Thermal degradation kinetics of poly(propylene succinate) prepared with the use of natural origin monomers*)

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Abstract: Linear bio-based polyester polyols were prepared with the use of succinic acid and 1,3-propanediol (both with natural origin). Tetraisopropyl orthotitanate (TPT) was used as a catalyst. In order to determine the effect of various synthesis temperature conditions on the thermal degradation kinetics, nine sequences of temperature conditions were used during two-step polycondensation reaction. Thermogravimetric analysis was conducted with the use of DSC-TG/QMS method (differential scanning calorimetry-coupled with thermogravimetry and quadrupole mass spectrometry). The results indicated high thermal stability of the obtained materials. They undergo a one-step thermal decomposition with the temperature of maximum rate of weight loss at *ca.* 405 °C. Moreover, the thermal degradation kinetics was determined with the use of Ozawa, Flynn and Wall as well as Kissinger methods. The highest thermal degradation activation energy was equal to 196.4 kJ/mol.

Keywords: poly(propylene succinate), bio-based polyester, thermal degradation kinetics, Ozawa, Flynn and Wall method, Kissinger method.

Kinetyka degradacji termicznej poli(bursztynianu propylenu) zsyntetyzowanego z monomerów pochodzenia naturalnego

Streszczenie: Liniowe bio-poliole poliestrowe syntetyzowano z wykorzystaniem substratów pochodzenia naturalnego: kwasu bursztynowego oraz 1,3-propanodiolu. W charakterze katalizatora stosowano ortotytanian tetraizopropylu (TPT). W celu określenia wpływu temperatury syntezy na kinetykę degradacji termicznej, podczas dwuetapowej reakcji polikondensacji zastosowano różne warunki temperaturowe w dziewięciu sekwencjach. Analizę termograwimetryczną prowadzono za pomocą metody różnicowej kalorymetrii skaningowej sprzężonej z termograwimetrią i kwadrupolową spektrometrią masową (DSC-TG/QMS). Wyniki badań potwierdziły dużą stabilność termiczną materiałów oraz jednoetapowość procesu rozkładu temperaturowego z temperaturą maksymalnego rozkładu wynoszącą ok. 405 °C. Określono też kinetykę degradacji termicznej metodami Ozawy, Flynna i Walla oraz Kissingera. Największa wartość energii aktywacji degradacji termicznej wyniosła 196,4 kJ/mol.

Słowa kluczowe: poli(bursztynian propylenu), bio-poliole poliestrowe, kinetyka degradacji termicznej, metoda Ozawy, Flynna i Walla, metoda Kissingera.

The primary reaction, which leads to the obtainment of polyester polyols, is a well-known two-step polycondensation reaction. The first step constitutes the esterification or transesterification reaction between carboxylic acid or carboxylic acid esters and the excess of the glycols. During the reaction, such by-products as water or alcohols, respectively, are formed. For shifting the reaction towards the main product, the by-product must be removed from the reaction mixture. The capability of the by-product elimination affects the reaction kinetics and productivity. After the by-product is removed, the second step – polycondensation reaction, can be started [1]. It is well-known that the reaction kinetics are also affected by the amount and chemical structure of the catalyst and monomers and by the temperature during both steps and reaction time [2]. The polyurethane materials obtained with the use of polyester polyols are less resistant to hydrolysis compared to the polyether polyols. However, it makes them more favorable due to the biodegradability [3–5]. Polyurethanes (PUR) based on polyester poly-

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ols have better thermal and fire resistance as well as superior solvent resistance than the polyether-based PUR. Furthermore, polyesters provide major possibilities for the preparation of biorenewable PUR material [6].

Currently, the biocomponents which allow producing polyester polyols derived entirely from bioresources are readily accessible [7]. One of the most important bio-based monomers for the synthesis of polyester polyols is succinic acid (SA). Since 2012, this compound can be obtained by a biotechnological process through the corn fermentation using such microorganisms as a fungi, yeasts or bacteria [8–11]. After fermentation, the product is purified which allows for a purification level of even 99.5 % [12]. The succinic acid based on the biomass fermentation is commercially available on a large-scale from such companies as BioAmber [13], Reverdia [14], Myriant [15] and BASF/Purac [16].

The second monomer taking part in the polycondensation reaction is a glycol. Bio-based glycol with the highest global usage is 1,3-propanediol (PDO) (Susterra, DuPont) [17]. Biosynthesis pathway for the bio-based PDO preparation involves the single-step fermentation process based on the glucose, sucrose, dextrose, and biomass sugars [18, 19]. The most commonly used bacteria to produce 1,3-propanediol are *Klebsiella* [18], *Clostridia* [20], *Citrobacter fruendii* [21], *etc*. These microorganisms allow for the industrial production of PDO with the 99.97 % purity [22, 23]. Other commonly available glycols made from renewable resources are bio-based 1,4-butanediol (bio-BDO) and ethylene glycol (bio-EG). Currently, the research on the bio-based 1,6-hexanediol (bio-HDO) and adipic acid (bio-AA) are carried out [13, 24, 25].

With the use of above-mentioned substances, we are able to synthesize fully bio-based polyester polyols with designed macromolecular structure and properties tailored to specific industrial requirements.

Recently, more and more substances can be obtained from biorenewable resources and substitute petrochemical-based counterparts. Researchers work on the synthesis of the bio-based polyester polyols with the use of these substances. Lu *et al*. [26] synthesized bio-based polyesters based on the bio-based 1,5-pentanediol and aliphatic diacids with 4, 5, 6, 9, 10, or 12 carbon atoms. Partially bio-based polyester were compared in terms of effects of dicarboxylate chain length on the crystalline structure and thermomechanical properties. All the polyesters are semicrystalline polymers, where the crystallization degree and melting temperature increase with dicarboxylate chain length. The results indicated also that all polyesters have sufficient thermal stability. Munoz-Guerra *et al*. [27] investigated bio-based aromatic polyesters prepared by ring-opening polymerization of cyclic ethylene and butylene 2,5-furandicarboxylate oligoesters. The polymerization of this two compounds led to furan-based polyesters: poly(ethylene furanoate) (PEF) and poly(butylene furanoate) (PBF). It was found that the oligo(butylene 2,5-furandicarboxylate) cycles are more reactive during polymerization than the ethylene ones, which required higher reaction temperature to reach similar conversions. Papageorgiou *et al*. [28] investigated synthesis of poly(propylene-2,5-furandicarboxylate) (PPF) as a new bio-based aromatic polyester. They described a comparative study of the thermal behavior and solid state structure of PPF, poly(propylene terephthalate) (PPT) and poly(propylene naphthalate) (PPN). The results indicated that macromolecular chains of PPF and PPT were rigid, due to their glass transition temperatures and thermal stability of these polymers was similar. The melting point of PPF was found at 180 °C when PPN and PPT revealed the melting point at higher temperatures, respectively 207 and 231 °C. Zhou *et al*. [29] studied aromatic polyesters synthesized from 2,5-furandicarboxylic acid (FDCA) and 1,4-butanediol (BDO), which were used for preparation of copolymer with poly(tetramethylene glycol) (PTMG). The results showed that glass transition temperature, melting point, melt crystallization temperature and crystallization ability decreased with increasing PTMG content. Moreover, PBF-PTMG copolymers exhibited good stress at break and outstanding elongation at break.

A range of articles describing bio-based polyurethane materials were published over the last decade. Petrović *et al*. [30] synthesized fast-responding shape-memory polyurethanes with the use of bio-based polyester polyols. Polyester polyols were synthesized with the use of 9-hydroxynonanoic acid and hexanediol. Dicarboxylic acid was obtained by ozonolysis of fatty acids extracted from soy oil and castor oil. The researchers indicated that due to the high crystallization rate of the soft segment, the obtained polyurethanes were characterized by unique properties suitable for shape-memory applications, such as adjustable transition temperatures and good mechanical strength. Moreover, they claimed that these materials were potentially biodegradable and biocompatible, which make them suitable for biomedical and environmental applications. Datta and Głowińska [31] investigated bio-based polyurethanes synthesized with the use of vegetable-oil based polyols. In their study, they used a mixture of commercial polyether and hydroxylated soybean oil with different ratios. Furthermore, they used two bio-based low molecular weight glycols: 1,2-propanediol and 1,3-propanediol as chain extenders. The results of thermomechanical analysis showed that the polyurethanes produced with bio-based 1,2-propanediol exhibited higher storage modulus and lower loss modulus than polyurethanes based on 1,3-propanediol as a chain extender. Moreover, they prepared bio-based polyurethane composites with microcrystalline cellulose [32, 33]. They confirmed good interfacial adhesion between the partially bio-based matrix and biofiller. The results of thermomechanical analysis showed a positive effect of the filler on the storage and loss modulus of the composites. The tensile strength and elongation at break decreased with increasing filler content, but the addition of microcrystalline cellulose improved the hardness of the obtained materials. Saralegi and Eceiza *et al*. [34] investigated segmented thermoplastic polyurethane materials based on the vegetable oil-based polyesters and corn sugar-based chain extender. They studied the effect of soft segment chemical structure and molecular weight on the morphology and properties of the final products. The results indicated that chemical structure and molecular weight of polyols strongly affect the properties of the synthesized polyurethanes. With the increasing soft segment molecular weight, the degree of segment crystallinity and microphase separation also increased, which gave enhanced mechanical properties and higher thermal stability.

One of the important features of polyester components is their good thermal stability, which promises to ensure a suitable behavior of the polyols during industrial processing. By conducting the measurements of thermal stability at various heating rates, the thermal degradation kinetics can be determined.

There are some methods which allow measuring the kinetics of the thermal decomposition. The first method is the Kissinger method [35]. This method makes it possible to determine the activation energy E without the precise knowledge about the mechanism of the reaction in accordance with the Equation (1):

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \text{const} \qquad (1)$$

where: β – heating rate [K/min], T_p – temperature corresponding to the inflection point (maximum reaction rate) of the thermal degradation curves [K], R – gas constant [$8.314 \cdot 10^{-3}$ kJ/(mol · K)].

Activation energy E of the decomposition can also be calculated by using isoconventional method of Ozawa, Flynn and Wall (OFW) [36]. This method consists of measurements of the temperatures, which are attributable to the constant value of conversion α from experiments carried out at different heating rate β. The assumption for this method is that the conversion function $f(\alpha)$ is constant for all values of conversion α with the alteration of the heating rate β. Plotting $\ln(\beta)$ against $1/T$ according to the Equation (2) allows determining the activation energy E.

$$\ln(\beta) = \ln\left[\frac{Af(\alpha)}{\frac{d\alpha}{dT}}\right] - \frac{E}{RT} \qquad (2)$$

where: β – heating rate [K/min], A – pre-exponential factor, that is assumed to be temperature-independent, $f(\alpha)$ – conversion function, α – conversion value, T – temperature [K], R – gas constant [$8.314 \cdot 10^{-3}$ kJ/(mol · K)].

Ozawa, Flynn and Wall developed also a model-free method for degradation kinetics study with the use of TG data [37]. This isoconversional method uses the following Equation (3):

$$\ln(\beta) = \ln\left[\frac{AE_{app}}{Rg(\alpha)}\right] - 0.4567\frac{E_{app}}{RT} - 2.315 \qquad (3)$$

where: $g(\alpha)$ – the integral reaction model, E_{app} – the approximate activation energy.

At each fixed degree of conversion α, plotting log β against $1/T$ creates linear trends. The slope of the plot's best-fit line is proportional to the approximate activation energy, according to the relation (4):

$$\text{slope} = -0.4567\frac{E_{app}}{R} \qquad (4)$$

In the present work, the synthesis of a series of linear bio-based aliphatic polyester polyols is described. The syntheses were designed to obtain the polyesters with proposed weight average molecular weight *ca*. 2000 g/mol and functionality $f = 2$. Tetraisopropyl orthotitanate (TPT) was used as a polycondensation catalyst. Thermal degradation characteristics of the obtained poly(propylene succinate)s was determined by the use of thermogravimetric analysis (TGA). Kinetics of the thermal degradation was determined by using Ozawa, Flynn and Wall as well as Kissinger methods.

EXPERIMENTAL PART

Materials

– Bio-based succinic acid (SA) (solid, molecular weight: 118.09 g/mol, purity: 98–100 %, relative density at 20 °C: 0.900 g/cm^3) used in this study was obtained from BioAmber Sarnia Inc. (Ontario, Canada).

– Susterra propanediol (1,3-propanediol) (liquid, molecular weight: 76.09 g/mol, purity: 99.98 %, water content by Karl Fischer: 12.1 ppm, relative density at 20 °C: 1.053 g/cm^3, dynamic viscosity at 20 °C: 52 mPa · s) was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA).

– Tetraisopropyl orthotitanate, Ti(O-*i*-Pr)$_4$ (TPT), (liquid, molecular weight: 284.22 g/mol, purity: 97 %) used as a catalyst was purchased from TCI Chemicals (India).

– All other materials and solvents used for analytical measurement methods for characterization of prepared bio-based polyester polyols were of analytical grade.

Bio-based polyesters synthesis

Aliphatic bio-based polyester polyols were prepared with the use of dicarboxylic acid, which was succinic acid, and glycol, 1,3-propanediol. Both used components were of natural origin. The catalyst was used in the same amount, 0.25 wt %, for all of the polyols. The catalyst mass was calculated as a glycol equivalent. All linear bio-based polyester polyols were synthesized in the bulk by two-step polycondensation method (esterification and polycondensation). The first step was represented by the esterification reaction between succinic acid (SA) and 1,3-propanediol (PDO). Glycol was always used in excess. The molar ratio SA : PDO equaled 1 : 1.2, was determined considering the final molar mass expected after full polycondensation (approximately number average molecular weight: $\overline{M}_n = 2000$ g/mol and functionality: $f = 2$). Both of the steps were carried out in the glass reactor, which consisted of three-neck flask equipped with nitrogen/vacuum inlet, mechanical stirrer, thermometer, and condenser. The glass reactor was placed into a heating mantle. The first step of the reaction was conducted under a nitrogen atmosphere. Succinic acid and 1,3-propanediol mixture (without catalyst) was stirred at 140, 150 or 160 °C, depending on the synthesis, and kept at this temperature, until at least 60 % of water as a by-product was received (application for patent in the Polish Patent Office, no. P418808). After the water distillation, the flow of nitrogen was stopped, the appropriate amount of catalyst was added to reaction mixture and the temperature was increased up to 160, 180, 190 or 200 °C, depending on the synthesis, under reduced pressure. The value of pressure amounted to *ca*. 6.67 kPa. During polycondensation, the acid number was measured. After achieving the acid number value of *ca*. or preferably below 1 mg KOH/g, the polycondensation was finished. The values of hydroxyl numbers have to range from 50 to 80 mg KOH/g – the scope of hydroxyl number of polyols dedicated for cast polyurethane elastomers.

Methods of testing

Acid and hydroxyl number

– Carboxyl end-group value measurements were performed in accordance with the Polish Standard PN-86/C45051. Samples about 1 g of the prepared polyesters were dissolved in *ca*. 30 cm^3 of acetone at room temperature. Thereafter, the solutions were titrated with the use of a standard solution of potassium hydroxide KOH in distilled water (0.1 mol/dm^3) and phenolphthalein as indicator.

– Hydroxyl group determination was performed with the use of sample about *ca*. 0.5 g of polyester. The sample was dissolved in 5 cm^3 of acetic anhydride solution prepared in accordance with the Polish Standard PN-88/C-89082. The solution was refluxed for 30 minutes. After that, 1 cm^3 of pyridine was added and heating continued for 10 minutes. Thereafter, 50 cm^3 of distilled water was added, the mixture was cooled to room temperature and titrated with the use of a standard solution of potassium hydroxide KOH in distilled water (0.5 mol/dm^3) and phenolphthalein as indicator.

Based on the results of the end-groups determination, the average molecular weights of bio-based polyols were calculated from following Equation (5):

$$\overline{M}_n = \frac{f \cdot 56.1 \cdot 1000}{L_k + L_{OH}} \quad (5)$$

where: $\overline{M}_n$ – average molecular weight calculated with the use of end-groups method [g/mol], f – bio-based polyols functionality, established value $f = 2$ [-], 56.1 – molar mass of the potassium hydroxide [g/mol], L_k – acid number [mg KOH/g], L_{OH} – hydroxyl number [mg KOH/g].

Dynamic viscosity

Dynamic viscosity measurements were performed with the use of rotary rheometer R/S-CPS+ produced by Brookfield Company, USA. The viscosity values at 80 °C were defined with the use of computer program Rheo3000. Measurements were conducted with controlled shear rate (CSR). The justification of the choice of temperature was based on temperature ranges in some industrial processes.

^{1}H NMR spectroscopy

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was carried out with the use of Bruker spectrometer. Operating frequency was 400 MHz for protons. The *ca*. 10 % w/v solutions of the poly(propylene succinate) polyesters were prepared in a $CDCl_3$ solvent at ambient temperature. The simulation and iteration of the obtained spectra were carried out using Bruker software.

Thermal characteristic

DSC-TG/QMS coupled method of thermogravimetric measurements were conducted using an STA 449 F1 Jupiter apparatus from NETZSCH-Feinmahltechnik GmbH Germany. Approximately 20 mg portions of dry samples were placed in corundum crucible and heated to 650 °C at various rates: 10, 15 and 20 deg/min and under helium flow. Under these conditions, the DSC-TG experiments of bio-based polyester polyols were sufficiently reproducible.

RESULTS AND DISCUSSION

Synthesis and characterization of the poly(propylene succinate)s

All prepared polyester polyols (PPS) were synthesized with the use of well-known two-step polycondensation method. The first step was the esterification reaction, which was conducted for 10 hours for all of the prepared polyester polyols without the use of catalyst. After removal of minimum 60 % water, the catalyst was added. The second step, which was the main polycondensation reaction, was carried out for individual time periods for all synthesized polyesters until achievement the acid number *ca*. or preferably lower than 1 mg KOH/g. The justification of the choice of end-point of the polycondensation reaction was based on the content of carboxyl end-groups corresponding to the acid number determined for some synthetic polyester polyols commonly used in the

T a b l e 1. Properties of the prepared polyester polyols

Sample	Synthesis temperature °C		Reaction time h	L_k mg KOH/g	L_{OH} mg KOH/g	$\overline{M}_n$ g/mol	Viscosity at 80 °C Pa · s
	I step	II step					
PPS 140/160	140	160	18	0.83	51.5	2200	3.43
PPS 140/190		190	16	1.05	58.5	1900	4.66
PPS 140/200		200	13	1.02	77.4	1400	2.76
PPS 150/180	150	180	17	0.96	63.4	1800	7.41
PPS 150/190		190	16	1.15	48.7	2300	3.47
PPS 150/200		200	14	0.80	70.4	1600	3.38
PPS 160/180	160	180	16	1.05	79.0	1400	4.76
PPS 160/190		190	14	1.00	64.7	1700	5.77
PPS 160/200		200	14	1.02	71.8	1600	4.34

T a b l e 2. Thermal degradation characteristics of the prepared polyester polyols at heating rate of 10 deg/min

Sample	Thermal degradation characteristics				
	$T_{5\%}$ °C	$T_{50\%}$ °C	$T_{90\%}$ °C	T_{max} °C	Residue at 650 °C %
PPS 140/160	323.2	393.9	415.5	403.2	0.35
PPS 140/190	323.8	394.1	417.7	403.9	0.67
PPS 140/200	326.0	395.9	418.5	401.0	0.96
PPS 150/180	320.8	395.9	418.5	401.0	0.99
PPS 150/190	327.5	395.6	418.4	403.6	0.67
PPS 150/200	318.2	396.0	417.2	403.2	0.94
PPS 160/180	318.9	394.9	417.8	403.9	0.61
PPS 160/190	321.0	395.0	417.3	401.3	0.30
PPS 160/200	313.2	395.2	417.1	403.2	0.89

polyurethane industry. Table 1 shows properties of the prepared polyols.

The conducted synthesis confirmed the influence of temperature conditions during both steps of the polycondensation on the reaction kinetics. Table 1 presents the shortest reaction time for polyols prepared at highest temperature conditions. The reaction time for PPS 140/200 was 13 hours. The synthesis was carried out until the acid number of the resulting polyol reached *ca.* 1 mg KOH/g. The hydroxyl number increased with the increasing synthesis temperature and the highest value was determined for polyol PPS 160/180. One of the most important properties for the industry, which gives information about probable behavior of polyol during industrial processing is viscosity. The lowest value at 2.76 Pa · s was measured for PPS 140/200.

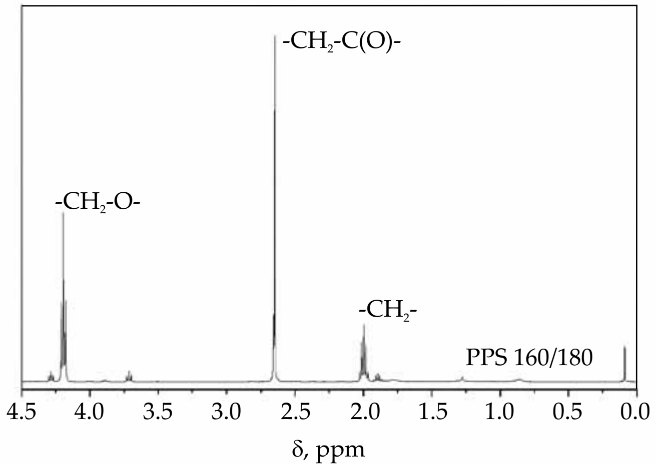

Fig. 1. ^{1}H NMR spectrum of PPS 160/180

^{1}H NMR spectroscopy

The structure analysis of received products was performed using ^{1}H NMR measurements. The resulted spectra verified that poly(propylene succinate)s were obtained. Figure 1 shows the exemplary ^{1}H NMR spectrum of PPS 160/180. The characteristic intensive single peak at 2.63 ppm is attributed to methylene protons from succinic acid [-C$\underline{\mathbf{H}}_2$-C(O)-] [38]. Peaks at 4.20 and 2.00 ppm are connected with a triple and multiple peaks corresponding to methylene protons from propylene glycol (1,3-propanediol), (-C$\underline{\mathbf{H}}_2$-O-) and (-C$\underline{\mathbf{H}}_2$-), respec-

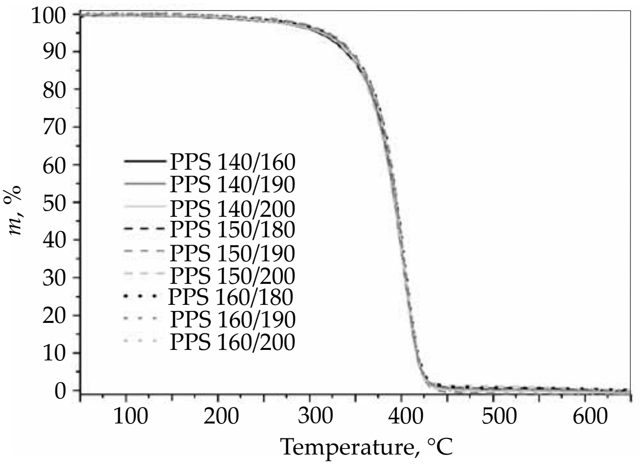

Fig. 2. TGA graph of the synthesized polyester polyols

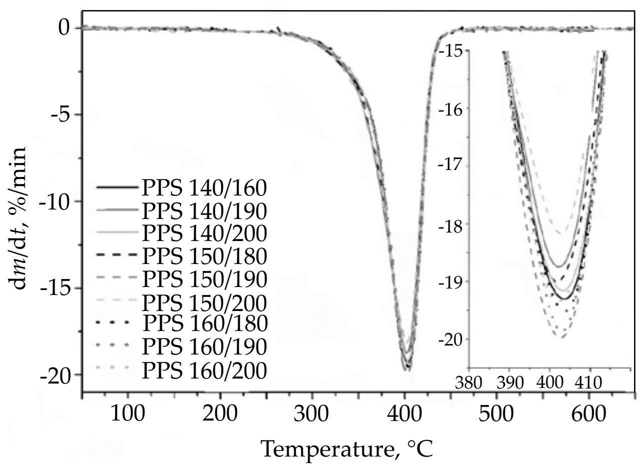

Fig. 3. DTG graph of the synthesized polyester polyols

tively [35]. More precise description can be found in references [39, 40].

Thermogravimetric analysis

Thermogravimetric analyses were performed to evaluate the thermal properties of the synthesized materials. The results confirmed their high thermal stability. Table 2 presents the characteristic temperatures of thermal decomposition of the prepared materials measured at the heating rate 10 deg/min. The characteristic temperatures of 5, 50 and 90 % of the weight loss and the temperature of the maximum rate of weight loss for all samples revealed similar values. The lowest value of $T_{5\,\%}$ at 313.2 °C which gives information about the beginning of the thermal decomposition was determined for PPS 160/200. The highest value of the $T_{5\,\%}$ at 327.5 °C was observed for PPS 150/190. The temperature of the maximum rate of weight loss was within the range from 401.0 to 403.9 °C.

Figures 2 and 3 present the TGA and DTG graphs for relevant materials. The results confirmed one-step mechanism of the thermal degradation and similarity of the thermal stability characteristics. The most visible differences are related to the intensity of the DTG curves what gives information about the rate of mass loss of materials.

Thermal degradation kinetics

Thermogravimetric analyses were conducted at different heating rates to determine the kinetics of thermal degradation. Table 3 presents the values of activation energy of polyester polyol decomposition calculated with the use of two primary methods: Kissinger as well as Ozawa, Flynn and Wall (OFW). The presented findings demonstrate that activation energy determined by OFW method shows distinct dependence on the synthesis temperature conditions. An increase in activation energy values calculated with this method was observed with increasing temperature conditions during the synthesis of polyols. Only for polyols prepared at 160 °C of the first step of the polycondensation, the activation energy decreased with the increase of the second step temperature. The highest E_a value was 196.4 kJ/mol for PPS 160/180. The lowest E_a equal to 154.2 kJ/mol was determined for the polyol PPS 150/180. In the case of Kissinger method results, there is no clear dependence of synthesis temperature conditions and thermal degradation kinetics. For the comparison between both methods and more precise study, the partitive activation energies for three selected polyols were calculated with the use of OFW method. Figures 4, 5 and 6 present the Ozawa, Flynn and Wall plots of the selected synthesized polyesters. The straight lines are given which slope is proportional to the activation energy ($-E_a/R$). When the activation energy E_a increases with the increase of the conversion degree, the complex reaction mechanism can be confirmed. The single-step reaction can be verified if the determined activation energy E_a is the same for the different α conversion values [35, 41, 42]. Figure 7 shows the dependence between the activation energy E_a and degradation conversion α for PPS 140/160, PPS 150/180 and PPS 160/180. It

Table 3. Activation energy (E_a) of thermal decomposition of the synthesized polyester polyols determined by Ozawa, Flynn and Wall as well as Kissinger methods

Sample	E_a, kJ/mol	
	Ozawa, Flynn and Wall method	Kissinger method
PPS 140/160	164.3	185.7
PPS 140/190	169.1	211.0
PPS 140/200	180.6	144.2
PPS 150/180	154.2	135.5
PPS 150/190	165.8	149.7
PPS 150/200	173.6	188.1
PPS 160/180	196.4	174.7
PPS 160/190	190.8	182.8
PPS 160/200	181.2	149.0

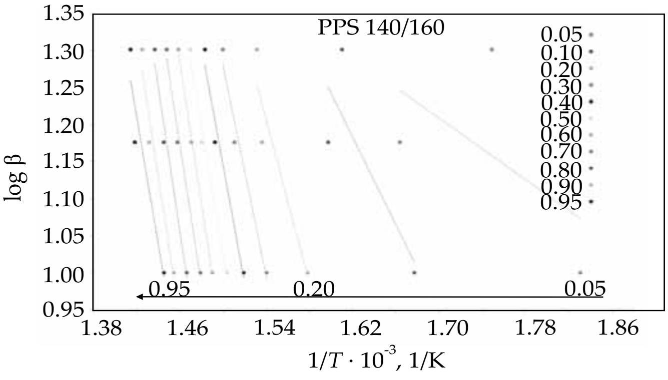

Fig. 4. Ozawa, Flynn and Wall plots of PPS 140/160

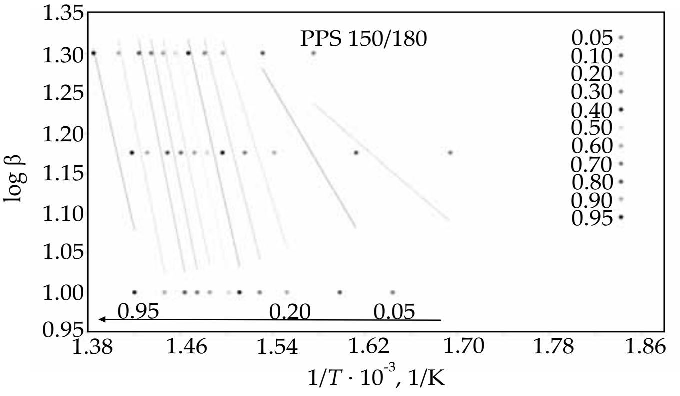

Fig. 5. Ozawa, Flynn and Wall plots of PPS 150/180

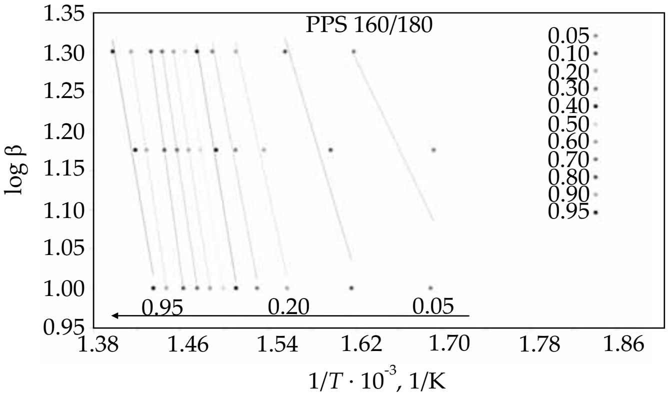

Fig. 6. Ozawa, Flynn and Wall plots of PPS 160/180

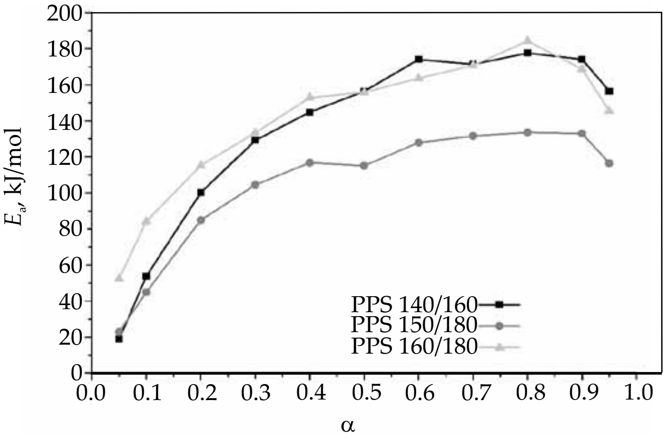

Fig. 7. Dependence of activation energy E_a and degradation conversion α for PPS 140/160, PPS 150/180 and PPS 160/180, determined by OFW method

is shown that with the increase of the conversion degree, the activation energy also increases.

After the conversion reached $0.8 < \alpha < 0.9$, the E_a decreased (see Fig. 7). Therefore, the results verified the existence of the multi-stage reaction during the thermal decomposition of the prepared polyols.

The conducted investigations allowed to verify the lower value of activation energy for fully bio-based poly(propylene succinate) than those of their petrochemical-based counterparts. Chrissafis *et al.* [35] and Bikiaris *et al.* [43] determined the activation energy of the petrochemical-based poly(propylene succinate) at *ca.* 220 kJ/mol.

CONCLUSIONS

A series of the linear bio-based polyester polyols were synthesized with the use of two-step polycondensation reaction conducted under the different temperature conditions. The reaction conditions and reagents ratio were selected for polyol production in accordance with the requirements of thermoplastic polyurethane industry. The differences of macromolecular structure were determined based on the values of acid and hydroxyl numbers, average molecular weights and viscosities. The thermal degradation kinetics of the synthesized polyols was also investigated. The results indicate the differences in the activation energy calculated with the use of two primary methods: Ozawa, Flynn and Wall as well as Kissinger. Based on the OFW method a distinct dependence between bio-based polyols synthesis conditions and kinetics of their thermal degradation was found. With the increasing temperature conditions, the increasing activation energy was observed. Only for polyols prepared at 160 °C at the first step of polycondensation revealed decreasing E_a with elevated temperature during the second step of polycondensation. The highest thermal degradation activation energy by OFW method and the most similar to that of petrochemical-based poly(propylene succinate), equal to 196.4 kJ/mol, was determined for polyol PPS 160/180. Moreover, the results verified the existence of the multi-stage reaction during thermal decomposition of the prepared polyols. The comparison between primary properties and activation energies allowed to select PPS 140/200 as one of the most suitable for use as a polyol for polyurethanes. The critical information was the lowest viscosity value and one of the highest activation energies from all of the prepared bio-based polyols.

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