

# Thermal degradation mechanism of poly(ethylene succinate) and poly(butylene succinate): Comparative study

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## Abstract

Two aliphatic polyesters that consisted from succinic acid, ethylene glycol and butylene glycol, —poly(ethylene succinate) (PESu) and poly(butylene succinate) (PBSu)—, were prepared by melt polycondensation process in a glass batch reactor. These polyesters were characterized by DSC, <sup>1</sup>H NMR and molecular weight distribution. Their number average molecular weight is almost identical in both polyesters, close to 7000 g/mol, as well as their carboxyl end groups (80 eq/10<sup>6</sup> g). From TG and Differential TG (DTG) thermograms it was found that the decomposition step appears at a temperature 399 °C for PBSu and 413 °C for PESu. This is an indication that PESu is more stable than PBSu and that chemical structure plays an important role in the thermal decomposition process. In both polyesters degradation takes place in two stages, the first that corresponds to a very small mass loss, and the second at elevated temperatures being the main degradation stage. The two stages are attributed to different decomposition mechanisms as is verified from the values of activation energy determined with iso-conversional methods of Ozawa, Flynn, Wall and Friedman. The first mechanism that takes place at low temperatures, is auto-catalysis with activation energy  $E = 128$  and  $E = 182$  kJ/mol and reaction order  $n = 0.75$  and  $1.84$  for PBSu and PESu, respectively. The second mechanism is  $n$ th-order reaction with  $E = 189$  and  $256$  kJ/mol and reaction order  $n = 0.68$  and  $0.96$  for PBSu and PESu, respectively, as they were calculated from the fitting of experimental results.

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## 1. Introduction

Continuous environmental surcharge due to domestic and industrial waste, as well as uncontrolled release of carbon dioxide in atmosphere, consist the major problems of nowadays growth. Plastic waste materials represent a high percentage of domestic wastes, while combustion techniques that are applied, in a controlled way in many countries or without any precaution in others, contribute in additional contamination, not only with carbon dioxide but also with various toxic volatiles, mainly dioxins. The only gain is energy upturn.

[1]. Plastics recycling may be a unique way for a decreasing influence on environment. Unfortunately, an abundance of polymers with different physical and chemical properties are utilized, and furthermore there are difficulties in their effective segregation. As a result, a very limited portion of plastics production is recycled. Besides, recycling demands activation of people and peculiar techniques. Due to these difficulties it is not possible to recover all the used plastic. Nowadays it is estimated that 150 million tonnes of plastics are annually produced all over the world while the production and consumption has an increasing trend [2]. The solid waste management crisis has generated a demand for environmentally friendly materials.

Biodegradable polymers have attracted considerable attention last decades due to their potential applications as

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green materials contributing to lower environmental pollution. Poly(butylene succinate) and its familiar polyester poly(ethylene succinate) are two of the commercially produced aliphatic polyesters and the most intensively studied members of this series. They have high melting points, 112–114 and 103–106 °C, respectively, and they present controllable biodegradation rate and high processability. Their mechanical properties such as elongation at break and tensile strength are comparable with those of PP and LDPE while their crystallization behavior is similar to that of polyethylene with well formed lamellar morphologies. The crystallization characteristics of PBSu were studied by DSC and optical microscopy and were found that they depend closely on the cooling rate [3]. Equilibrium melting point and the glass transition temperatures were found to be at about 132 and –38 °C, respectively while enthalpy of fusion is 200 J/g. By isothermal crystallization using DSC, equilibrium melting point of PBSu was found at 140 °C and multiple melting peaks (up to three) were also reported [4]. The existence of two kinds of crystals, perfect that were formed at higher temperatures and imperfect that were formed at low crystallization temperatures is characteristic of all semicrystalline polyesters. Similar triple melting peaks were also found in PESu revealing that at low crystallization temperatures imperfect crystals were formed, which were melted and recrystallized during progressive heating [5]. This behavior could also be reflected on the cold crystallization temperature of polyesters. For non-isothermal crystallization of PESu, there were two crystallization exotherms upon heating the amorphous state. One major crystallization exotherm, located at low temperatures that corresponds to the real cold crystallization of PESu, while the other minor one, located at high temperature may correspond to the melt-crystallization of the unstable crystals formed in advance, during the non-isothermal crystallization. [6]. The equilibrium melting point for PESu was found at 115.6 °C [7]. A dependence of thermal properties on molecular weight was also mentioned. Melting point ( $T_m$ ) and crystallization temperature ( $T_c$ ) are decreasing by increasing the molecular weight of PBSu [8].

In our previous work concerning the biodegradation rate of succinic acid polyesters, it was found that poly(propylene succinate) biodegrades faster than, poly(ethylene succinate) or poly(butylene succinate), which may have the lowest biodegradability [9]. Since chemical composition plays an important role on the biodegradation rates, it was expected that PBSu should biodegrade faster than the other two familiar polyesters. Fields et al. studied polyesters prepared from diacids containing C<sub>2</sub>–C<sub>12</sub> and diols with C<sub>4</sub>–C<sub>12</sub> and it was found that the distance between ester groups affected the biodegradation rate [10]. Taking this into account in the studied succinate polyesters increasing the spacing between the ester groups by introducing higher number of methylene groups, the polyesters could become more susceptible to enzymatic hydrolysis. However, this was not in case. In the aliphatic polyesters many researchers have found that the

degree of crystallinity, spherulite size and lamellar structure can influence the biodegradation rate [11–14]. This seems to be also the dominant factor affecting the biodegradation rate of poly(alkylene succinate)s. Thus, PPSu which has the lowest crystallinity degrades faster than PESu and PBSu.

PESu and PBSu are two of the extensively studied biodegradable synthetic polyesters. Although the crystallization and biodegradation behaviour has been examined [3,4,15,16], limited work has been reported so far, in the literature, about their thermal stability and their degradation kinetics [17]. The purpose of this work is to examine in more details the thermal degradation and understand its mechanism at elevated temperatures.

## 2. Kinetic methods

Activation energy  $E$  can be calculated by various methods. The first method, the isoconversional method of Ozawa, Flynn and Wall (OFW) [18,19] is in fact, a “model free” method which assumes that the conversion function  $f(\alpha)$  does not change with the alteration of the heating rate for all values of  $\alpha$ . It involves the measuring of the temperatures corresponding to fixed values of  $\alpha$  from experiments at different heating rates  $\beta$ . Therefore, plotting  $\ln(\beta)$  against  $1/T$  in the form of

$$\ln(\beta) = \ln \left[ \frac{Af(\alpha)}{d\alpha/dT} \right] - \frac{E}{RT} \quad (1)$$

should give straight lines and its slope is directly proportional to the activation energy ( $-E/R$ ). If the determined activation energy is the same for the various values of  $\alpha$ , the existence of a single-step reaction can be concluded with certainty. On the contrary, a change of  $E$  with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis [20]. These complications are significant, especially in the case that the total reaction involves competitive mechanisms.

The second method is also an isoconversional one. Friedman [21] proposed the use of the logarithm of the conversion rate  $d\alpha/dt$  as a function of the reciprocal temperature, in the form of

$$\ln \left( \frac{d\alpha}{dT} \right) = \ln \left( \frac{A}{\beta} \right) + \ln(f(\alpha)) - \frac{E}{RT} \quad (2)$$

It is obvious from Eq. (2) that if the function  $f(\alpha)$  is constant for a particular value of  $\alpha$ , then the sum  $\ln(f(\alpha)) + \ln A/\beta$  is also constant. By plotting  $\ln(d\alpha/dT)$  against  $1/T$ , the value of the  $-E/R$  for a given value of  $\alpha$  can be directly obtained. Using this equation, it is possible to obtain values for  $E$  over a wide range of conversions.

### 3. Experimental

#### 3.1. Materials

Succinic acid (purum 99%), ethylene glycol (purum 99%) and butylene glycol (purum 99%) and were purchased from Aldrich Chemical Co. Tetrabutoxytitanium used as catalyst was analytical grade and purchased from Aldrich Chemical Co. Polyphosphoric acid (PPA) used as heat stabilizer was supplied from Fluka. All other materials and solvents which were used for the analytical methods were of analytical grade.

#### 3.2. Synthesis of polyesters

Aliphatic polyesters were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [22]. In briefly, the proper amount of succinic acid and appropriate glycols in a molar ratio 1/1.1 and the catalyst ( $10^{-3}$  mol TBT/mol SA) were charged into the reaction tube of the polyesterification apparatus. The apparatus with the reagents was evacuated several times and filled with argon in order to remove the whole oxygen amount. The reaction mixture was heated at 190 °C under argon atmosphere and stirring at a constant speed (500 rpm). This first step (esterification) is considered to be completed after the collection of theoretical amount of H<sub>2</sub>O, which was removed from the reaction mixture by distillation and collected in a graduate cylinder.

In the second step of polycondensation, PPA was added ( $5 \times 10^{-4}$  mol PPA/mol SA), in order to prevent side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period time of about 30 min, to avoid excessive foaming and to minimise oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was slowly increased at 230 °C while stirring speed was increased at 720 rpm. The polycondensation continued for about 60 min for all prepared polyesters. After the polycondensation reaction was completed, the polyesters were easily removed, milled and washed with methanol.

### 4. Measurements

#### 4.1. Gel permeation chromatography (GPC)

Molecular weight determinations were performed by GPC method using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastyrigel (103, 104, 105 Å) columns in series. CHCl<sub>3</sub> was used as the eluent (1 ml/min) and the measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

#### 4.2. End group analysis

Carboxyl end-group content (–COOH) of the resins was determined as follows. About 0.1 g of polyesters was dis-

solved in chloroform at room temperature and the solution was titrated by using a standard NaOH in methanol (N/10) and phenol red as indicator.

For hydroxyl groups (–OH) determination 1 g of polyester was dissolved in 50 ml of chloroform. Acetic anhydride solution in pyridine was added and the mixture refluxed for 1 h. After that, 2 ml of water were added and heating was continuous for 10 min. The solution was titrated by using NaOH in methanol (1 N) and phenol red as indicator. For the calculations a blank titration was also became while the content of carboxyl groups was also taken into account.

#### 4.3. Nuclear magnetic resonance (NMR)

<sup>1</sup>H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. Deuterated chloroform (CDCl<sub>3</sub>) was used as solvent in order to prepare solutions of 5% w/v. The number of scans was 10 and the sweep width was 6 kHz.

#### 4.4. Thermal analysis

A Perkin-Elmer, Pyris 1 Differential Scanning Calorimeter (DSC), calibrated with indium and Zinc standards, was used. A sample of about 10 mg was used for each test, placed in an aluminium seal and heated to 35 °C above the melting point of particular polyester at a heating rate 20 °C/min. The sample remained at that temperature for 5 min in order to erase any thermal history. After that it was quenched into liquid nitrogen and scanned again using the same heating rate as before. The glass transition temperature ( $T_g$ ), the melting temperature ( $T_m$ ) and the heat of fusion ( $\Delta H_m$ ) were measured.

Thermogravimetric analysis was carried out with a SETARAM SETSYS TG-DTA 1750 °C. Samples ( $11 \pm 0.5$  mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 500 °C in a 50 ml/min flow of N<sub>2</sub>. Nominal heating rates of 5, 10, 16 and 22 °C/min were used and continuous records of sample temperature, sample weight, its first derivative and heat flow were taken.

### 5. Results and discussion

The polymerization process of the studied polymers involves two different steps according to the well-known process used for polyester synthesis as described in our previous study concerning synthesis of poly(propylene succinate) [23]. The prepared polyesters have white colour and PESu is harder than PBSu. In order to study the influence of molecular structure of the polyesters on thermal decomposition rates, samples of about the same molecular weight were prepared. Thus, effect of molecular weight on degradation rates can be ignored. To achieve this, several polymerizations for each polyester were performed lasting different times. Among the

Table 1  
Structure and properties of prepared polyesters

	Mn (g/mol)	T <sub>m</sub> (°C)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	ΔH <sub>m</sub> (J/g)	X <sub>c</sub> (%)	[–COOH] (eq/10 <sup>–6</sup> )	[–OH] (eq/10 <sup>–6</sup> )
PESu	6810	104	–11.5	55	67.7	37.6	80	85
PBSu	6820	112	–44	–6	96.3	45.8	79	58

prepared samples, those having the same molecular weight as determined by intrinsic viscosity and GPC measurements, were chosen. The intrinsic viscosity of the chosen samples measured in chloroform at 25 °C is 0.28 dL/g and it corresponds to molecular weight values about 7000 g/mol as were determined with GPC (Table 1). Furthermore, from this Table it is clear that the prepared polyesters have similar carboxyl end groups. This is crucial since end groups and mainly carboxyl groups can accelerate the thermal decomposition of polyesters and accordingly an additional factor of effect would enter into our measurements. [24,25].

The <sup>1</sup>H NMR spectra of studied polyesters PESu and PBSu are shown in Fig. 1. <sup>1</sup>H NMR spectrum of PESu is very simple, containing only two characteristic peaks at 2.55–2.67 and 4.18–4.3 ppm attributed to methylene proton *a* of succinic acid and *b* of ethylene glycol, respectively. PBSu <sup>1</sup>H NMR spectrum has a multiple peak at 1.8–2 ppm attributed to *d* proton groups and a triple at 4–4.2 attributed to *c* proton groups.

DSC thermograms for the as received polyesters from the glass reactor have shown that these are crystalline materials

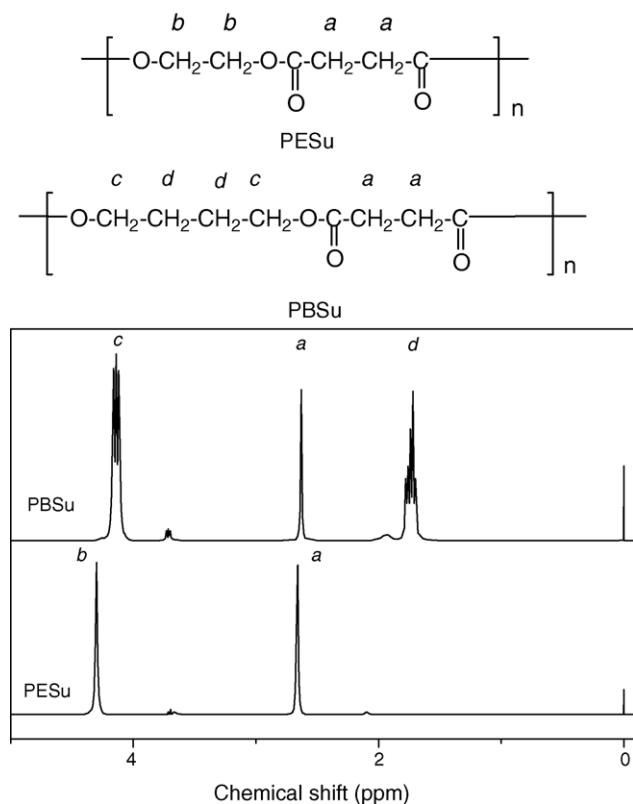


Fig. 1. <sup>1</sup>H NMR spectra of studied polyesters PESu and PBSu.

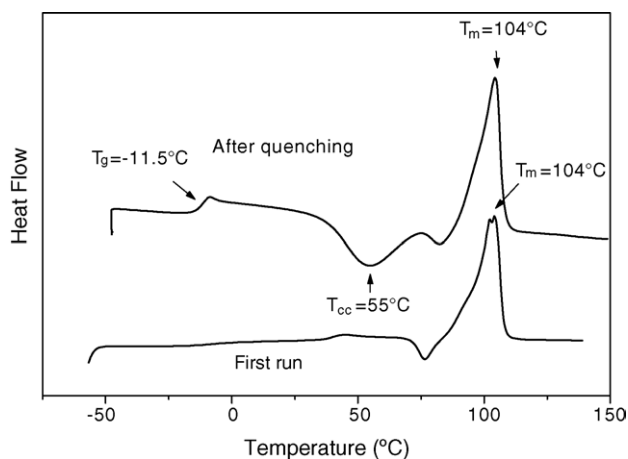


Fig. 2. DSC thermograms of PESu as received from glass reactor and after quenching in liquid nitrogen.

since their melting temperatures are recorded (Figs. 2 and 3). PESu has a melting point at 104 °C while PBSu melts at higher temperature 112 °C, although it has higher number of methylene groups and thus lower melting temperature was expected. Beyond this, for a series of samples crystallized at different conditions, the heat of fusion and the corresponding crystallinity were always lower for PESu than for PBSu samples [26]. In the same study was found that the heat of fusion for pure crystalline material (equilibrium heat of fusion) was 180 J/g for PESu and 210 J/g for PBSu. Thus, the degree of crystallinity for the used polyesters is 37 and 45 %, respectively. After melt-quenching the two polyesters in liquid nitrogen can be taken fully amorphous, despite PBSu has very high crystallization rate and crystallizes rapidly at

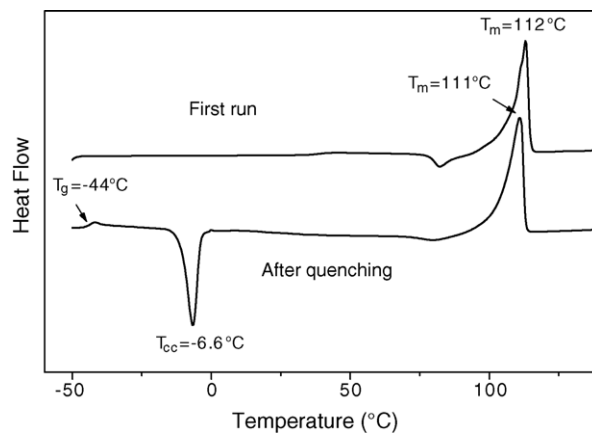


Fig. 3. DSC thermograms of PBSu as received from glass reactor and after quenching in liquid nitrogen.

room temperature. The glass transition temperatures of amorphous samples are more distinguishable after quenching in liquid N<sub>2</sub> and are recorded at  $-44\text{ }^{\circ}\text{C}$  for PBSu and  $-11.5\text{ }^{\circ}\text{C}$  for PESu. PBSu showed a sharp cold-crystallization peak at  $-6\text{ }^{\circ}\text{C}$ , compared to the corresponding broad peak for PESu at  $55\text{ }^{\circ}\text{C}$ , which is further evidence that crystallizes slowly. The cold-crystallization exotherms were accompanied by recrystallization exotherms as shown in the PESu and PBSu thermograms just before the melting point. This behavior is well known for these polyesters and can be also recorded in the as received samples from the reactor. Melting points of both polyesters during the second heating run are almost identical to the  $T_m$  of the crystalline materials.

Regarding thermal degradation behavior of the prepared polyesters, it has been studied the influence of chemical structure on thermal stability, through thermogravimetric analysis (TGA).

## 6. Thermogravimetric analysis

Thermal degradation of PBSu and PESu was studied by determining their mass loss during heating. In Figs. 4 and 5 are presented the mass loss (TG%) and the derivative mass loss (DTG) curves at heating rate  $10\text{ }^{\circ}\text{C}/\text{min}$  for the two polyesters. From the thermogravimetric curves it can be seen that PBSu and PESu present a relatively good thermostability since no significant weight loss, 0.8% for PBSu and 0.5% for PESu, occurred until  $300\text{ }^{\circ}\text{C}$ . A temperature  $T_d$  ( $-2\text{ wt.}\%$ ), at which 2.0 wt.% of the original polyester sample has already been thermally degraded and lost, was hereby taken as index to express its thermal stability. This temperature is  $329\text{ }^{\circ}\text{C}$  for PBSu and  $326\text{ }^{\circ}\text{C}$  for PESu.

In both TG-thermograms (Fig. 4) one stage of mass loss can be followed, while in the DTG-diagrams, very small divergences from the peak regularity can be observed (Fig. 5). These may be due to a second peak corresponding to a small mass loss, taking place at the initial stages of thermal degradation, and thus it presents a particularly big covering (over-

lapping) with the peak that is corresponding to the main mass loss. As it can be seen in the curves of DTG, in the early stages of the decomposition, there is a small shoulder probably due to a slight difference in the slope of decomposition curve of TG. Such a pre-major weight loss stage was also mentioned in poly(propylene terephthalate), where this first decomposition step that corresponded to small weight loss was attributed to the volatilization of small molecules, residual catalysts, 1,3-propanediol and carbon dioxide that devaluated from chain ends. [27]. From preliminary studies of the monomers it was found that succinic acid degrades at temperatures close to  $200\text{ }^{\circ}\text{C}$  while ethylene glycol and butylene glycol evaporate at slightly higher temperatures, nevertheless lower than  $300\text{ }^{\circ}\text{C}$ . These data strengthens our hypothesis that the first decomposition step is due to oligomer degradation. Furthermore, from kinetic studies of poly( $\epsilon$ -caprolactone) (PCL) which also degrades in two steps, it was verified with TGA/FTIR and mass spectroscopy that water, carbon dioxide and hexanoic acid are the volatile products of the first decomposition step taking place at lower temperatures [28].

After that temperature the polyesters under study decompose quickly and lose almost their whole weight, about 99.5 wt.% for PBSu until  $460\text{ }^{\circ}\text{C}$  and 98 wt.% for PESu until  $470\text{ }^{\circ}\text{C}$ . As can be seen from the peak of the first derivative, the temperatures at which PBSu and PESu decomposition gain the highest rate are at  $399$  and  $413\text{ }^{\circ}\text{C}$ , respectively, for heating rate  $10\text{ }^{\circ}\text{C}/\text{min}$ . According to the predominant mechanism proposed by Buxbaum for polyesters, a random cleavage of the ester bond takes place due to the  $\beta$ -CH hydrogen transfer. Carboxylic end groups and vinyl groups are formed during this chain scission [29]. Of course the tendency for chain scission is higher in the polyesters in which monomers with higher number of methylene groups are used. This was verified from decomposition rates of model compounds, which differ by one or more methylene groups, like ethylene dibenzoate and butylene dibenzoate. Thermal and thermo-oxidative degradation of the second is higher than that of the first one [30]. For this reason the decomposition rates of PBT or PPT are higher compared to that of PET, as

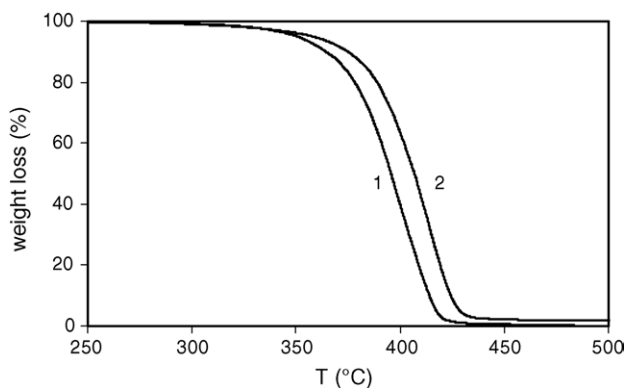


Fig. 4. Mass loss (TG%) vs. temperature with heating rate  $\beta = 10\text{ }^{\circ}\text{C}/\text{min}$ : (1) PBSu; (2) PESu.

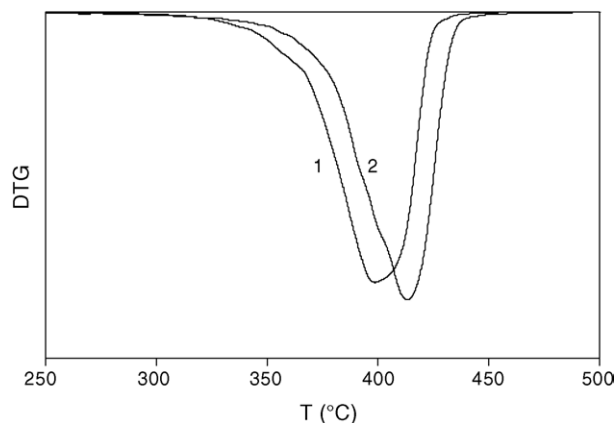


Fig. 5. Derivative mass loss (DTG) vs. temperature with heating rate  $\beta = 10\text{ }^{\circ}\text{C}/\text{min}$ : (1) PBSu; (2) PESu.

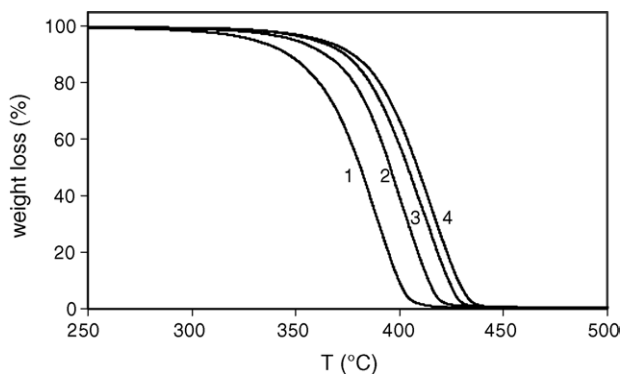


Fig. 6. TG curves of PBSu at different heating rates  $\beta$ : (1) 5 °C/min; (2) 10 °C/min; (3) 16 °C/min; (4) 22 °C/min.

this contains one or two methylene groups less and is more stable to decomposition [31].

From the above results it is noticeable that PESu presents higher thermal stability than the PBSu. Furthermore, from our previous study it was verified that the maximum rate of mass loss of the familiar aliphatic polyester poly(propylene succinate) appears at a decomposition temperature 408 °C [23]. This temperature lies between the corresponding decomposition temperatures of PESu and PBSu. Consequently, it can be concluded that the number of methylene groups of used diol for polyester preparation has a crucial effect on its thermal stability. As the number of methylene groups increases, thermal stability decreases. However, these temperatures and especially that of PESu, are very high taking into account that the polyesters are aliphatic and the values of temperature are comparable to decomposition temperatures reported for aromatic polyesters of terephthalic (PET, PBT, PPT) and naphthalic acid like PEN [32,33]. Furthermore, these temperatures are much higher compared to other aliphatic polyesters like poly(L-lactide) in which major degradation step appears at temperatures lower than 370 °C, as well as from poly[(R)-3-hydroxybutyrate] and poly( $\epsilon$ -caprolactone) [34–36].

In order to be analyzed more deeply the degradation mechanisms of PBSu and PESu it is important kinetic parameters (activation energy  $E$  and pre-exponential factor  $A$ ) and conversion function  $f(\alpha)$  to be evaluated. The relationship between kinetic parameters and conversion ( $\alpha$ ) can be found by using the mass loss curves recorded in TG dynamic thermograms. The thermogravimetric curves of PBSu heated in N<sub>2</sub> atmosphere, at different heating rates are shown in Figs. 6 and 7 from temperature above melting point till 500 °C. Analogous results are received for PESu. It is clear from the DTG plots that the peak temperature,  $T_p$ , shifts to higher values with increasing heating rate; an increase of 29 °C for PBSu and 18 °C for PESu, in the initial thermal decomposition temperature is measured.

The activation energy of degradation of the studied polyester was estimated using Ozawa, Flynn and Wall (OFW) and Friedman methods. Firstly, the isoconversional Ozawa method was used to calculate the activation energy for differ-

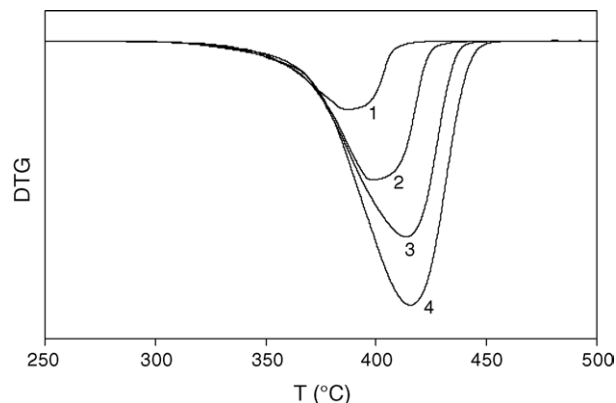


Fig. 7. DTG curves of PBSu at different heating rates  $\beta$ : (1) 5 °C/min; (2) 10 °C/min; (3) 16 °C/min; (4) 22 °C/min.

Table 2  
Activation energies of PBSu using Ozawa and Friedman methods

Conversion $a$	Activation energy (kJ/mol) Ozawa method	Activation energy (kJ/mol) Friedman method
0.02	126 ± 17	146 ± 15
0.05	135 ± 15	136 ± 15
0.10	146 ± 13	177 ± 10
0.20	165 ± 13	200 ± 11
0.30	177 ± 12	191 ± 5
0.40	182 ± 10	186 ± 11
0.50	186 ± 8	181 ± 16
0.60	186 ± 8	178 ± 12
0.70	186 ± 8	183 ± 8
0.80	187 ± 8	184 ± 7
0.90	188 ± 8	185 ± 4
0.95	190 ± 7	206 ± 12
0.98	203 ± 4	320 ± 38

ent conversion values by fitting the plots of  $\log \beta$  versus  $1/T$ . Some of the Ozawa plots for PESu are shown in Fig. 10 and all data are summarized in Tables 2 and 3 for PBSu and PESu, respectively. The straight lines fitting the data are nearly parallel being an indication that the activation energies at the different degree of conversion are similar (Fig. 8).

Table 3  
Activation energies of PESu using Ozawa and Friedman methods

Conversion $a$	Activation energy (kJ/mol) Ozawa method	Activation energy (kJ/mol) Friedman method
0.02	136 ± 11	136 ± 43
0.05	186 ± 24	219 ± 29
0.10	206 ± 28	223 ± 29
0.20	239 ± 26	246 ± 16
0.30	256 ± 14	297 ± 18
0.40	265 ± 7	269 ± 8
0.50	267 ± 7	264 ± 18
0.60	268 ± 6	262 ± 13
0.70	265 ± 7	246 ± 16
0.80	260 ± 10	237 ± 17
0.90	254 ± 11	227 ± 16
0.95	250 ± 12	228 ± 11
0.98	247 ± 12	245 ± 24

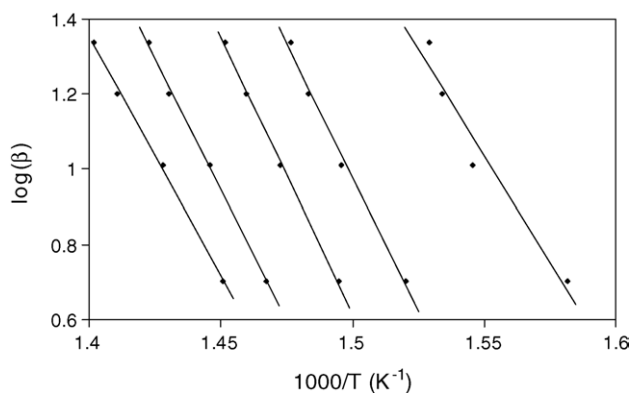


Fig. 8. Ozawa plots of PESu at fractional extent of reaction: (1)  $\alpha=0.95$ ; (2)  $\alpha=0.8$ ; (3)  $\alpha=0.5$ ; (4)  $\alpha=0.3$ ; (5)  $\alpha=0.1$ .

Secondly, Friedman method was used by plotting  $\ln(d\alpha/dT)$  against  $1/T$  for a constant  $\alpha$  value and the activation energy is calculated. The results are shown also in Tables 2 and 3. The difference in the  $E$  value calculated by the two methods can be explained by a systematic error due to improper integration. The method of Friedman employs instantaneous rate values being, therefore very sensitive to experimental noise. In Ozawa method the equation used is derived assuming constant activation energy, introducing systematic error in the estimation of  $E$  in the case that  $E$  varies with  $\alpha$ , error that can be estimated by comparison with the Friedman results [37]. It is followed from Table 2 for PBSu that the dependence of  $E$  on  $\alpha$  value, as calculated with Ozawa method, can be separated in two main distinct regions, the first for values of  $\alpha$  up to 0.2, in which  $E$  presents a monotonous increase and the second ( $0.2 < \alpha < 0.95$ ) in which  $E$  can be considered as having a constant average value. From Table 3 for PESu, the dependence of  $E$  from  $\alpha$  is more complicated, presenting a first augmentative region for  $\alpha < 0.2$ , and then a region with relatively constant value of  $E$  for  $0.2 < \alpha < 0.8$  which is followed by a region with monotonous decrease of  $E$ . This dependence of  $E$  on  $\alpha$  is an indication of a complex reaction with the participation of at least two different mechanisms, from which the one has quite small effect in mass loss. This conclusion is associated with the already mentioned at the beginning observation about a possible presence of overlapped peak in DTG diagram with a very small contribution in mass loss. Although, the “two mechanisms” – as a result of the increasing  $E$  with  $\alpha$  – is a rather typical phenomenon for many polymers [38], this assumption is based on the multi-step TG curve. This is not clear in our case and the conclusion is extracted through the combined examination of overlapped peak in DTG diagram. From the two mechanisms, the first corresponds to the part where small loss appears while the second part, where the substantial mass loss takes place, is attributed to the main decomposition mechanism, each one mechanism presenting different activation energy. This is in accordance with other studies in biodegradable polyesters such as PCL, in which two mechanisms were recorded with different activation energies each other [28,34,39].

In order to determine the nature of these two mechanisms through the comparison of the experimental and theoretical data, initially it is considered that the degradation of PBSu and PESu can be described only by a single mechanism that corresponds to the main mass loss, without presuming the exact mechanism. Then, knowing this mechanism ( $f(\alpha)$ ), are determined the data of the other mechanism corresponding to the small mass loss, in order the better possible agreement between experimental and theoretical data to be achieved. To determine the conversion function  $f(\alpha)$  we used a method referred to as the “model fitting method” [40]. This method that does not assume the knowledge of  $E$  and  $f(\alpha)$  in advance, was applied simultaneously on the experimental data taken at the heating rates  $\beta = 5, 10, 16$  and  $22$  °C/min. It has been shown that model-fitting to multiple heating rate data gives activation energies similar to the values estimated by the iso-conventional methods [41]. For the fitting were used sixteen different kinetic models. In Fig. 9 can be seen the results of this fitting for PESu, the results for PBSu being analogous. The form of the conversion function, obtained by fitting is  $f(\alpha) = (1 - \alpha)^n$  for both the polyesters and the parameters of the mechanisms were: for PBSu, the exponent value  $n$  is equal to 0.57, activation energy  $E = 180$  kJ/mol, pre-exponential factor  $\log A$  ( $s^{-1}$ ) = 11.8 and the correlation coefficient was 0.99955, while for PESu were, exponent value  $n$  equal to 0.97, activation energy  $E = 230$  kJ/mol, pre-exponential factor  $\log A$  ( $s^{-1}$ ) = 15.6 and correlation coefficient 0.999. Comparing these results, the nature of mechanism can be evaluated and it can be defined as  $n$ th-order reaction mechanism, which coincides with the mechanism that is generally used for the description of mass loss in polyesters [42]. The value of the activation energy is between the limits of the calculated values from the Ozawa and Friedman methods for PBSu and it is lower for PESu. Exponent value  $n$  in the PBSu diverges considerably from the value 1, which is usually used for the kinetic description of mass loss in polyesters, in a first-order reaction mechanism. As it can be seen, the fitting to the experimental data is very good for the area where mass loss takes values higher than 20%, while the divergence is important for

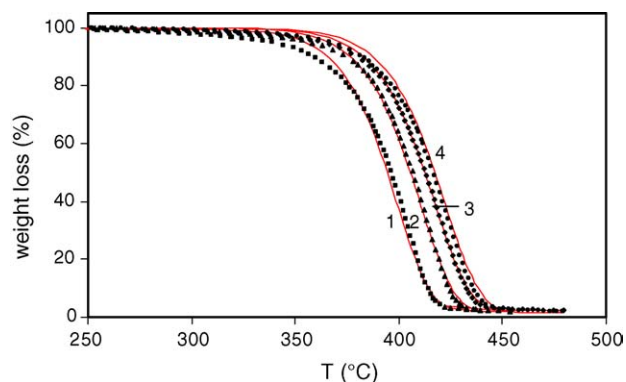


Fig. 9. Fitting and experimental data TG curves of PESu for all the different heating rates  $\beta$  for one reaction mechanism: (1)  $5$  °C/min; (2)  $10$  °C/min; (3)  $16$  °C/min; (4)  $22$  °C/min.

Table 4

Calculated values of activation energy, pre-exponential factor and exponent  $n$  for the two reaction mechanisms of PBSu and PESu

Sample	Activation energy of first decomposition mechanism (kJ/mol)	$n$	Pre-exponential factor $\log A$ ( $s^{-1}$ )	Activation energy of second decomposition mechanism (kJ/mol)	$n$	Pre-exponential factor $\log A$ ( $s^{-1}$ )
PBSu	128	0.75	8.3	189	0.68	12.6
PESu	182	1.84	13.4	256	0.96	17.6

the region where the mass loss takes lower values, especially for the PESu as it is, also, realized from correlation factor of the fitting in this polyester. This deviation is followed mainly in the starting temperatures area, where it has been noticed possible overlapped peak in the DTG curve.

For the determination of the first stage mechanism are assumed the followings: (a) the two mechanisms follow each other, (b) this mechanism which we try to identify corresponds to small mass loss, according to the experimental results, (c) this mechanism according to the literature [43,44] is mechanism of autocatalysis  $n$ -order that is described by equation  $f(\alpha) = f(\alpha) = (1 - \alpha)^n \alpha^m$ .

The agreement of experimental and theoretical results (Fig. 10), leads to a further improvement of fitting that is remarkable mainly in the first stages of mass loss. The improvement due to identification is noticeable particularly for PESu. The data of the fitting for the two polyesters are presented in Table 4. In this stage of identification for the best possible results, we left the parameters ( $E$ ,  $A$  and  $n$ ) of the examined mechanism to be recalculated and the results are included in Table 4.

Therefore, for PBSu, the activation energy  $E$  of the first decomposition mechanism is 128 kJ/mol while for the second decomposition mechanism it was increased from 180 kJ/mol in 189 kJ/mol, remaining in the limits of corresponding values that were calculated with Ozawa method.

The activation energy of the first decomposition stage is similar to that reported for poly(butylene terephthalate) (PBT) 117 kJ/mol and corresponds to the production of tetrahydrofuran (THF) [45]. The initiating mechanism is ionic decomposition taking place at low temperatures while after THF evolution, which is the main product during PBT

thermal decomposition, ester pyrolysis predominates yielding to 1,3-butadiene through an intermediate cyclic transition state. The activation energy of this second stage was reported at 208 kJ/mol, which is very close to that found in the present study for PBSu (189 kJ/mol). Thus a similar mechanism may be also speculated for PBSu since activation energies for initial and main decomposition stages are similar to that reported for PBT.

From the other side the PESu value of  $E$  is considerably increased concerning the one that was calculated considering only one decomposition mechanism, from 230 to 256 kJ/mol. This value is henceforth inside of the value limits that were calculated with Ozawa method. Exponent  $n$  for the main mechanism was increased from 0.57 to 0.68 in the PBSu, having however a considerably smaller value from 1, while in PESu the exponent value remained almost constant, from 0.97 to 0.96.

## 7. Conclusions

In the present study two aliphatic and biodegradable polyesters—poly(ethylene succinate) and poly(butylenes succinate)—were prepared and studied. Both polyesters, have the same molecular weight and carboxylic end groups, the latter being very important when comparing their thermal degradation kinetics. PESu presents melting at 104 °C, glass transition at −11.5 °C and cold crystallization at 55 °C, while for PBSu the parameters take the values, melting at 112 °C, glass transition at −44 °C and cold crystallization at 6.6 °C.

According to TG and DTG analysis it was found that mass loss of PESu and PBSu is accomplished in two stages, from which the small one is slightly distinguishable only in DTG diagrams with the overlapped contributions. The two stages are attributed to different degradation mechanisms that take place during polyesters thermal decomposition at different temperatures.

The activation energies for all values of  $\alpha$ , were determined with iso-conversional methods of Ozawa, Flynn, Wall and Friedman. From the dependence of activation energy on the  $\alpha$  value, it was identified the existence of two regions for  $E$  values: The first for  $\alpha < 0.2$ , where the value of  $E$  is increased monotonously, and a second one for  $\alpha > 0.2$  with the value of  $E$  remaining rather constant, mainly in the PBSu. This constitutes a clear indication that the kinetic description of mass loss can be accomplished through at least two different mechanisms, and this conclusion is consistent with the appearance of an overlapped peak (shoulder) in DTG diagrams.

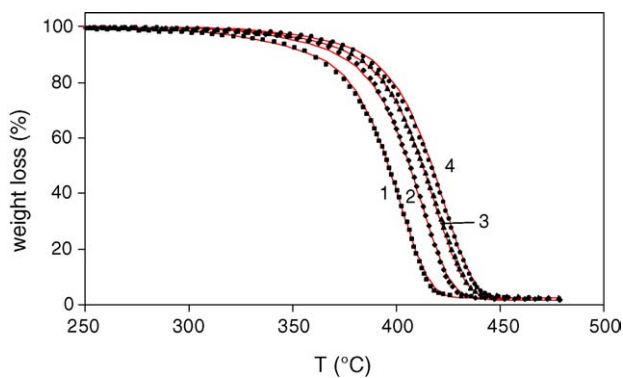


Fig. 10. Fitting and experimental data TG curves of PESu for all the different heating rates  $\beta$  for two reaction mechanisms: (1) 5 °C/min; (2) 10 °C/min; (3) 16 °C/min; (4) 22 °C/min.



The first mechanism that takes place at lower temperatures and is related to the much smaller mass loss, is  $n$ th-order autocatalysis, described by the equation  $f(\alpha) = (1 - \alpha)^n \alpha^m$  with the parameter values being -for PBSu and PESu, respectively, activation energy  $E = 128$  and  $182$  kJ/mol, pre-exponential factor  $\log A$  ( $\text{s}^{-1}$ ) =  $8.3$  and  $13.4$ , and exponent  $n = 0.75$  and  $1.84$ . The second mechanism of mass loss can be better described by the equation  $f(\alpha) = (1 - \alpha)^n$ , with values of activation energy  $E = 189$  and  $256$  kJ/mol, pre-exponential factor  $\log A$  ( $\text{s}^{-1}$ ) =  $12.6$  and  $17.6$  and exponent value  $n$  equal to  $0.68$  and  $0.96$  for PBSu and PESu, respectively.

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