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Structure and properties comparison of poly(ether-urethane)s based on nonpetrochemical and petrochemical polyols obtained by solvent free two-step method

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ABSTRACT

The application of thermoplastic polyurethanes (TPU) is becoming more and more extensive, and the decreasing of used petrochemical monomers and reduction of energy for the polymerization and processing processes is getting increasingly important. In this paper, we confirmed the positive influence of high bio-based monomers contents (by replacing petrochemical polyol and glycol by bio-based counterparts) on processing and properties of obtained materials. A series of partially bio-based thermoplastic poly(ether-urethane)s (bio-based TPU) were obtained from bio- and petrochemical-based polyols, bio-based 1,4-butanediol, and 4,4′-diphenylmethane diisocyanate by the two-step method without using any solvents. Both the monomers' origin and polyurethane prepolymer processing parameters were taken into account in characterization of the obtained materials. The TPUs' chemical structure was analyzed by FTIR spectroscopy and ^{1}H NMR and the number average molecular weight was examined by ^{1}H NMR and GPC. The measurements of dynamic mechanical thermal analysis, tensile test, hardness, density method, and rheological behavior provided useful information about the properties of prepolymers and TPUs. The processing properties and an activation energy of prepared materials was examined using the melt-flow index. It has been confirmed that despite the origin of polyols obtained thermoplastic poly (ether-urethanes) exhibited comparably good mechanical and thermo-mechanical properties, and an appropriate melt flow index facilitates their processing. Nevertheless, the use of high amount of bio-based monomers resulted in obtaining more eco-friendly materials.

1. Introduction

Thermoplastic polyurethanes (TPUs) interest scientists not solely because these materials exhibit a wide spectrum of excellent and versatile properties, but also because they combine the advantages of thermoplastic and elastomeric materials, including facilitated processing [1]. TPUs are synthesized by the reaction between diisocyanate, polyol and low-molecular chain extender by two different methods, namely a one-shot or two-shot method [2,3]. In the two-shot method, which is called the prepolymer method, prepolymer is synthesized by the reaction of polyol with stoichiometric excess of diisocyanate [4]. Subsequently, the obtained prepolymers are used in the synthesis of polyurethane materials, such as thermoplastics, elastomers, foams, coatings, adhesives and sealants by the reaction with glycol or diamine [5-7].

In spite of the different types of polyurethanes, until recently most substrates used for the preparation of prepolymers and polyurethanes were derived from petroleum only (non-renewable petroleum, natural gas, coal, etc.) [8]. As a result, it leads to serious environmental and energy problems and limits the sustainable development of polymer materials. Nevertheless, in recent times growing interest in applying bio-based substrates as a primary component in the polyurethane synthesis is distinctly visible [9-15]. This tendency is determined by the disadvantageous forecast of oil consumption [10,16]. Moreover, according to the literature, the substitution of the petrochemical component provides a decrease in the synthesis cost with an increasing amount of production and made for the reduction of energy consumption during synthesis, the reduction of greenhouse gas emissions (including decreased CO_2 emissions), and the biodegradability improvement. As a result, a few years ago this contributed to the search for new, renewable monomers, which can replace the typical petrochemical monomers [17,18]. Therefore, nowadays the bio-based components have become more accessible,

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including polyols, glycols, and diisocyanates from bio-resources, which allows the production of bio-polyurethanes [19,20]. Additionally, nowadays it is crucial to save energy in the industrial processes and this is possible by decreasing the viscosity of processing liquid systems. Selected features can be controlled by the proper selection of monomers and the molar ratio of diisocyanate group to a hydroxyl group during their polymerization [20-22].

Polyols have a large impact on the processing of prepolymers and polyurethanes, and properties of obtained materials. In general, polyols constitute more than half of the total polyurethanes composition. Usually application of polyether polyols lead to lowering of the viscosity of urethane prepolymers and polyurethane composition too, which is beneficial during industrial processing. Depend on the polyether polyol structure (linear or branch) or molecular weight, the resulted polyurethanes exhibit different properties. For instance linear structure of polyols influences on the tendency of creation of ordered soft phase in the structure of polyurethane. Branched polyols due to the creation of amorphous soft segments. Among commonly used polyether polyols are: poly(ethylene glycol) (PEG) poly(propylene glycol) (PPG), poly(tetramethylene glycol) (PTMG) or poly(tetrahydrofuran) (polyTHF) and all of them are petrochemical origin. Nowadays, bio-based polyols are used more often for polymers production. As an example of bio-based counterparts of mentioned polyether polyols is bio-based polytrimethylene ether glycol (PO3G). This polyol is produced with different molecular weights in the acid-catalyzed polycondensation reaction of bio-based 1,3-propanediol (product obtained in fermentation process of corn-based glucose) [23]. In the market, this polyol is available under the trade name Velvetol and produced by Allesa company [17,24].

PO3G can be successfully applied for polyether-urethanes synthesis [1,25,26] and for the synthesis of bis(cyclic carbonate)s for non-isocyanate polyurethane materials (NIPU) preparation [27]. Next example of bio-based polyols based on 1,3 propylene glycol is bio-based poly(1,3-propylene succinate) glycol (PPS), product of the polycondensation reaction of 1,3-propanediol and succinic acid. Molecular mass of mentioned polyol ranging from 1000 to 4000 g/mol. The properties of thermoplastic polyurethanes obtained with the use of mentioned PPS via solvent free one shot method depended on molecular weight. Bio-based polyurethanes based on PPS exhibited glass transition temperature in the range of −2.16 to 18.25 °C. Melt flow index, hardness and tensile strength increased with increasing of molecular weight because of to many secondary bonds and the high molecular chain entanglement [28].

Parcheta et al. obtained by series of bio-based polyester polyols: poly(1,3-propylene succinate) glycol (PPS), poly(1,4-buthylene succinate) glycols (PBS) and copolyester polyols poly(propylene succinate-co-butylene succinate)s (SPB) [10,29,30]. Polyols were synthesized via polycondensation of bio-based substrates such: succinic acid, 1,4-butanediol and 1,3-propanediol. Obtained PPS polyols were used for thermoplastic polyurethane elastomer preparation without catalyst usage. Bio-based thermoplastic polyurethane elastomers characterized by glass transition temperature ranging from ca. 0–5 °C, hardness ca. 40 °ShD and tensile strength ca. 30 MPa [31].

Other example of usage corn-based products is bio-based polyol which was synthesized using corn oil and 2-mercaptoethanol via thiol-ene reaction using UV irradiation. Such kind of polyol with a hydroxyl number and an acid value of 176 mg KOH/g and 1.77 mg KOH/g, was used for preparation of flame retardant rigid polyurethane foam. Dimethyl methyl phosphonate was added in different amount to the polyurethane systems as a flame retardant, In the result foams characterized by higher closed cell content, moderate compression strength and improved flame retardancy were obtained [32].

As was mentioned earlier polyurethanes can be obtained via two-shot method known as prepolymer method. The properties of the prepolymer which is obtained in the first step synthesis of TPUs depend on the molar ratio of isocyanate to a hydroxyl group, viscosity, the presence or absence of water, and the properties of diisocyanates and polyols. The viscosity of the prepolymer is one of the most important factors, which determines the future processing methods of a given system [6]. In general, fluids can be described by the Newtonian fluid model or by non-Newtonian fluid models. In the case of the rheological characterization of polyurethane prepolymers, these fluids are usually described by the Ostwald-de Waele and Herschel-Bulkley models which are assigned based on rheograms and depended on the monomers (including their viscosity) used for their synthesis. The mentioned models are applicable to non-Newtonian fluids [33,34].

Polyurethane prepolymers are considered pseudoplastic fluid chemicals. These pseudoplastic fluids become thinner when the shear rate increases until reaching the plateau of limit viscosity. The elements suspended in the fluid follow the direction of the current, which is caused by a raised shear rate [6]. Determination of polyurethane prepolymers' rheological properties allows to properly adjust the further processing parameters. Polyurethane prepolymers and liquid polyurethane systems are often processed by the reaction injection molding technique, gravity molding or rotary molding and coating.

Along with changing the monomers used in polyurethane prepolymers and polyurethanes, the processing and further properties can be also changed, and are related with theirs molecular weight. The presence of complicated polymer structures and branches caused their viscosity to not have to be proportional to the molecular weight [35]. That is why it is worth determining the molecular weight based on gel permeation chromatography (GPC) or nuclear magnetic resonance (NMR), while their processing behavior can be effectively determined by melt flow index measurements.

TPUs can be processed by thermoplastic techniques such as injection molding, extrusion or blow molding. When it comes to practical application of these materials, melt flow index (MFI) is an essential factor influencing the melt processability, requirements of customers, and, due to the simplicity of operation, good reproducibility of results and low cost [36]. The MFI depends on the polymer structure, number and weight average molecular weight, and polydispersity index. The MFI is determined by measuring the melt mass flow rate (MFR) or melt volume flow rate (MVR) [37,38]. The weight (g) or the volume (cm^3) of a polymer extruded in a defined period of time through a capillary of a specific diameter and length by the pressure applied by a weight at a certain time is determined during the measurement of MFI (according to the standard EN ISO 1133–1).

In this work we developed environmental-friendly bio-based thermoplastic poly(ether-urethane)s by incorporating to their synthesis high amount of bio-based monomers. We investigated the effect of bio-based polyols and bio-glycols on the chemical structure and rheological behavior of prepolymers and poly(ether-urethane)s obtained with their use and to compare their properties with petrochemical analogues. For each sample mechanical and physicochemical properties and also processing parameters of liquid ether-urethane prepolymers and bio-based thermoplastic poly(ether-urethane)s were determined.

2. Experimental

2.1. Materials

Thermoplastic poly(ether-urethane)s were synthesized using 4,4′-diphenylmethane diisocyanate (MDI; BorsodChem, Hungary), bio-based 1,4-butanediol derived from corn sugar as a chain extender (kindly provided by BASF, Germany) and two different polyols (Fig. 1**a**), bio-based polytrimethylene ether glycol (PO3G, M_n = 2000 g/mol) and petrochemical-based polytetramethylene ether glycol (PTMG, M_n = 2000 g/mol) supplied by Allesa (Germany) and BASF (Germany), respectively. 1,4-diazabicyclo[2.2.2]octane (DABCO), used as a catalyst, was purchased from Sigma-Aldrich.

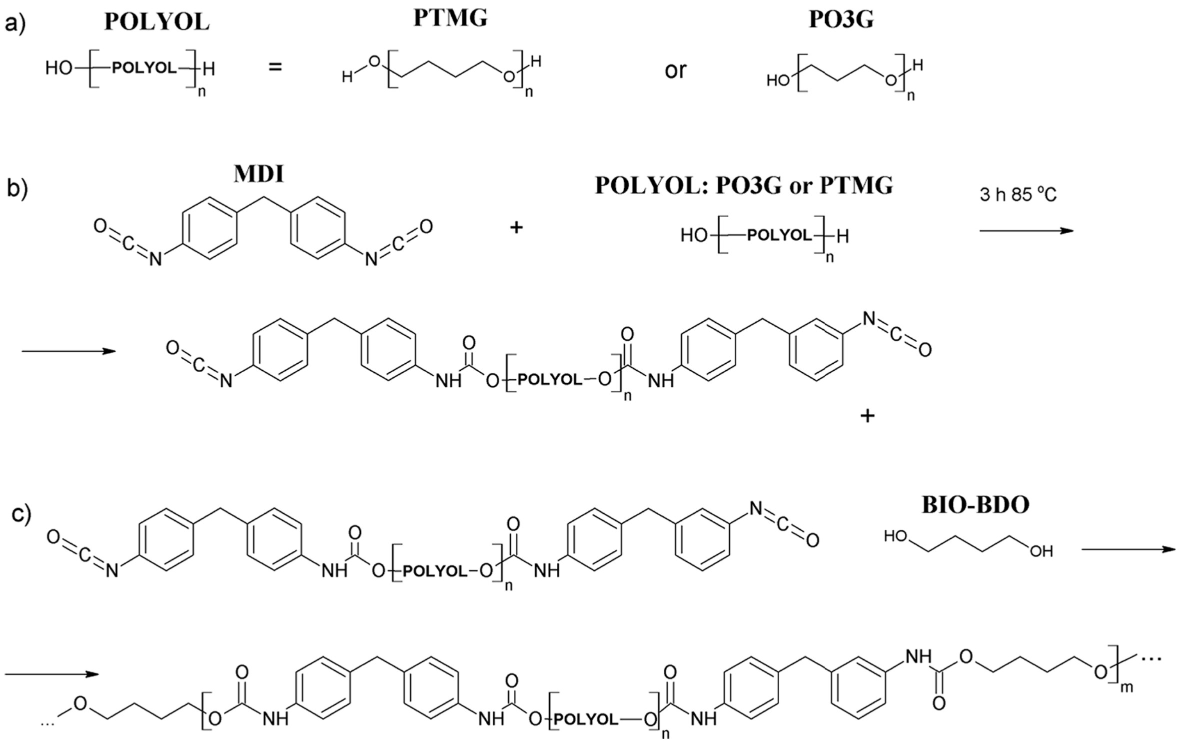

Fig. 1. a) Structure of polyols used, and the synthesis of partially bio-based thermoplastic poly(ether-urethane)s by the prepolymer method; b) synthesis of the prepolymer by the reaction of diisocyanate with polyol; c) extension of ether-urethane prepolymer chains by using bio-based glycol.

2.2. Synthesis

The thermoplastic poly(ether-urethane)s were synthesized by a two step-method (prepolymer method) which was presented in Fig. 1**b-c**. The prepolymer was synthesized by the reaction of polyol (which was dried for 2 h at 95 °C under the vacuum) with the molar excess of diisocyanate at 85 °C for 3 h, resulting in the isocyanate-terminated prepolymer. The amount of isocyanate groups equaled 8.0% (determined according to ISO 14896 standard). In the second step, the obtained prepolymer chains were extended by using a mixture of bio-based 1,4-butanediol (Bio-BDO) and catalyst (0.3 wt%). The extension of prepolymer chains was conducted at three different ([NCO]/[OH]) molar ratios of 0.9, 0.95, and 1.0, respectively. In order to insure the completeness of the reaction, the obtained thermoplastic poly(ether-urethane)s were cured at 100 °C for 24 h in a laboratory oven.

The schematic structure of the used monomers and the scheme of the reactions are presented below (Fig. 1**a–c**).

2.3. Characterization of the synthesized materials

2.3.1. Fourier Transform Infrared spectroscopy (FTIR)

The chemical structure of all obtained materials was investigated by Fourier Transform Infrared Spectroscopy by means of a Nicolet FTIR 8700 spectrophotometer (Thermo Electron Corporation, USA). Spectra were registered at the wavenumber range from 500 to 4500 cm^{-1}, with a resolution of 4 cm^{-1}. Each spectrum was acquired with 64 scans. Measurements were taken at room temperature.

2.3.2. Rheological measurements of prepolymers

The rheological measurements were performed with the use of an R/S-CPS + rotary rheometer (Brookfield Company, USA). The viscosity values at 60, 70 and 90 °C and mathematical models for rheological behavior description were defined with the use of the computer program Rheo3000. The measurements were conducted with controlled shear rate (CSR). The following program was applied: increasing shear rate from 1 to 200 s^{-1} for 120 s; constant shear rate of 200 s^{-1} for 120 s; and decreasing shear rate from 200 to 1 s^{-1} for 120 s.

2.3.3. Nuclear magnetic resonance (^{1}H NMR)

The hydrogen proton nuclear magnetic resonance (^{1}H NMR) spectra of the prepared thermoplastic poly(ether-urethane)s were obtained with the use of a Varian Mercury Vx spectrometer in order to determine the chemical structure and the number average molecular weights. The ^{1}H NMR spectra were recorded at room temperature and at a frequency of 400 MHz by applying C_5D_5N as a solvent.

End-group analysis and estimating surface areas under the resonance peaks in the ^{1}H NMR spectra which are proportional to the molar concentration of the species in the materials [39] enabled to determine of the number average molecular weights of TPUs.

The following equations (2), (3) and (4) are used to calculate the degree of polymerization (n) and the number average molecular weight (M_n) of partially bio-based thermoplastic poly(ether-urethane)s. The chemical structure of the analyzed materials is given in Fig. 2. Synthesized TPUs are terminated by a residue of a bio-based BDO glycol used as a chain extender, where three different CH_2 groups (differing in adjoining protons) can be identified. Peaks “F” and “E” correspond to CH_2 groups which are enclosed by four hydrogen atoms [40].

$$(\boldsymbol{E}+\boldsymbol{F})\ \left(\boldsymbol{n}\ \ 4\boldsymbol{H}_{\boldsymbol{repeated\ \ unit}}+4\boldsymbol{H}_{unit\ \ at\ \ the\ \ end\ \ of\ \ the\ \ chain}\right) \tag{2}$$

$$\boldsymbol{I}\ \left(4\boldsymbol{H}_{\boldsymbol{on\ \ the\ \ chain\ \ end}}\right) \tag{3}$$

$$\boldsymbol{n}=\frac{(\boldsymbol{E}+\boldsymbol{F})-\boldsymbol{F}}{\boldsymbol{I}} \tag{4}$$

where: “F’ and “I” are the areas of the peaks of CH_2 end groups and “E” is the intensity of the peak of CH_2 end groups in the repeating unit. Because “I” and “F” have the same meaning and occur in the same equation (5), it takes the form expressed as:

$$\boldsymbol{n}=\boldsymbol{E}/\boldsymbol{F} \tag{5}$$

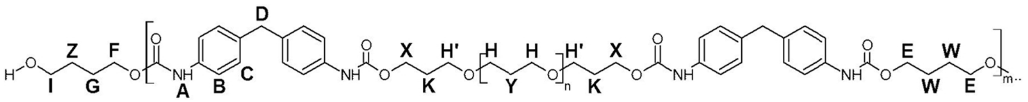

Fig. 2. The chemical structure of TPU with assigned protons.

Determining the degree of polymerization allows to calculate the number average molecular weight of the obtained bio-based thermoplastic materials as below (equation (6)).

$$M_n = n\left(M_{n(repeated\quad unit)}\right) + M_{n(end\quad unit)} \tag{6}$$

2.3.4. *Gel permeation chromatography (GPC)*

GPC was carried out using a GPC system equipped with two detectors: a refractive index detector (Shodex, Japan) and a UV–Vis detector ($\lambda = 254$ nm, LCD 2084, Ecom, Czech Republic). A set of three columns (PLgel with particle size of 10 μm, pore size: 50/10E3/10E4 Å, 300 × 7.5 mm, Polymer laboratories, UK) was applied. As an eluent tetrahydrofuran was used with a 1 ml/min flow rate. The polystyrene standards were used for calibration. The number average (M_n) and weight average (M_w) molecular weights, as well as the polydispersity were determined.

2.3.5. *Melt flow index (MFI)*

The values of MFI (as MFR - melt mass-flow rate and MVR – melt volume-flow rate) and an energy activation (E_a) were measured in the samples of the obtained thermoplastic poly(ether-urethane)s using a Zwick/Roell plastometer, according to ISO 1133. The reported MFI values are averages from at least five determinations. The measuring procedure was conducted at different temperatures (from 170 °C to 210 °C) by applying a 5.0 kg load.

2.3.6. *Dynamic mechanical thermal analysis (DMTA)*

DMTA measurements of the obtained poly(ether-urethane)s were performed according to the ASTM D 4065 standard with the use of DMA Q800 Analyzer (TA Instruments). Rectangular samples (length 40 mm × width 10 × 2 mm thickness) were used for the test. Measurements were conducted in the standard temperature range between −100 and 150 °C at a heating rate of 4 °C min^{-1} and a frequency of 10 Hz. Based on the results the glass temperature of soft segments (T_{gSS}); the damping coefficient (tangent delta); storage modulus (E′) at T_{gSS}; and loss modulus (E″) were determined.

2.3.7. *Mechanical properties*

Testing of mechanical properties (tensile strength (TS_b) and elongation at break (E_b)) were investigated in accordance with ISO 37. Tensile test was carried out with a Zwick/Roell Z020 universal testing machine with cross-head speed 100 mm/min at room temperature. The dumbbell specimens type 1 were used.

2.3.8. *Hardness*

The hardness of the materials was measured using an electronic Shore type D Durometer at room temperature, according to the ISO 868 standard. The presented results are averages calculated from ten points per one type of sample.

2.3.9. *Density*

The density of the prepared materials was measured with a RADWAG analytical balance by a hydrostatic method. The methanol was used as an immersion medium. The measurements were carried out at room temperature, in accordance with the ISO 2781 standard. Five measurements were obtained for each sample.

3. Results and discussion

3.1. *Rheological behavior of prepolymers*

Based on the rheological measurements, the viscosity (Fig. 3) and flow curves (Fig. 4), were determined. The results demonstrate that all prepared isocyanate-terminated prepolymers are non-Newtonian fluids. The prepared prepolymers are fluids displaying nonlinear flow.

The viscosity curves presented in Fig. 3 were obtained at 60, 70 and 90 °C. The shape of a viscosity curve depends on the shear rate and viscosity of a given system. The viscosity of all prepared isocyanate-terminated prepolymers decreased with increasing shear rate in the analyzed temperature range. This finding was confirmed by the pseudoplastic character of the prepared isocyanate-terminated polyurethane prepolymers, which can be explained by changes in the orientation of molecules caused by a flow field. The particles of prepolymers change direction by rotation and become parallel to the flow direction. As a result, the viscosity and frictional resistance decrease [6,41].

Taking into consideration the origin of polyols it was observed that the bio-based prepolymer synthesized from the PO3G displayed decreased viscosity. In all cases viscosity decreased with increasing temperature. Probably this was caused by differences in the length of polyol monomeric units (one $-CH_2$ group less between ether groups than the petrochemical polyol does). Higher length of monomeric units in the case of PTMG can lead to stress-induced crystallization, what is revealed in higher viscosity. Because the bio-based prepolymers show lower viscosity, their processing is easier compared to petrochemical-based prepolymers.

The shear stress of synthesized prepolymers decreased with increasing temperature (see Fig. 4). A decrease in their viscosity with temperature was also observed. The maximum values of shear stress were observed at 60 °C for the prepolymer prepared with the use of petrochemical-based polyols (656 Pa) and for the prepolymer coded PO3G_prep (508 Pa). At a higher temperature of 70 °C, the shear stress was lower, reaching 459 and 358 Pa for PTMG_prep and PO3G_prep, respectively. At 90 °C, the shear stress was the lowest as it amounted to 254 and 183 Pa for the prepolymers prepared with the use of PTMG and PO3G, respectively.

The characteristic hysteresis loops were obtained by measuring the shear stress for a controlled shear rate from 1 to 200 s^{-1}, and for a decreasing shear rate from 200 to 1 s^{-1}. The flow curves showed linear behavior for the high values of shear stress [6]. The hysteresis loops were small and narrow for all prepared prepolymers, but the petrochemical prepolymer exhibited smaller hysteresis loops compared to the bio-based prepolymer. With increasing temperature, the hysteresis loops became bigger (Fig. 4). The prepared prepolymer displayed thixotropic behavior because the rising curves were located under the return curves. All the obtained flow curves showed linear behavior for high shear rate values. However, the initial parts of viscosity curves (shear stress vs shear rate) were not linear. Due to the above, it was concluded that all prepared prepolymers were pseudoplastic fluids.

Based on obtained results the Herschel-Bulkley mathematical model, which is applicable to nonlinear behavior, was applied to describe the prepared prepolymers (Table 1).

The Herschel-Bulkley model was suitable for describing the prepared prepolymers because the value of stability index R was close to 1. The Herschel-Bulkley model is described by equation (7):

$$\tau = \tau_0 + K^*\gamma^n \tag{7}$$

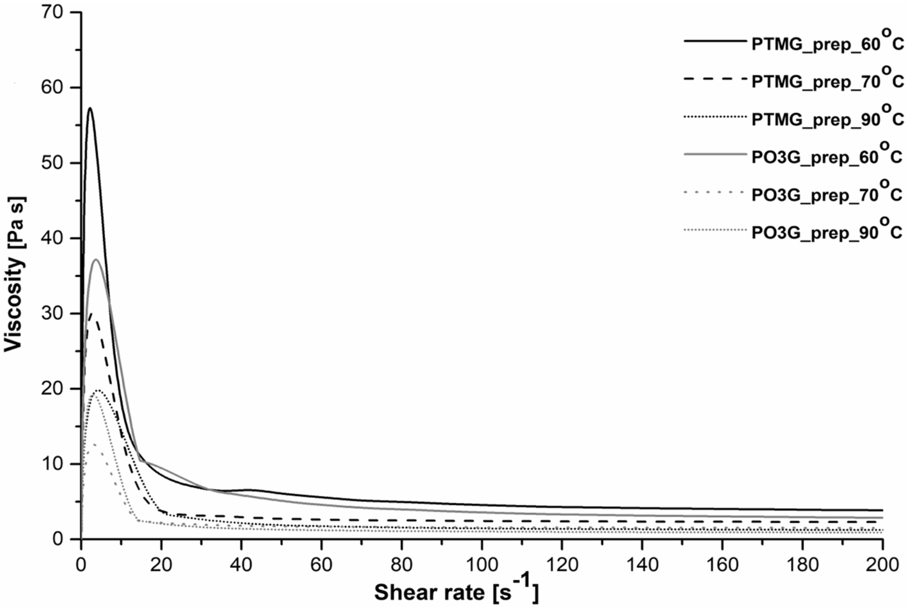

Fig. 3. The viscosity curves of prepared isocyanate-terminated prepolymers at 60, 70 and 90 °C.

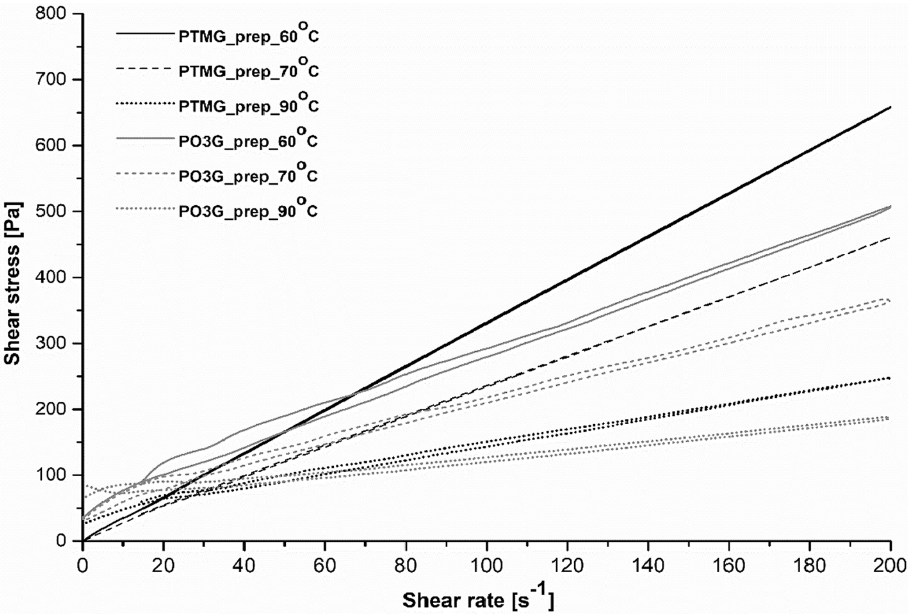

Fig. 4. The flow curves of prepared isocyanate-terminated prepolymers at 60, 70 and 90 °C.

where τ – shear stress [Pa], τ_0 – yield stress [Pa], γ – shear rate [s^{-1}], **K** – consistency index [Pa s^n], **n** – flow behavior index [−].

Analysis of the equation coefficients provides the information about the rheological behavior of fluids (Newtonian behavior, pseudoplastic behavior, dilatant behavior or Bringham plastic behavior), and leads to their classification as shear thinning or shear thickening fluids.

The value of flow index lower than 1 means that the prepolymers are shear thinning fluids [42,43]. The highest value of consistency coefficient was observed at a temperature of about 60 °C, which confirms that at this temperature the prepolymer has the highest viscosity. The viscosity values of all prepolymers decreased with increasing temperature. Based on the obtained results it was noticed that the PO3G_prep is characterized by higher values of yield stress, which increase with increasing of temperature. Such results of rheological measurements are helpful in ensuring diffusion of reagents during the industrial processing of the ether-urethane prepolymers obtained with the use of bio-monomers. What is more, a decrease in viscosity of a prepolymer based on a bio-polyether polyol has an additional benefit. Industrial processing of such a system could be conducted at a lower temperature, and the same with lower energy, which is consistent with green chemistry principles.

3.2. Polymer characterization

3.2.1. Fourier Transform Infrared spectroscopy

The overall chemical structure of prepared thermoplastic poly(ether-urethane)s was analyzed by Fourier Transform Infrared Spectroscopy and the registered spectra are presented in Fig. 5. Beginning with the spectra analysis from the lowest wavenumbers (from 4500 cm^{-1} to 500 cm^{-1}) a very flat peak in the 3300–3250 cm^{-1} range was assigned to the

Table 1
The Herschel-Bulkley linear function based on the rheological data of prepared isocyanate-terminated prepolymers.

Sample						
T [°C]	**Function**	**τ_0 [Pa]**	**μ_{om} [Pas^n]**	**n [–]**	**R^2 [–]**	**Behavior**
PTMG_prep						
60	$y = 1.41 + 3.31 * (x^{0.99})$	1.41	3.31	0.99	0.9998	Bingham plastic
70	$y = 4.99 + 2.46 * (x^{0.98})$	4.99	2.46	0.98	0.9998	Bingham plastic
90	$y = 26.02 + 1.66 * (x^{0.99})$	26.02	1.66	0.99	0.9977	Bingham plastic
PO3G_prep						
60	$y = 125.30 + 3.09 * (x^{0.87})$	125.30	3.09	0.87	0.9957	Bingham plastic
70	$y = 128.78 + 2.33 * (x^{0.98})$	128.78	2.33	0.98	0.9939	Bingham plastic
90	$y = 148.33 + 0.45 * (x^{1.09})$	148.33	0.45	1.09	0.9915	Bingham plastic

y – shear stress [Pa], **x** – shear rate [s^{-1}], **τ_0** – yield stress [Pa], **μ_{om}** – consistency index [Pas^n], **n** – flow behavior index [–], **R^2** – stability index [–].

–NH stretching vibrations of the urethane groups. It is widely known that the –NH bond of the urethane group manifests itself as two separate bands at 3400 and 3300 cm^{-1}. The peak occurring at the higher wavenumber value is associated with the free –NH bond, while the peak at the lower wavenumber corresponds to the hydrogen-bonded –NH groups. For all prepared materials, the vibration intensity of N-H bond increased with decreasing [NCO]/[OH] molar ratio applied during the chain extension of prepolymer. At the range of wavenumber from 2980 to 2760 cm^{-1} strong absorption bands correspond to the symmetric CH and asymmetric stretching bands in the CH_2 groups, respectively. Analyzing the FTIR spectra in a wavenumber of 2270 cm^{-1} no peak of absorption was detected, which confirmed the completeness of the reaction between the isocyanate-terminated prepolymer and chain extender. Next, the intensive multiple peak visible at a wavenumber of 1738–1648 cm^{-1} is attributable to carbonyl groups —C═O. It is commonly known that the signal associated with the —C═O bond can be observed in two or sometimes three separate bands, e.g. the hydrogen-bonded carbonyl groups in the less ordered amorphous regions display the absorbance band at 1718–1714 cm^{-1}, the hydrogen-bonded carbonyl groups in ordered crystalline regions are present at 1706–1685 cm^{-1}, and finally the free carbonyl groups display absorbance at 1730 cm^{-1} [44]. The two characteristic peaks observed in the 1160–990 cm^{-1} range are assigned to ether groups. The maximum at 1063 cm^{-1} is related to the hydrogen-bonding interaction between the —NH and —C—O—C groups, while the maximum at 1100 cm^{-1} is associated with the stretching vibrations of non-associated ether groups [45,46].

FTIR spectra of each TPU materials were used for determining fractions of free carbonyl, H-bonded carbonyl in the amorphous region and H-bonded carbonyl in the ordered region. Detailed results of the C═O peak analysis for the prepared thermoplastic polyurethanes are shown in Table 2. The exact position of the C═O peaks indicates only slight differences in the analyzed materials containing two different polyols, i.e. bio- and petrochemical-based polyols. It can be concluded that more than 70% of the urethane hard segments were well microphase-separated, while only 30% of these segments appeared to be well mixed or dispersed within the polyol matrix. The bio-based thermoplastic polyurethanes obtained based on PO3G contained a slightly higher fraction of hydrogen-bonded carbonyl groups (in both amorphous and order phase) in comparison to the materials prepared with the use of PTMG. These phenomena can be caused by lower number of methylene groups between ether groups in soft segments and higher Van der Waals forces which are molecular-distance dependent and greater in structures that closely pack [47,48]. It was noticed that with increasing [NCO]/[OH] molar ratio during the prepolymer chain extension step, the fraction of hydrogen bonded C═O groups decreased.

3.2.2. *Average molecular weight*

Two different methods were applied to determine the average molecular weight of thermoplastic polyurethanes: ^1H NMR spectroscopy and GPC chromatography. The first mentioned method lead to determine the absolute molecular weight and the second one is relative to polystyrene reference.

In Figs. 6 and 7, ^1H NMR and ^1H COSY spectrum of the PO3G NCO/OH 0.95 TPU sample were shown. The protons derived from CH_2 groups of the used bio-based chain extender are located on the ends of the molecules and those from the main chain ("F" and "E" signals respectively) were separated from CH_2 protons on the ends of the polymer chain ("I" signal). Signals "F" and "E" correspond to CH_2 groups which are enclosed by four hydrogen atoms. Simultaneously, these groups are correlated with protons of the CH_2 "I" group located on the ends of polymer. Analogous analyses were conducted in the case of PTMG_0.95

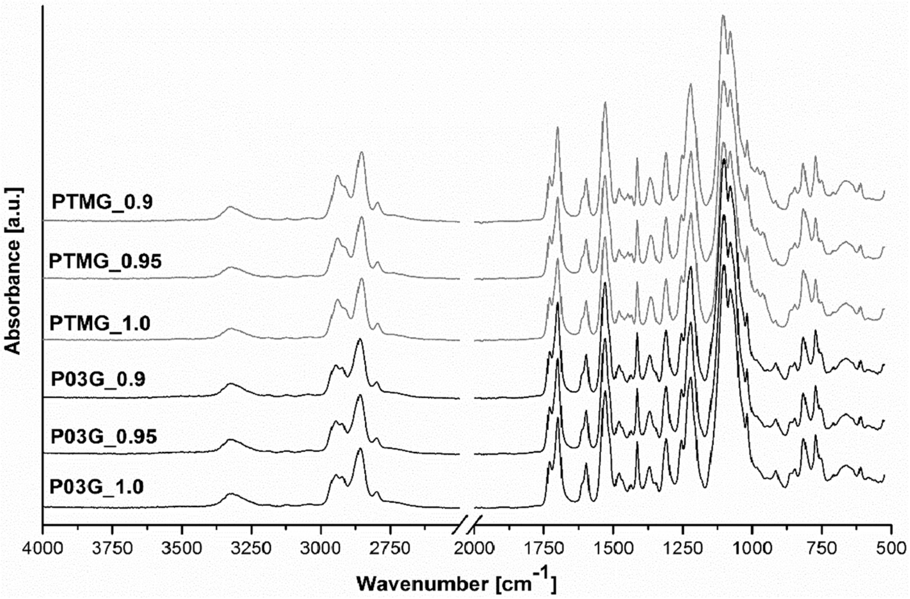

Fig. 5. FTIR spectra of synthesized bio-based thermoplastic poly(ether-urethane)s.

Table 2
The location of carbonyl peaks and a fraction of curve fitting peaks for the carbonyl region for all prepared samples, calculated by the deconvolution of absorption bands.

Samples	Peak I: free C=O		Peak II: H-bonded in —C=O in amorphous region		Peak II: H-bonded in —C=O in order region	
	Location [cm^{-1}]	Fraction [%]	Location [cm^{-1}]	Fraction [%]	Location [cm^{-1}]	Fraction [%]
PTMG_0.9	1730.24	18.82	1716.89	3.35	1700.18	77.83
PTMG_0.95	1730.08	20.95	1716.18	3.10	1700.57	75.95
PTMG_1.0	1730.67	21.65	1718.75	2.32	1699.62	76.03
PO3G_0.9	1730.38	18.60	1717.38	5.03	1699.77	76.37
PO3G_0.95	1730.31	20.14	1717.31	4.64	1699.80	75.22
PO3G_1.0	1729.78	21.10	1716.09	4.00	1700.10	74.90

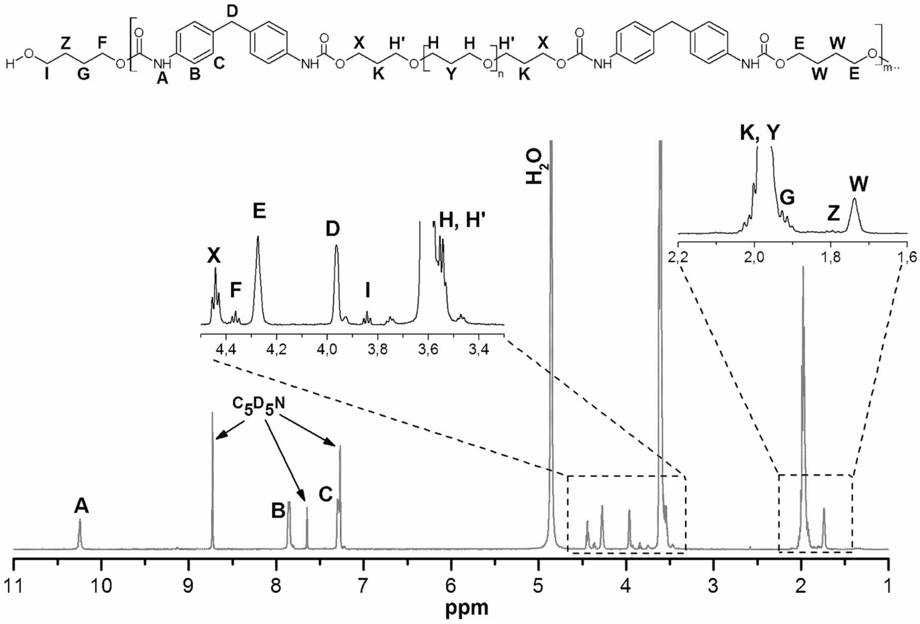

Fig. 6. Demonstrative ^{1}H NMR spectrum of the PO3G_0.95 sample.

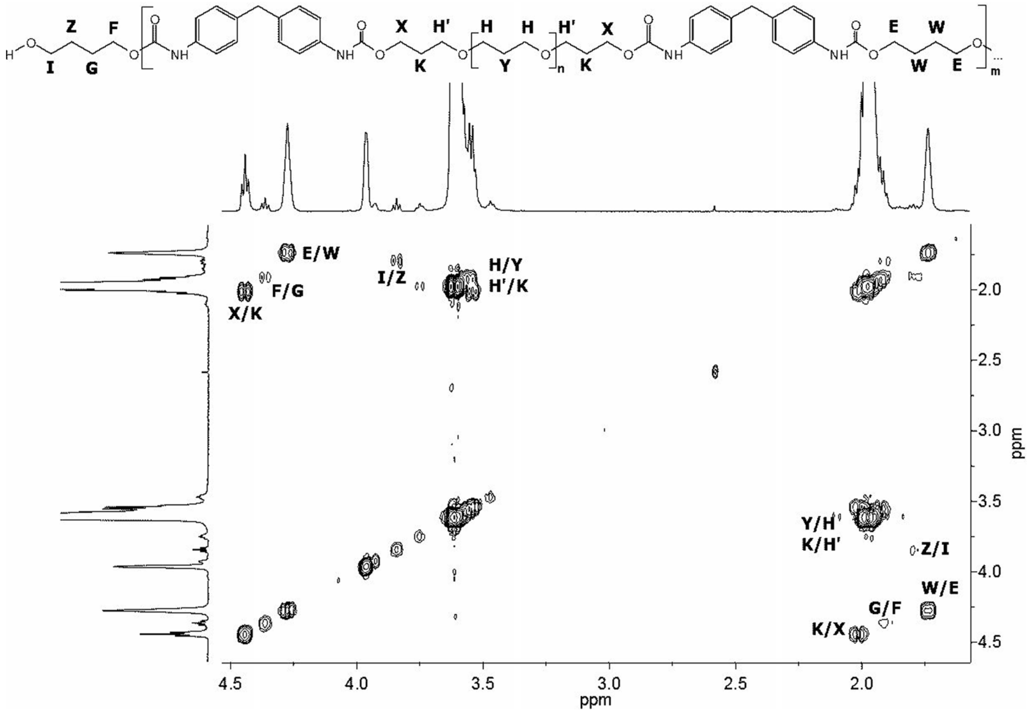

Fig. 7. ^{1}H COSY spectrum of the PO3G_0.95 sample.

TPU (Fig. 8).

Based on equations (2)–(6) provided in Section 2.3.3 the number average molecular weight of repeating unit and end units was calculated and equaled 2596 g/mol and 95 g/mol, respectively. The calculated number average molecular weights of the prepared thermoplastic poly (ether-urethane)s are presented in Table 3. With increasing [NCO]/[OH] molar ratio the number of molecular average molecular weights also increased. Poly(ether-urethane)s synthesized using PTMG polyol have higher M_n than TPU obtained with a bio-based polyol that resulted from the chemical structure of PTMG. According to literature [49], with an increase of M_n, there is an increase in tensile strength, hardness and density, which was also confirmed in this work. The results of M_n and M_w calculated using ^{1}H NMR and GPC are very similar. Based on GPC measurements the polydispersity index was determined which is less than 1.72.

3.2.3. Melt flow index

The values of MFR and MVR for the prepared thermoplastic polyurethanes are shown in Figs. 9 and 10. Each material was assessed at different temperatures, but with the same load of 5.0 kg. It is clearly visible that the MFI values steadily increased with increasing temperature. Moreover, the MFI values decreased with increasing [NCO]/[OH] molar ratio, which may be due to the higher average molecular weight of the materials prepared of a higher molar ratio [NCO]/[OH] groups [38]. Differences in the MFI values due to the molar ratios of the samples being more pronounced for the materials obtained with the use of petrochemical-based polyols. In conclusion, the MFI depends on the origin of the polyols. For a given temperature, the materials prepared using petrochemical polyol displayed lower values of MFI than the materials prepared using bio-based polyol. The bio-based thermoplastic polyurethanes obtained with the usage of PO3G polyol required lower temperature and lower pressure to be processed. This finding is in good agreement with the values of activation energy presented in Table 4. The E_a values increased with decreasing [NCO]/[OH] molar ratio, which can be correlated with the structure of the obtained materials and resulted from a different phase order, both of soft and hard segments. This finding can be confirmed by DMA analysis (storage modulus as a function of temperature), where, at a temperature of 135C°, a relation between the temperature of melting of hard segments and their number was observed. As a result, the processing of bio-thermoplastic poly (ether-urethane)s based on PO3G polyol obtained in the [NCO]/[OH] molar ratio from 0.95 to 1.0 is cost-effective.

Table 3
Results of molecular weight determination by ^{1}H NMR spectroscopy and GPC.

Sample	*^{1}H NMR*	*GPC*		
	M_n	**M_n**	**M_w**	**Đ**
PTMG_0.9	19,400	20,300	34,100	1.68
PTMG_0.95	29,700	32,600	52,800	1.62
PTMG_1.0	39,200	42,800	66,700	1.55
PO3G_0.9	17,100	19,400	33,400	1.72
PO3G_0.95	26,300	31,900	51,040	1.60
PO3G_1.0	36,200	38,200	60,300	1.58

Mn - number average molecular weight; **Mw -** weight average molecular weight; **Đ –** polydispersity index.

3.2.4. Dynamic mechanical thermal analysis

The results of DMTA analysis for the synthesized materials are shown in Figs. 11 and 12. The highest values of storage modulus (E′) were observed in the TPUs synthesized using bio-based polyol, which suggests a higher degree of stiffness of these samples (Fig. 11). This finding is most likely connected to the physical crosslinking due to the larger number of hydrogen bonds in the analyzed material. In the case of TPUs synthesized using petrochemical PTMG polyols, the E′ values remained in the range between 2250 and 2550 MPa. For the TPUs prepared with the use of the bio-based polyol, the storage modulus varied from 3490 to 3850 MPa. The storage modulus values below −50 °C remain nearly constant, which is due to the fact that the molecular motions become restricted to vibrations and short-range rotations of the soft phase. Then, gradual decreasing of storage modulus at around −50 °C corresponds to the glass transition temperature of soft segments for all prepared thermoplastic polyurethanes. The obtained TPUs displayed a short and distinctly temperature-sensitive rubbery plateau, especially in the case of TPUs obtained using bio-based polyols, which was followed by the visible softening of the material, which also suggested less ordered structure at the range of the ordered phase. The materials prepared with the use of petrochemical-based polyols showed a wider rubbery plateau modulus and a wider temperature window than the materials prepared with the use of the bio-based polyol. The described situation occurs due to differences in the strength of hydrogen bonding within the HS of the two materials, and probably due to a better degree of microphase separation in the bio-based thermoplastic polyurethane compared to the

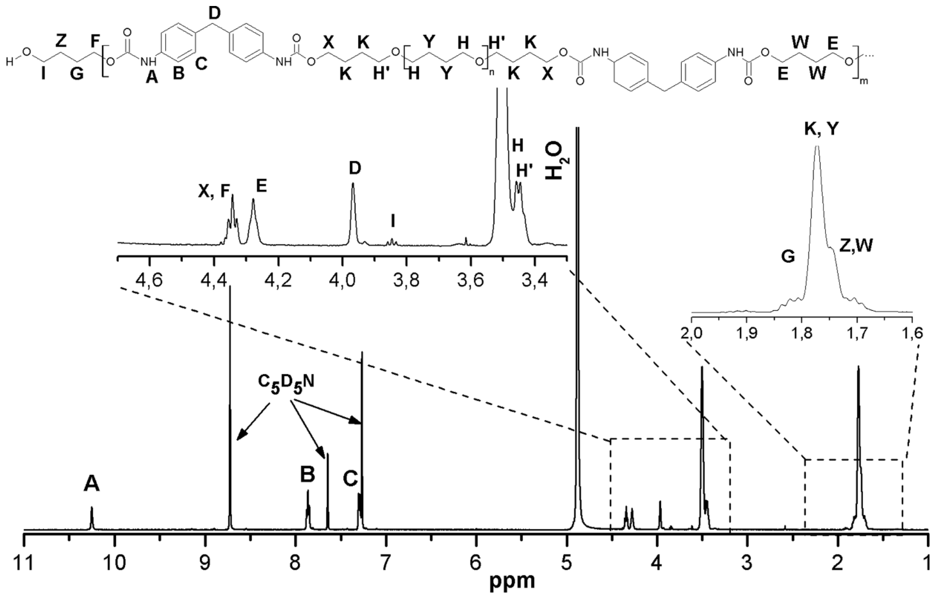

Fig. 8. Demonstrative ^{1}H NMR spectrum of the PTMG_0.95 sample.

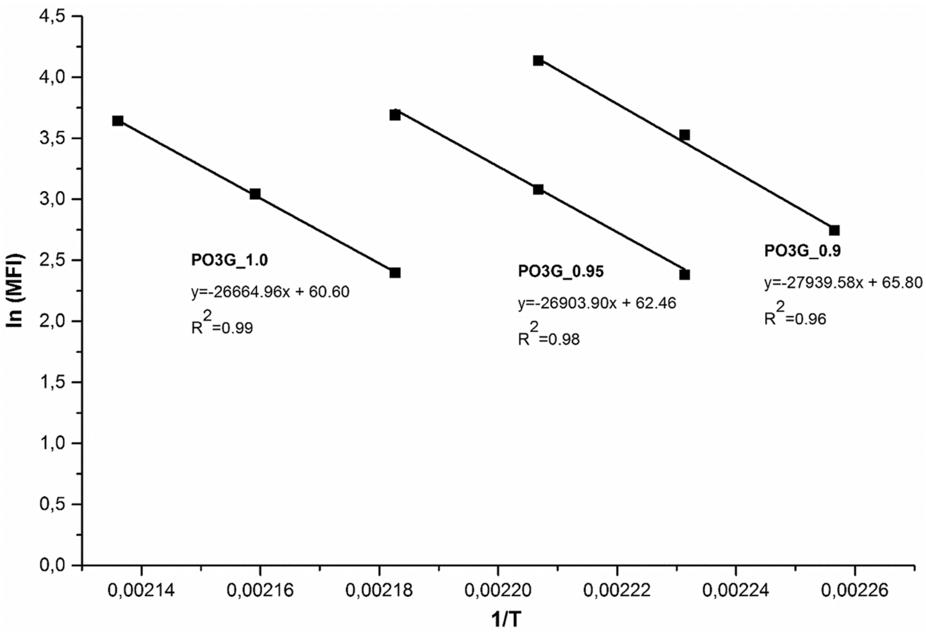

Fig. 9. Determination of energy activation for bio-based thermoplastic polyurethanes obtained with the use of PO3G polyol.

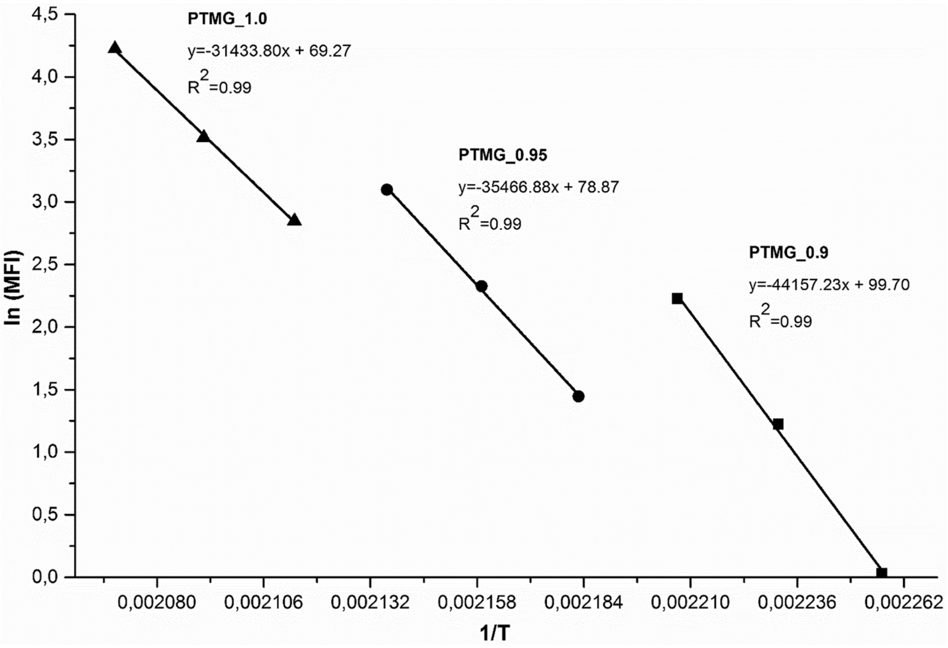

Fig. 10. Determination of energy activation for thermoplastic polyurethanes obtained with the use of PTMG polyol.

petrochemical materials, although these differences are small. A lower number of hydrogen bonds in the ordered region has been observed in the materials obtained from the petrochemical polyol, which is related to the presence of longer carbon chains in the petrochemical-based polyol. According to the literature, softening of the hard segments in thermoplastic materials leads to a drop in E′ after the rubbery plateau region [50], which is easily visible on the storage curve.

The loss modulus (E″) of the prepared thermoplastic poly(ether-urethane)s remained in the range between 434 and 446 MPa for the samples produced with the use of PO3G as a polyol, and between 214 and 240 MPa for the samples produced with the use of PTMG as a polyol (Fig. 12). The highest values of E″ were observed in the samples synthesized using PO3G as a polyol and at the [NCO]/[OH] molar ratio of 0.9 during the prepolymer chain extension step.

The glass transition temperature of the soft segment was established as the temperature at which the damping factor achieves a maximum value. The produced materials showed two thermal transitions, i.e. the glass transition temperature of SSs (T_{gSS}), and the melting temperature of SSs (T_{mSS}) [46,51,52]. However, the two thermal transitions were less visible in the samples of TPUs obtained using bio-based polyols, especially in PO3G_0.95 and PO3G_1.0 samples. The values of T_{gSS} ranged from −41.6 to 39.9 °C for TPUs obtained using PTMG as a polyol, and from −38.2 to −35.4 °C for materials produced with the use of PO3G as a polyol. The melting temperature (T_{mSS}) of the synthesized thermoplastic poly(ether-urethane)s was about −10 and 0 °C for TPUs prepared with the use of PTMG or PO3G as a polyol, respectively. Both transition

Table 4
The MFR and MVR values of bio-based thermoplastic polyurethanes prepared with the use of two different polyols.

Sample	I conditions (T [^{o}C]; load [kg])		II conditions (T [^{o}C]; load [kg])		III conditions (T [^{o}C]; load [kg])		E_a [kJ/mol]
	MFR [g/10 min]	MVR [cm^3/10 min]	MFR [g/10 min]	MVR [cm^3/10 min]	MFR [g/10 min]	MVR [cm^3/10 min]	
PTMG_0.9	1.1 ± 0.2 (170; 5)	1.3 ± 0.1 (170; 5)	3.4 ± 0.3 (175; 5)	3.8 ± 0.2 (175; 5)	9.3 ± 0.3 (180; 5)	9.5 ± 0.2 (180; 5)	367.1
PTMG_0.95	4.3 ± 0.2 (185; 5)	4.7 ± 0.3 (185; 5)	10.3 ± 0.1 (190; 5)	10.4 ± 0.2 (190; 5)	22.1 ± 0.2 (195; 5)	22.5 ± 0.3 (195; 5)	294.9
PTMG_1.0	17.3 ± 0.3 (200; 5)	17.1 ± 0.2 (200; 5)	33.7 ± 0.2 (205; 5)	34.6 ± 0.2 (205; 5)	68.2 ± 0.4 (210; 5)	69.5 ± 0.5 (210; 5)	261.3
PO3G_0.9	14.9 ± 0.8 (170; 5)	14.6 ± 0.3 (170; 5)	36.1 ± 0.2 (175; 5)	40.42 ± 0.7 (175; 5)	60.2 ± 0.3 (180; 5)	60.8 ± 0.4 (180; 5)	232.2
PO3G_0.95	10.8 ± 0.2 (175; 5)	11.1 ± 0.1 (175; 5)	24.0 ± 0.2 (180; 5)	24.5 ± 0.3 (180; 5)	40.1 ± 0.3 (185; 5)	41.8 ± 0.2 (185; 5)	223.6
PO3G_1.0	10.9 ± 0.3 (185; 5)	11.2 ± 0.1 (185; 5)	20.9 ± 0.2 (190; 5)	20.0 ± 0.1 (190; 5)	38.2 ± 0.4 (195; 5)	39.1 ± 0.2 (195; 5)	221.7

MFR - melt mass-flow rate; **MVR –** melt volume-flow rate; **E_a -** energy activation.

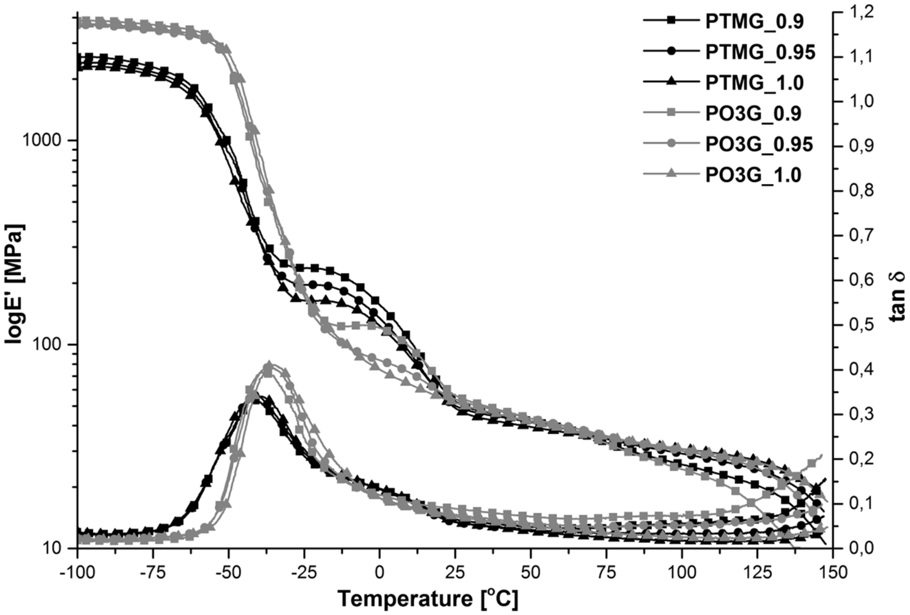

Fig. 11. Storage modulus (as logE′) and tan delta as a function of temperature for the prepared materials.

temperatures of soft segment increased with increasing [NCO]/[OH] molar ratio.

The thermoplastic poly(ether-urethane)s obtained using PO3G as a polyol displayed higher maximum values of tan delta than the materials prepared using a petrochemical PTMG polyol. The materials prepared using PO3G had a higher ability to damp vibrations. The TPUs synthesized using PTMG displayed the broader and flatter tangent delta peak than the materials prepared using bio-based polyols. According to the literature, materials displaying broader and flatter tan delta peak possess a limited flexibility of soft segments [50].

3.2.5. *Mechanical properties*

The values of characteristic mechanical properties of the prepared materials, such as tensile strength (TS_b), elongation at break (E_b), Young Modulus (E), hardness (H) and density (ρ), are presented in Table 5.

The results of the tensile test showed that samples containing the petrochemical-based polyol and synthesized in the [NCO]/[OH] molar ratio equaled 1.0 and 0.95 were characterized by higher tensile properties compared to the samples containing the bio-based polyol. As can be seen in Table 5, the tensile strength and elongation at break increased with increasing [NCO]/[OH] molar ratio. This was due to the increase of molar mass of the prepared materials. The highest TS_b value of 32.7 MPa was observed for the material coded PTMG_1.0 and was slightly higher than for bio-based TPU obtained at the same [NCO]/[OH] molar ratio (32.3 MPa). In general, the thermoplastic poly(ether-urethane)s obtained using PO3G polyols and synthesized at [NCO]/[OH] molar ratio of 0.9, 0.95, and 1.0 displayed tensile strength values ranging from 12.1 to 32.2 MPa, and the elongation at break between 220 and 780%. TPUs prepared with the use of PTMG were characterized by tensile strength between 16.3 and 32.7 MPa, and the elongation at break ranging from 534 to 680 %. The parameter values of mechanical properties were comparable for both material types. i.e. the materials prepared using PO3G and PTMG.

Hardness of polymers characterized the resistance of material to indentation which causes permanent deformation or damage [53]. This property is related to the yield stress and can define as a stress which is needed to the plastically deform the material [54]. Many different factors (e.g. morphological structure or tendency to phase separation) influence on the hardness which resulted from the intermolecular cohesive forces between the polymer chains. In the case of analyzed materials it was observed that TPUs prepared using the PTMG as polyol showed higher hardness than those synthesized with the use of the bio-based polyol and ranging from 32.3 to 40.7 Sh^{o}A. This is result of morphological structure of obtained bio-based TPU by increasing the crystallinity of soft segments built from residue of PTMG [26] and also creation of higher amount of hydrogen bonds in order region of urethane groups

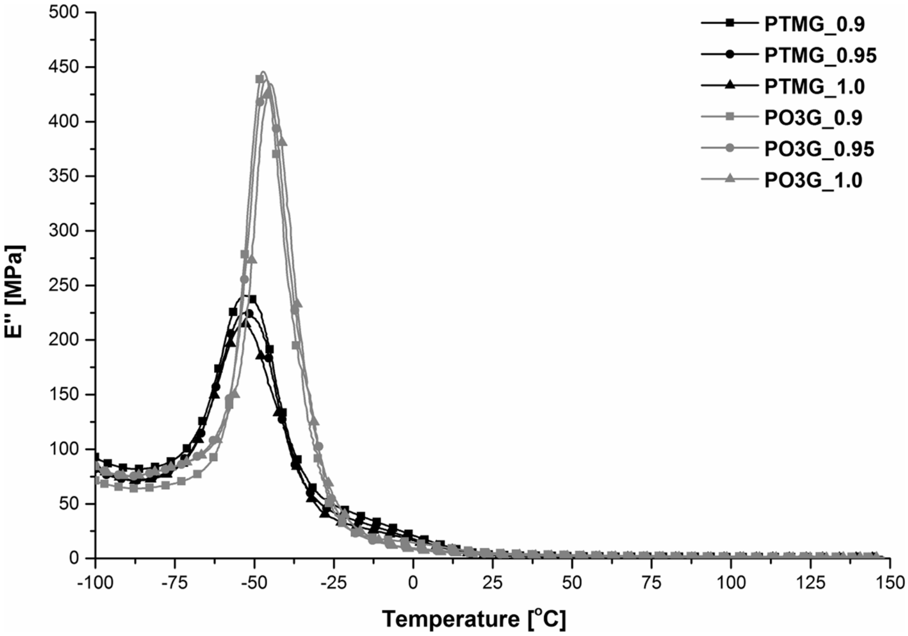

Fig. 12. Loss modulus (E″) as a function of temperature for the prepared materials.

Table 5
Mechanical properties, hardness, and density of the prepared bio-based thermoplastic poly(ether-urethane)s.

Sample	TS_b [MPa]	E_b [%]	H [°ShD]	ρ [g/cm^3]
PTMG_0.9	16.3 ± 1.1	534 ± 21	32.3 ± 0.1	1.0967 ± 0.0013
PTMG_0.95	27.1 ± 2.1	659 ± 34	37.8 ± 0.2	1.0963 ± 0.0011
PTMG_1.0	32.7 ± 1.2	680 ± 23	40.7 ± 0.3	1.0954 ± 0.0011
PO3G_0.9	12.1 ± 0.3	220 ± 12	26.2 ± 0.1	1.1196 ± 0.0002
PO3G_0.95	23.4 ± 2.1	679 ± 14	27.3 ± 0.2	1.1185 ± 0.0004
PO3G_1.0	32.2 ± 1.3	780 ± 23	28.2 ± 0.4	1.1179 ± 0.0001

TS_b - tensile strength; **E_b** – elongation at break; **H** – hardness; **ρ** – density.

(confirmed by FTIR results). It was also noticed that the hardness increased with increasing [NCO]/[OH] molar ratio. The materials prepared using bio-based polyol, that is, PO3G_0.9 and PO3G_1.0 displayed the hardness values in the range from 26.2 to 28.2 Sh°A, respectively. The lower hardness in the case of PO3G based materials is caused by less ordered structure of bio-TPU in comparison to materials based on PTMG. What is more, the bio-based TPUs prepared using the PO3G polyol exhibited slightly higher density than those produced with the use of PTMG as a polyol.

4. Conclusions

Therefore, in this work, via free solvents and via a two-step method of synthesis, it was demonstrated that some bio-based polyol can successfully replace petrochemical polyol with many benefits such as lower viscosity of urethane prepolymers, which leads to easier further processing or comparable tensile properties of the obtained polymers. In general, it was found that the properties of novel, partially bio-based thermoplastic poly(ether-urethane)s depend on their chemical structure, the [NCO]/[OH] molar ratio of reagents and the number average molecular weight. It was found that the obtained prepolymers had a similar chemical structure and were non-Newtonian fluids, which can be described by the Herschel-Bulkley model and suggests that both prepolymers can be processed using the same processing methods. The structure analysis by the FTIR method has confirmed that the [NCO]/[OH] molar ratio during the prepolymer chain extension step affects the number of hydrogen bonds in the prepared bio-based thermoplastic poly(ether-urethane)s. With increasing [NCO]/[OH] molar ratio, the number of hydrogen bonds decreased. The ^{1}H NMR spectra confirmed the predicted structure of the prepared bio-based TPUs and allowed to calculate the number average molecular weight what needed to choose the such solvent which can clearly separate hydrogen protons of the used polyols and glycol. In comparison to the materials obtained with the use of petrochemical polyol, the materials produced using bio-based polyol showed lower glass transition temperature. The bio-TPUs based on PTMG polyol displayed higher values of tensile strength and elongation at break. However, the mechanical properties of the prepared materials were comparable. It has been demonstrated that the energy activation and MFR are strongly dependent on the [NCO]/[OH] molar ratio during the prepolymer chain extension step and the origin of the used polyol. The materials prepared from the PO3G polyol showed lower energy activation than those prepared from petrochemical PTMG, which is a significant advantage from an industry point of view. Furthermore, the bio-based thermoplastic poly(ether-urethane)s obtained with the usage of PO3G polyol were characterized by a higher value of melt flow index. This results show that TPU based on PO3G polyol and obtained at the [NCO]/[OH] molar ratio from 0.9 to 1.0 processing using the RIM method needs less pressure and probably the polymer system will better fill the molds than other systems. Additionally, the bio-based TPUs seem to be good materials for the application in FDM 3D printing, since it presented an ideal MFI value.

Summarizing, the synthesis of bio-based TPUs synthesized with the usage of PO3G polyol can provide economical, universal and green production of TPUs that display many advantageous properties. Through analysis of these experiments, a lot of useful information for the polymer industry was found, which will be very significant.

CRediT authorship contribution statement

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

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.

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2021.110673.

References

[1] P. Kasprzyk, H. Beneš, R.K. Donato, J. Datta, The role of hydrogen bonding on tuning hard-soft segments in bio- based thermoplastic poly (ether-urethane)s, J. Cleaner Prod. 274 (2020) 122678, https://doi.org/10.1016/j.jclepro.2020.122678.

[2] X. Kong, G. Liu, J.M. Curtis, Novel polyurethane produced from canola oil based poly(ether ester) polyols: synthesis, characterization and properties, Eur. Polym. J. 48 (12) (2012) 2097–2106, https://doi.org/10.1016/j.eurpolymj.2012.08.012.

[3] P. Król, Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers, Prog. Mater. Sci. 52 (6) (2007) 915–1015, https://doi.org/10.1016/j.pmatsci.2006.11.001.

[4] C.P. Buckley, C. Prisacariu, C. Martin, Elasticity and inelasticity of thermoplastic polyurethane elastomers: sensitivity to chemical and physical structure, Polymer 51 (2010) 3213–3224, https://doi.org/10.1016/j.polymer.2010.04.069.

[5] P. Jutrzenka Trzebiatowska, A. Santamaria Echart, T. Calvo Correas, A. Eceiza, J. Datta, The changes of crosslink density of polyurethanes synthesised with using recycled component. Chemical structure and mechanical properties investigations, Prog. Org. Coat. 115 (2018) 41–48, https://doi.org/10.1016/J.PORGCOAT.2017.11.008.

[6] E. Głowińska, J. Datta, A mathematical model of rheological behavior of novel bio-based isocyanate-terminated polyurethane prepolymers, Ind. Crops Prod. 60 (2014) 123–129, https://doi.org/10.1016/j.indcrop.2014.06.016.

[7] X. Chen, W. Wang, C. Jiao, A recycled environmental friendly flame retardant by modifying para-aramid fiber with phosphorus acid for thermoplastic polyurethane elastomer, J. Hazard. Mater. 331 (2017) 257–264, https://doi.org/10.1016/j.jhazmat.2017.02.011.

[8] L. Ren, X. Ma, J. Zhang, T. Qiang, Preparation of gallic acid modified waterborne polyurethane made from bio-based polyol, Polymer 194 (2020) 122370, https://doi.org/10.1016/j.polymer.2020.122370.

[9] L. Zhang, M. Huang, R. Yu, J. Huang, X. Dong, R. Zhang, J. Zhu, Bio-based shape memory polyurethanes (Bio-SMPUs) with short side chains in the soft segment, J. Mater. Chem. A 2 (29) (2014) 11490, https://doi.org/10.1039/c4ta01640h.

[10] P. Parcheta, J. Datta, Structure-rheology relationship of fully bio-based linear polyester polyols for polyurethanes - Synthesis and investigation, Polym. Test. 67 (2018) 110–121, https://doi.org/10.1016/j.polymertesting.2018.02.022.

[11] T.A. Phung Hai, M. Tessman, N. Neelakantan, A.A. Samoylov, Y. Ito, B.S. Rajput, N. Pourahmady, M.D. Burkart, Renewable polyurethanes from sustainable biological precursors, Biomacromolecules (2021), https://doi.org/10.1021/acs.biomac.0c01610.

[12] T.A. Phung Hai, N. Neelakantan, M. Tessman, S.D. Sherman, G. Griffin, R. Pomeroy, S.P. Mayfield, M.D. Burkart, Flexible polyurethanes, renewable fuels, and flavorings from a microalgae oil waste stream, Green Chem. 22 (10) (2020) 3088–3094, https://doi.org/10.1039/D0GC00852D.

[13] E. Głowińska, P. Parcheta, P. Kasprzyk, J. Datta, Polyisocyanates from Sustainable Resources, 2021. https://doi.org/10.1021/bk-2021-1380.ch003.

[14] E. Głowińska, P. Kasprzyk, J. Datta, The green approach to the synthesis of bio-based thermoplastic polyurethane elastomers with partially bio-based hard blocks, Materials. 14 (9) (2021) 2334, https://doi.org/10.3390/ma14092334.

[15] E. Głowińska, W. Wolak, J. Datta, Eco-friendly route for thermoplastic polyurethane elastomers with bio-based hard segments composed of bio-glycol and mixtures of aromatic-aliphatic and aliphatic-aliphatic diisocyanate, J. Polym. Environ. 29 (7) (2021) 2140–2149, https://doi.org/10.1007/s10924-020-01992-5.

[16] T. Calvo-Correas, A. Santamaria-Echart, A. Saralegi, L. Martin, Á. Valea, M. A. Corcuera, A. Eceiza, Thermally-responsive biopolyurethanes from a biobased diisocyanate, Eur. Polym. J. 70 (2015) 173–185, https://doi.org/10.1016/j.eurpolymj.2015.07.022.

[17] P. Parcheta, J. Datta, Environmental impact and industrial development of biorenewable resources for polyurethanes, Crit. Rev. Environ. Sci. Technol. 47 (20) (2017) 1986–2016, https://doi.org/10.1080/10643389.2017.1400861.

[18] R. Mülhaupt, Green polymer chemistry and bio-based plastics: dreams and reality, Macromol. Chem. Phys. 214 (2) (2013) 159–174, https://doi.org/10.1002/macp.201200439.

[19] Arvind S. More, Thomas Lebarbé, Lise Maisonneuve, Benoit Gadenne, Carine Alfos, Henri Cramail, Novel fatty acid based di-isocyanates towards the synthesis of thermoplastic polyurethanes, Eur. Polym. J. 49 (4) (2013) 823–833, https://doi.org/10.1016/j.eurpolymj.2012.12.013.

[20] P. Kasprzyk, J. Datta, Effect of molar ratio [NCO]/[OH] groups during prepolymer chains extending step on the morphology and selected mechanical properties of final bio-based thermoplastic poly(ether-urethane) materials, Polym. Eng. Sci. 58 (S1) (2018) E199–E206, https://doi.org/10.1002/pen.v58.S110.1002/pen.24874.

[21] L. Bartolomé, J. Aurrekoetxea, M.A. Urchegui, W. Tato, The influences of deformation state and experimental conditions on inelastic behaviour of an extruded thermoplastic polyurethane elastomer, Mater. Des. 49 (2013) 974–980, https://doi.org/10.1016/j.matdes.2013.02.055.

[22] D.B. Klinedinst, I. Yilgör, E. Yilgör, M. Zhang, G.L. Wilkes, The effect of varying soft and hard segment length on the structure–property relationships of segmented polyurethanes based on a linear symmetric diisocyanate, 1,4-butanediol and PTMO soft segments, Polymer 53 (23) (2012) 5358–5366, https://doi.org/10.1016/j.polymer.2012.08.005.

[23] M.A. Harmer, D.C. Confer, C.K. Hoffman, S.C. Jackson, A.Y. Liauw, A.R. Minter, E. R. Murphy, R.E. Spence, H.B. Sunkara, Renewably sourced polytrimethylene ether glycol by superacid catalyzed condensation of 1,3-propanediol, Green Chem. 12 (2010) 1410–1416, https://doi.org/10.1039/c002443k.

[24] J. Datta, P. Kasprzyk, Thermoplastic polyurethanes derived from petrochemical or renewable resources: a comprehensive review, Polym. Eng. Sci. 58 (S1) (2018) E14–E35, https://doi.org/10.1002/pen.v58.S110.1002/pen.24633.

[25] P. Kasprzyk, E. Głowińska, P. Parcheta-Szwindowska, K. Rohde, J. Datta, Green TPUs from prepolymer mixtures designed by controlling the chemical structure of flexible segments, Int. J. Mol. Sci. 22 (2021) 7438, https://doi.org/10.3390/ijms22147438.

[26] P. Kasprzyk, K. Błażek, P. Parcheta, J. Datta, Green thermoplastic poly(ether-urethane)s - synthesis, chemical structure and selected properties investigation, Polimery/Polymers. 65 (2020) 672–680. https://doi.org/10.14314/polimery.2020.10.2.

[27] K. Błażek, H. Beneš, Z. Walterová, S. Abbrent, A. Eceiza, T. Calvo-Correas, J. Datta, Synthesis and structural characterization of bio-based bis(cyclic carbonate)s for the preparation of non-isocyanate polyurethanes, Polym. Chem. 12 (11) (2021) 1643–1652, https://doi.org/10.1039/D0PY01576H.

[28] C. Pattamaprom, C.-H. Wu, P.-H. Chen, Y.-L. Huang, P. Ranganathan, S.-P. Rwei, F.-S. Chuan, Solvent-free one-shot synthesis of thermoplastic polyurethane based on bio-poly(1,3-propylene succinate) glycol with temperature-sensitive shape memory behavior, ACS Omega 5 (8) (2020) 4058–4066, https://doi.org/10.1021/acsomega.9b0366310.1021/acsomega.9b03663.s001.

[29] P. Parcheta, J. Datta, Influence of chemical structure on physicochemical properties and thermal decomposition of the fully bio-based poly(propylene succinate-co-butylene succinate)s, Polym. Test. 83 (2020) 106337, https://doi.org/10.1016/j.polymertesting.2020.106337.

[30] P. Parcheta, I. Koltsov, E. Głowinska, J. Datta, Thermal degradation kinetics of poly (propylene succinate) prepared with the use of natural origin monomers, Polimery. 63 (2018) 700–707. https://doi.org/10.14314/polimery.2018.10.6.

[31] P. Parcheta, E. Głowińska, J. Datta, Effect of bio-based components on the chemical structure, thermal stability and mechanical properties of green thermoplastic polyurethane elastomers, Eur. Polym. J. 123 (2020) 109422, https://doi.org/10.1016/j.eurpolymj.2019.109422.

[32] S. Ramanujam, C. Zequine, S. Bhoyate, B. Neria, P. Kahol, R. Gupta, Novel biobased polyol using corn oil for highly flame-retardant polyurethane foams, C. 5 (2019) 13, https://doi.org/10.3390/c5010013.

[33] P. Kopczynska, J. Datta, Rheological characteristics of oligomeric semiproducts gained via chemical degradation of polyurethane foam using crude glycerin in the presence of different catalysts patrycja, Polym. Eng. Sci. 57 (2017) 891–900, https://doi.org/10.1002/pen.

[34] P. Kosmela, K. Gosz, P. Kazimierski, A. Hejna, J. Haponiuk, Ł. Piszczyk, Chemical structures, rheological and physical properties of biopolyols prepared via solvothermal liquefaction of Enteromorpha and Zostera marina biomass, Cellulose 26 (10) (2019) 5893–5912, https://doi.org/10.1007/s10570-019-02540-8.

[35] P. Król, A. Zmihorska-Gotfryd, Studies on synthesis of oligomeric urethane prepolymers as intermediates to make linear pulyurethanes, Polimery. 45 (11/12) (2000) 775–785.

[36] S.D.C. Guerreiro, I.M. João, L.E. Pimentel Real, Evaluation of the influence of testing parameters on the melt flow index of thermoplastics, Polym. Test. 31 (8) (2012) 1026–1030, https://doi.org/10.1016/j.polymertesting.2012.07.008.

[37] P. Kasprzyk, J. Datta, Novel bio-based thermoplastic poly(ether-urethane)s. Correlations between the structure, processing and properties, Polymer. 160 (2019) 1–10, https://doi.org/10.1016/j.polymer.2018.11.032.

[38] P. Kasprzyk, E. Sadowska, J. Datta, Investigation of thermoplastic polyurethanes synthesized via two different prepolymers, J. Polym. Environ. 27 (11) (2019) 2588–2599, https://doi.org/10.1007/s10924-019-01543-7.

[39] J.U. Izunobi, C.L. Higginbotham, Polymer molecular weight analysis by 1H NMR spectroscopy, J. Chem. Educ. 88 (8) (2011) 1098–1104, https://doi.org/10.1021/ed100461v.

[40] P. Parcheta, J. Datta, Kinetics study of the fully bio-based poly(propylene succinate) synthesis. Functional group approach, Polym. Degrad. Stability. 155 (2018) 238–249, https://doi.org/10.1016/j.polymdegradstab.2018.07.025.

[41] K. Wilczyński, Reologia w przetwórstwie tworzyw sztucznych, Wydawnictwo Naukowo-Techniczne, Warszawa, 2001.

[42] Z. Kłembowski, Reometria płynów nienewtonowskich, Wydawnictwo Naukowo-Techniczne, Warszawa, 1973.

[43] A. Bjorn, P. Segura de La Monja, A. Karlsson, J. Ejlertsson, B.H. Svensson, Rheological Characterization, Intech. (2012) 64–76. https://doi.org/10.5772/32596.

[44] K.A. Barrera-Rivera, L. Peponi, Á. Marcos-Fernández, J.M. Kenny, A. Martínez-Richa, Synthesis, characterization and hydrolytic degradation of polyester-urethanes obtained by lipase biocatalysis, Polym. Degrad. Stab. 108 (2014) 188–194, https://doi.org/10.1016/j.polymdegradstab.2014.04.004.

[45] Lahorija Bistričić, Goran Baranović, Mirela Leskovac, Emi Govorčin Bajsić, Hydrogen bonding and mechanical properties of thin films of polyether-based polyurethane-silica nanocomposites, Eur. Polym. J. 46 (10) (2010) 1975–1987, https://doi.org/10.1016/j.eurpolymj.2010.08.001.

[46] L. Ugarte, B. Fernández-d'Arlas, A. Valea, M.L. González, M.A. Corcuera, A. Eceiza, Morphology-properties relationship in high-renewable content polyurethanes, Polym. Eng. Sci. 54 (2014) 2282–2291, https://doi.org/10.1002/pen.

[47] M. Fuensanta, J.M. Martín-Martínez, Viscoelastic and adhesion properties of new poly(ether-urethane) pressure-sensitive adhesives, Front. Mech. Eng. 6 (2020), https://doi.org/10.3389/fmech.2020.00034.

[48] GRANTRADE, Polyurethane Elastomer: Blends of PTMEG and PPG Polyols, (2020). Polyurethane Elastomer: Blends of PTMEG and PPG Polyols (accessed June 11, 2021).

[49] Z. Wirpsza, Poliuretany. Chemia. Technologia. Zastosowanie, Wydawnictwo Naukowo-Techniczne, Warsaw, 1991. https://doi.org/S0960-9822(00)00846-0 [pii] ET - 2001/01/04.

[50] J.P. Sheth, A. Aneja, G.L. Wilkes, E. Yilgor, G.E. Atilla, I. Yilgor, F.L. Beyer, Influence of system variables on the morphological and dynamic mechanical behavior of polydimethylsiloxane based segmented polyurethane and polyurea copolymers: a comparative perspective, Polymer 45 (20) (2004) 6919–6932, https://doi.org/10.1016/j.polymer.2004.06.057.

[51] David M. Guptill, Jacob P. Brutman, Thomas R. Hoye, Thermoplastic polyurethanes from β-methyl-δ-valerolactone-derived amidodiol chain extenders, Polymer 111 (2017) 252–257.

[52] P.A. Gunatillake, G.F. Meijs, S.J. Mccarthy, R. Adhikari, Poly(dimethylsiloxane)/Poly(hexamethylene oxide) Mixed Macrodiol Based Polyurethane Elastomers. I. Synthesis and Properties, J. Appl. Polym. Sci. 76 (14) (2000) 2026–2040.

[53] T. Koch, S. Seidler, Correlations between indentation hardness and yield stress in thermoplastic polymers, Strain 45 (2009) 26–33, https://doi.org/10.1111/j.1475-1305.2008.00468.x.

[54] Francisco José Baltá Calleja, Strucutre-microhardness correlation of polymers and blends, (n.d.). https://digital.csic.es/bitstream/10261/242314/1/Structure-microhardness%20correlation.pdf (accessed July 18, 2021).