1.0	3.45 ± 0.47	17 ± 2	2.93 ± 0.84	23.3 ± 1.2	1.018 ± 0.005

Table 6 Properties of bio-based TPUs in relation to the isocyanate index, including molecular mass of bio-based polyester polyol

Properties	Influence of isocyanate index and/or polyol molecular mass on bio-TPU
Hydrolytic stability	Bio-TPUs based on polyol P1 and P2 undergo the hydrolytic degradation activated via acid and alkali environment
Thermal properties	DSC analysis confirm influence of polyol molecular mass and acidic and alkali treatment on the glass temperatures and melting/crystallization behavior of bio-TPUs TGA revealed that the thermal stability of bio-TPUs increases with increasing isocyanate index
Termomechanical properties	With increasing in molecular mass of polyols, glass transition temperature of soft segments decreased
Mechanical properties	Tensile strength and elongation at break Increases with increasing isocyanate index
Physical properties	Hardness increases with increasing isocyanate index and decreases with increasing of molecular mass of polyol. Regardless NCO/OH molar ratio and polyol molecular mass bio-TPUs exhibit similar density

Overall, bio-TPUs based on polyol type P1 exhibit better tensile properties compared to bio-TPUs series P2. A similar trend was observed in the case of the permanent elongation. Among all the bio-TPUs, P1_1.0 is outstanding—it reaches the highest tensile strength and relative and permanent elongation. For comparison, materials based on polyol P2 and synthesized in equimolar [NCO]/[OH] exhibit lower T_{Sb} , ϵ_{break} and ϵ indicate on durable nature of this bio-TPUs. Enhancement in tensile properties of P1-based bio-TPUs may be related to the molecular mass of polyol. As was mentioned increase in molecular mass of polymer, due to increase in tensile properties. Nevertheless, there might be a specific limit in molecular mass of bio-TPU, which caused decrease in the chain mobility because of chain entanglements and thereby in elongation at break and tensile strength [33].

In the case of hardness similar trend to tensile properties was noticed. With increasing of molar ratio of isocyanate groups to hydroxyl groups, increase in hardness was observed (see Table 5). In general, hardness is related to the intermolecular interactions in the material. The stronger the interactions, the greater the hardness of the material. Taking into account the higher content of amorphous phase in bio-TPUs based on polyol P2, these set of materials exhibited lower hardness. The densities of both bio-TPUs are higher than 1.0 g cm^{-3} , but in the case of materials obtained from bio-polyol P2 slightly higher densities regardless of the [NCO]/[OH] molar ratio was observed. It is caused by higher molecular mass of resulting bio-TPUs by the incorporation of branched polyester polyols.

Conclusions

The hydrolytic and thermal stability of bio-TPUs might be controlled by the types of monomers and also by the molar ratio of the main components. The research results evaluate the effect of molecular mass of bio-based polyester polyol and hard segment content on the selected properties of

bio-based thermoplastic polyurethanes (Table 6). Both variables revealed their effect on thermal stability and mechanical properties of bio-TPUs. Based on conducted measurements it can be stated that a polyol with a mass of $\sim 2000 \text{ g mol}^{-1}$ (polyol P1) improved the mechanical properties and thermal stability of the bio-TPUs. The bio-TPUs mentioned, based on polyol P1, are characterized by a slightly lower density than the bio-TPUs based on polyol P2. The effect of the [NCO]/[OH] molar ratio and thereby hard segments content on bio-TPU was revealed as an increase in hardness, tensile strength and thermal stability. An increase in the molecular mass of the polyols leads to a decrease in the glass temperature. Due to the structure of branched polyester polyols, it is possible to reduce the tendency of hydrolytic degradation compared to polyester-urethanes based on linear polyols.

Summarizing, application of vegetable-based polyols can efficiently improve selected properties of bio-based polyurethanes. Obtained materials exhibited quite good hydrolytic resistance, thermal stability and thermomechanical properties.

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