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Effect of molar ratio on thermal mass loss kinetics of poly(ε-caprolactone-b-propylene adipate) copolymers

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ABSTRACT

Poly(ε-caprolactone-b-propylene adipate) copolymers were synthesized using a combination of polycondensation and ring opening polymerisation. GPC was used for molecular weight determination. ^{1}H-NMR and ^{13}C-NMR spectroscopy was also used for copolymer characterization and composition, which was found similar to the feeding ratio. DSC study was used in order to define T_g, T_m and ΔH_m values of neat polymers and copolymers. Mass loss upon heating kinetics of neat polymers and their copolymers were studied by using thermogravimetric analysis (TGA). It was found that copolymers have almost the same thermal stability as PCL, which is the most stable part. The influence of PPAd in copolymers can mainly be seen at the beginning of mass loss where a small overlapped peak can be observed. The kinetic parameters of mass loss upon heating of all polyesters were calculated while the activation energies were estimated using the Ozawa, Flynn and Wall (OFW) and Friedman methods. Mass loss upon heating was found to be described by two mechanisms that follow each other. The first mechanism is attributed to a small mass loss, while the second mechanism is attributed to the main mass loss as in autocatalysis n^{th}-order (reaction model Cn) or n^{th} order (reaction model Fn).

1. Introduction

Aliphatic polyesters like poly(L-lactic acid), poly(ε-caprolactone), poly(3-hydroxy butyrate), poly(3-hydroxy valerate), etc., due to their favorable features of biodegradability and biocompatibility, constitute a very important class of biodegradable polymers. They are nowadays commercially available in a variety of types used for several applications. Among them, aliphatic polyesters have found applications in medicine and pharmaceutical technology, for example, in drug delivery systems, surgical sutures, implants, and tissue engineering [1–4].

Poly(ε-caprolactone) (PCL) occupies a head position due to its properties; it is a semicrystalline polymer with high mechanical properties, it is a flexible material with low melting temperature ($T_m = 60\,^\circ$C), low glass transition temperature ($T_g = -60\,^\circ$C) and good solubility in most solvents [5]. It is used in multiple biomedical and environmental applications, as prostheses, bandages or controlled release matrix for active principles (e.g. drugs, pesticides and surgery repair materials) [6,7] as well as packaging materials. However, high crystallinity and hydrophobicity of PCL decreases its compatibility with soft tissues and diminishes its *in vivo* and *in vitro* hydrolysis rate. This can be solved using plasticizers or by copolymerization with other comonomers with higher hydrolysis rate. Biodegradability can also be improved dramatically [8].

Nowadays, there is a renewed interest in 1,3-propanediol-based polyesters, due to their unique properties, such as high light and thermal stability, high mechanical properties and good spinning machinability. In the past, the synthesis of 1,3-propanediol was carried out by hydrolysis of acrolein and subsequent catalytic hydrogenation, which gave low yields, reducing its technological and economic importance. Recently, the price of 1,3-propanediol has been steadily decreasing, due to the ability of producing it by microbial conversion from glycerol [9], and this fact gave a strong impulse to the diffusion of propanediol-based polymers for many industrial applications. Such aliphatic polyesters have been recently used as effective drug carriers in the form of nanoparticles and solid state dispersions [10–13]. Poly(propylene adipate) (PPAd) is a novel biodegradable aliphatic polyester, which has gained an increasing interest, since it has high mechanical properties and higher biodegradation rate, compared to other poly(propylene alkanedicarboxylate)s [14,15]. Also, it has low cytotoxicity and thus, can be used as drug carrier. Due to its low crystallinity, it also degrades faster than most of polyesters used as pharmaceutical excipients, including polycaprolactone (PCL) [15] and thus copolymers between them could be of high interest.

It is known that homopolymers in many cases do not present the "optimal" set of properties. Therefore, copolymers have become more and more important, since their characteristics can be more

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easily tailored to fit specific applications. Their physical properties are strongly affected by copolymer composition, structural arrangement of molecular units, sample crystallinity, etc. These physical properties may affect the application and the behaviour of these copolymers. In our previous study, copolymers of ε-CL with propylene succinate (PSu) were synthesized and used as candidate polymers towards the development of effective nanoparticles as drug delivery systems. [8] These nanoparticles are self organized into core/shell structures, driven by differences in hydrophobicity and, mainly, physical state (amorphous vs. crystalline, respectively) between the poly(propylene succinate) (PPSu) and PCL segments. The advantage of these nanoparticles is that they are free from burst effects and can release the drug over a relatively short period of time, typically less than 2 days. Similar copolymers could be of high interest as fast biodegradable materials in agriculture applications as well as packaging materials [16].

The aim of the present work was to synthesize neat PPAd and PCL as well as their copolymers with different molar ratios in order to correlate the physical and mainly thermal properties to copolymer composition. Additional scope was to reveal the mechanisms by which mass loss upon heating occurs. This is very important in the case that these copolymers would be used as solid dispersion drug carriers prepared by melt mixing technique. For this purpose copolymers containing PPAd in mass ratios 30 and 65 wt% were synthesized.

2. Experimental

2.1. Materials

Adipic acid (purum >99.5%) was purchased from Fluka. 1,3-Propanodiol (purum 99.6+%) and ε-caprolactone (purum 99%) was purchased from Aldrich Chemical co. ε-caprolactone was distilled at 94–95 $^{\mathrm{O}}$C under reduced pressure at about 5 mmHg, prior to use, in order to remove the inhibitor contained. Titanium (IV) butoxide [$\mathrm{Ti(OBu)_4}$] (purum 97%) was used as catalyst and was also purchased from Aldrich Chemical co. Polyphosphoric acid (PPA) used as heat stabilizer was supplied from Fluka. All other materials and solvents used were of analytical grade.

2.2. Synthesis of polyesters

Synthesis of poly(propylene adipate) (PPAd) was performed following the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. In brief, the proper amount of adipic acid and the one of 1,3-propanediol in a molar ratio 1/1.2 and catalyst $\mathrm{Ti(OBu)_4}$ (3×10^{-4} mol/mol adipic acid) were charged into the reaction tube of the polycondensation apparatus. The apparatus with the reagents was evacuated several times and filled with nitrogen in order to remove the total amount of oxygen preventing other side reactions. The reaction mixture was heated at 180 °C under nitrogen atmosphere while stirring at a constant speed (255 rpm) was applied. The first step (esterification) is considered to complete after the collection of almost the theoretical amount of H_2O, which was removed from the reaction mixture by distillation and collected in a graduated cylinder. At this stage poly(propylene adipate) oligomers were produced. In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol adipic acid). A vacuum (5.0 Pa) was applied slowly over a period of about 15 min in order to avoid excessive foaming and to minimize oligomer evaporate. The temperature was gradually increased to 240 °C while stirring speed was slowly increased to 720 rpm. The polycondensation reaction time was 2 h.

Synthesis of PCL was performed by bulk polymerization of ε-caprolactone (ε-CL) in a 250 mL round bottomed flask equipped with a mechanical stirrer and a vacuum apparatus. The initiator was added as a solution in toluene at a final concentration of 1×10^{-4} mol $\mathrm{Ti(OBu)_4}$/mol ε-CL. The polymerization mixture was purged with nitrogen three times. The reaction was carried out at 180 °C for 2 h. Unreacted monomer was removed through distillation by applying a vacuum (≈5 Pa) over a period of 15 min. Polymerization was stopped by fast cooling to room temperature.

Synthesis of poly(ε-caprolactone-co-propylene adipate) copolymers, at mass ratios 70/30 w/w and 35/65 w/w respectively, was performed following the procedures described in our previous paper [8]. In brief, PPAd was added into the same apparatus used for PCL synthesis and the proper amounts of ε-CL monomer were added, as well as $\mathrm{Ti(OBu)_4}$ [1×10^{-4} mol $\mathrm{Ti(OBu)_4}$/mol ε-CL]. Polymerization took place at 180 °C under nitrogen flow for 60 min while the stirring rate was kept stable at 500 rpm. Unreacted monomer was also removed through distillation by applying vacuum (≈5 Pa), slowly to avoid excessive foaming, over a period of 15 min.

2.3. Characterization of polymers and co-polymers

2.3.1. Intrinsic viscosity

Intrinsic viscosity [η] measurements were performed using an Ubbelohde viscosimeter at 25 °C. All polymers prepared were dissolved in chloroform at room temperature in order to prepare solutions of 1% w/v concentration.

2.3.2. Gel permeation chromatography (GPC)

GPC analysis was used in order to determine the molecular weights. It was performed using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastyragel (10^3, 10^4, 10^5 Å) columns in series. Tetrahydrofuran (THF) 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.

2.3.3. Nuclear magnetic resonance (NMR)

^{1}H-NMR and ^{13}C-NMR spectra of polyesters were obtained using a Bruker spectrometer operating at a frequency of 400 MHz and 75.5 MHz respectively. Deuterated chloroform ($\mathrm{CDCl_3}$) was used as solvent in order to prepare solutions of 5% w/v and the spectra were internally referenced to tetramethylsilane.

2.3.4. Differential scanning calorimetry (DSC)

Thermal analysis study was performed using Differential scanning calorimeter (DSC) on a Perkin–Elmer, Pyris Diamond DSC, calibrated with Indium and Zinc standards. Samples of 5 ± 0.1 mg were used in tests. They were sealed in aluminium pans and heated 50 °C above the melting point at a heating rate 20 °C/min under nitrogen atmosphere. The samples were held at that temperature for 5 min in order to erase any thermal history and then cooled to −75 °C at a cooling rate 200 °C/min under nitrogen atmosphere in order to prevent crystallization. The sample was heated again at the same condition and glass transition temperature (T_{g}), melting temperature (T_{m}) and heat of fusions (ΔH_{m}) were recorded. An Intracooler 2P cooling device was used to achieve high cooling rates over the temperature region of interest, which was from −75 to 120 °C.

2.3.5. Thermogravimetric analysis

Thermogravimetric analysis was carried out with a SETARAM SETSYS TG-DTA 16/18. Samples (6.0 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. PPAd, PCL and PCL/PPAd copolymers were heated from ambient temperature to 550 °C in a 50 mL/min flow of N_2 at heating rates

Table 1
Theoretical concentrations (wt%, mol%), real concentrations (mol% ^{1}H-NMR and ^{13}C-NMR), intrinsic viscosities and molecular weights of neat polymers and prepared copolymers.

Sample	wt%	mol%	mol% ^{1}H-NMR	mol% ^{13}C-NMR	[η] (dL/g)	Average M_n (g/mol)	Average M_w (g/mol)	M_w/M_n
PCL	0/100	0/100	0/100	0/100	0.53	15300	47700	3.12
PCL/PPAd 70/30	70/30	79.20/20.80	76.69/23.31	78.73/21.27	0.40	13200	34300	2.60
PCL/PPAd 35/65	35/65	46.76/53.24	44.55/55.45	44.67/55.33	0.42	19400	38600	1.99
PPAd	100/0	100/0	100/0	100/0	0.57	13700	28900	2.10

of 5, 10, 15 and 20 °C/min. Continuous recordings of sample temperature, sample weight, its first derivative and heat flow were performed.

3. Results and discussion

3.1. Polyester synthesis and characterization

The aliphatic polyester PPAd was synthesized following the two stage melt polycondensation method (esterification and polycondensation). According to this procedure at the first stage oligomer synthesis occurred by an esterification reaction of a diol and a dicarboxylic acid. At the second stage, that of polycondensation, the temperature was raised in order to increase the molecular weight of the polyester. Poly(ε-caprolactone-b-propylene adipate) copolyesters, in concentrations 70/30 w/w and 35/65 w/w respectively, were synthesized using the proper amount of the synthesized PPAd and ε-CL monomer following the procedures described by Papadimitriou et al. [8]. The intrinsic viscosities of the prepared polymers were ranged between 0.4 and 0.57 dL/g and the recorded molecular weights form GPC are between 13200 and 19400 g/mol (Table 1). All samples showed unimodal distribution in GPC (data not shown), i.e. only a single broad peak, an indication that only one type of polyester at each sample was formed. Oligomers of both polymers were not observed.

In order to establish the copolymerization process as well as the composition of synthesized copolymers, ^{1}H-NMR and ^{13}C-NMR spectra were recorded. The ^{1}H-NMR spectra of PCL, PPAd and their PCL/PPAd 35/65 w/w copolymer are shown in Fig. 1.

For PCL there are the typical signals, a multiple peak at 1.32–1.39 attributed to methylene group c, an eightfold peak at 1.58–1.66 attributed to methylene groups b, a triple peak at 2.26–2.31 owing to methylene d next to carbonyl group and a triple peak at 4.02–4.06 due to methylene a standing next to oxygen atom. These peaks are in accordance with same ones detected to related studies [8,17,18]. The ^{1}H NMR spectra of PPAd shows a triple peak at 4.12–4.14 attributed to methylene groups e, a quintuple peak at 1.92–1.98 attributed to methylene group f, a single peak at 2.32 owing to methylene groups g and a quintuple peak at 1.62–1.65 attributed to methylene groups h. These peaks have also been detected in previous studies [16]. At ^{1}H-NMR spectra of PCL/PPAd copolymers 30/70 and 65/35 w/w there are present both the characteristic peaks of PCL and PPAd. The mol% concentrations of the copolymers were calculated using (i) the peaks attributed to methylene groups c and f corresponding to PCL and PPAd respectively for ^{1}H-NMR and (ii) the peaks attributed to diol carbons bonded to the ester oxygen for ^{13}C-NMR. All these results are presented in Table 1 and as can be seen the theoretical data according to the feedings are almost identical with the calculated ones. Similar are also the results from ^{13}C-NMR spectra. Fig. 2 represents the ^{13}C-NMR spectra of neat polymers PCL and PPAd and their copolymer 70/30 w/w.

As can be seen from the spectrum of copolymer PCL/PPAd 70/30 w/w, the peaks of both homopolymers are present at the same position. A closer look at region 173–174 ppm proves the formation of two new smaller peaks between those assigned to neat polymers (Fig. 3). The peaks of the copolymer at that region can be identified as follows: (i) the peak at 173.56 ppm is attributed to carbonyl carbon of PCL moiety, (ii) the new peak at 173.40 ppm corresponds to carbonyl carbon of PCL which is bonded to carbonyl carbon of PPAd, (iii) the second new peak at 173.36 ppm corresponds to carbonyl carbon of PPAd which is bonded to carbonyl carbon of PCL and (iv) the peak at 173.21 can be ascribed to carbonyl carbon of PPAd moiety.

Integration of these four peaks can be performed to characterize the chemical microstructures of the synthesized copolymers [19,20]. The total areas of the four peaks were normalized and the percentage values of each peak corresponding to each copolymer were calculated. From normalized areas three possible triad sequences were calculated, Cl–Cl–Cl, Cl–Ad–Cl or Ad–Cl–Ad and Ad–Ad–Ad. By using the possible triad sequences, the number of different length of PCL (LnPCl) and PPAd (LnPPAd) segments in macromolecule chain can be calculated, which is named as average number sequence length. It was found that for copolymer 70/30 w/w the values LnPCl and LnPPAd were 27.53 and 7.72

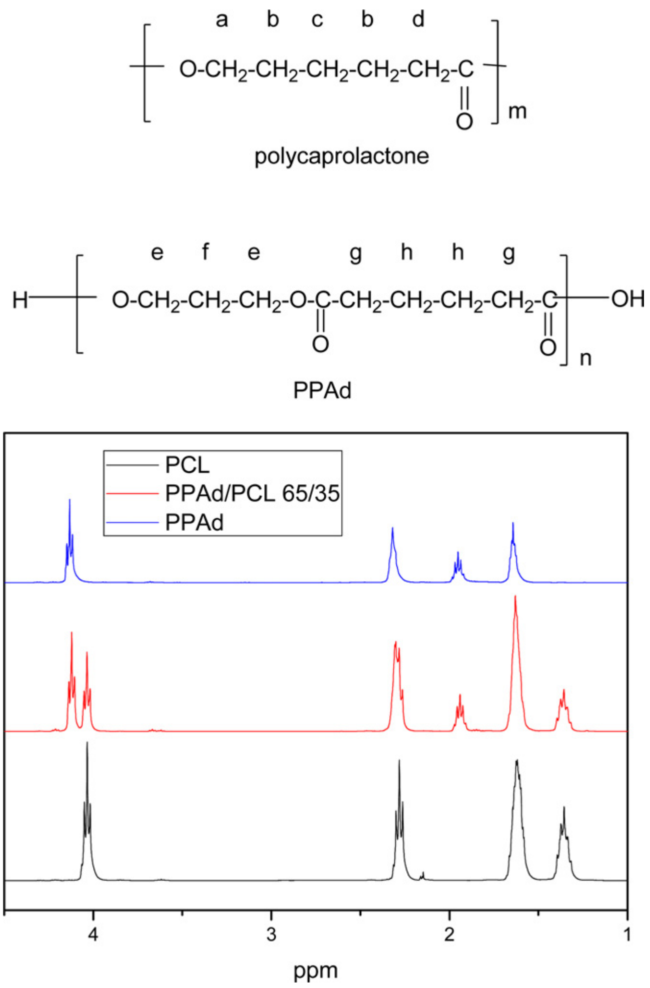

Fig. 1. ^{1}H-NMR spectra of PCL, PPAd and copolymer PCL/PPAd 35/65 w/w.

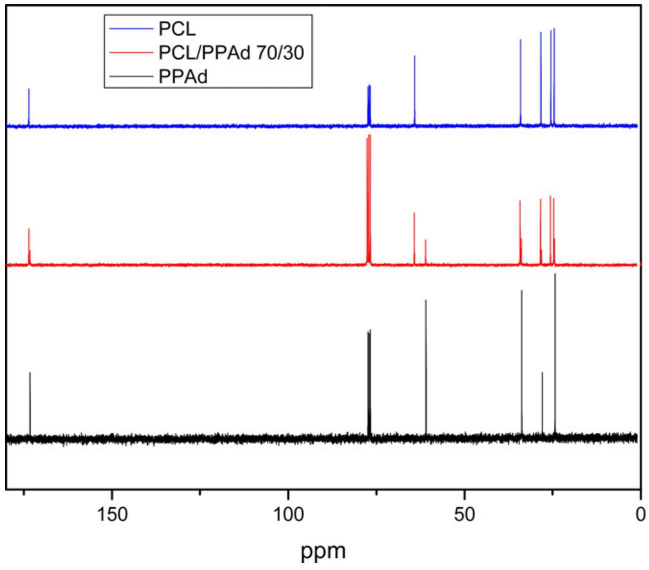

Fig. 2. ^{13}C-NMR spectrum of PCL, PPAd and their copolymer PCL/PPAd 70/30 w/w.

Table 2
T_g, T_m and ΔH_m values of PCL, PPAd and their copolymers.

Sample	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
PCL	−68.2	54.8	58.1	68.66
PCL/PPAd 70/30	−64.4	40.0	48.7	56.98
PCL/PPAd 35/65	−64.3	21.9	36.1	44.93
PPAd	−56.1	31.1	41.8	35.93

respectively, while for copolymer 35/65 w/w the correspondent values were 13.84 and 16.24 respectively.

The randomness β of the copolymers was also calculated. When $\beta = 1$ the copolymer has a random distribution, the value $\beta = 0$ represents blends and when $\beta < 1$ the copolymer has a block distribution. The values calculated for copolymers PCL/PPAd 70/30 w/w and 35/65 w/w are 0.17 and 0.13 respectively, indicating that block copolymers have been synthesized.

In order to define T_g and T_m values of neat polymers and synthesized copolymer DSC studies were performed. All samples were initially heated at 50 °C above the melting point and held at that temperature for 5 min in order to erase any thermal history. After cooling, the sample was heated again and glass transition temperature (T_g) and melting temperature (T_m) were recorded. Data are shown in Table 2.

As can be seen one T_g was recorded in all samples. PCL showed a T_g at −68.2 °C while PPAd has $T_g = -56.1$ °C. Their copolymers showed intermediate values between these of neat polymers and as can be seen these are unaffected from PPAd content since their T_g is closer to that of neat PCL. The behaviour of copolymers regarding their T_m and ΔH_m, is completely different. A double peak appears in all samples and the recorded peaks are affected from copolymer ratio. The double melting peak corresponds either to the formation of two different crystals after quenching from its melt either to the formation of block copolymers [21]. However, double melting points are also recorded in the neat polymers and thus it can be said that the two melting points correspond to two types of different crystals. PCL has higher crystallinity than PPAd and considering the fact that polymers crystallize as metastable lamellae, it is possible for PCL to form different types of crystals or with different perfection. Similarly is the behaviour of PPAd. It is rather typical for polyesters to present multiple melting peaks in their DSC heating curves after the crystallization from their melt [22]. Examining the melting points of the copolymers it can be seen that in the case of PCL/PPAd 70/30 w/w they are recorded between the melting points of neat PCL and PPAd. However, in PCL/PPAd 35/65 w/w the recorded melting points are even lower than the corresponding of PPAd, which compared with PCL has the lowest melting point. This is a usual phenomenon in copolymers in which the crystal formation of the main component, in this case PPAd, is affected by the existence of the other monomer. Examining the ΔH_m values of copolymers, it can be seen that these are reducing gradually as the amount of PPAd increases. This was expected since PCL has higher crystallinity that PPAd, which is a polymer that crystallizes slowly [15].

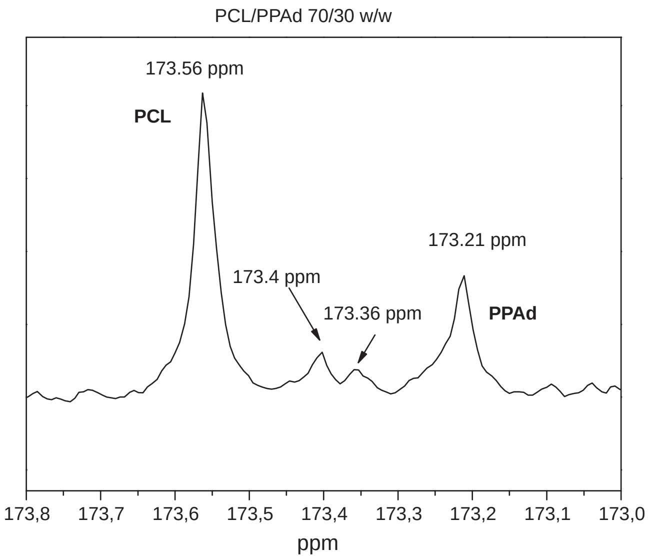

Fig. 3. ^{13}C-NMR spectrum at region 173-174 ppm of PCL/PPAd 70/30 w/w.

3.2. Kinetics of mass loss upon heating

Mass loss upon heating of PPAd, PCL and PCL/PPAd copolymers was studied by determining their mass loss during heating. Figs. 4 and 5 show the mass (%) and the derivative mass (DTG) curves respectively, of PCL/PPAd 70/30 w/w and PCL/PPAd 35/65 w/w in comparison with the curves of PPAd and PCL, at a heating rate of 10 °C/min.

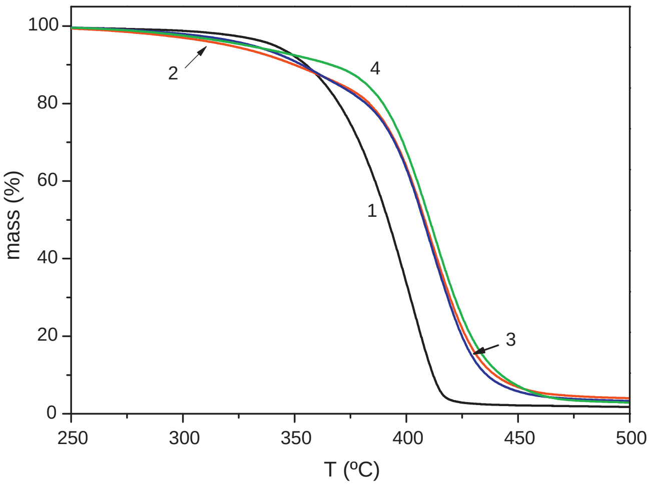

Fig. 4. Mass loss versus temperature with heating rate $\beta = 10$ °C/min. 1: PPAd, 2: PCL/PPAd 70/30 w/w, 3: PCL/PPAd 35/65 w/w, 4: PCL.

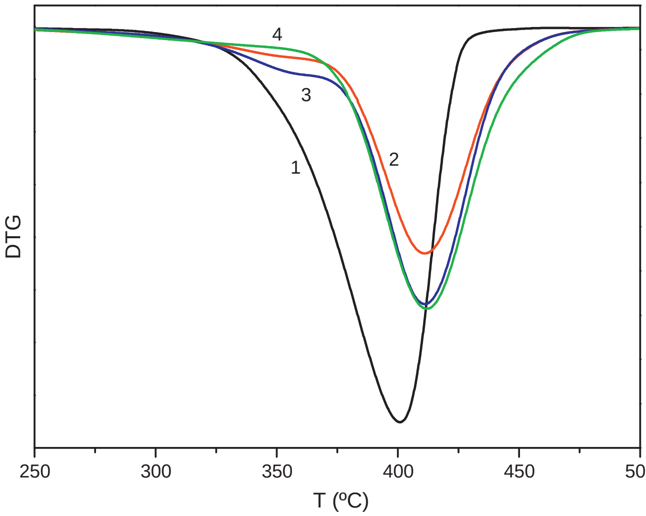

Fig. 5. Derivative mass loss versus temperature with heating rate $\beta = 10\,^{\circ}$C/min. 1: PPAd, 2: PCL/PPAd 70/30 w/w, 3: PCL/PPAd 35/65 w/w, 4: PCL.

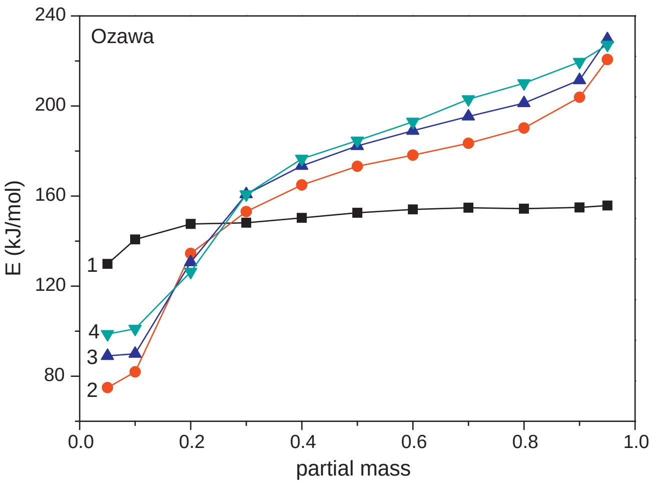

Fig. 6. The dependence of the activation energy on the degree of conversion (partial mass loss) resulted from OFW method. The lines are guide to the eye. 1: PPAd, 2: PCL, 3: PCL/PPAd 70/30 w/w, 4: PCL/PPAd 35/65 w/w.

Thermal degradation of PCL, as also reported in literature, occurs in two degradation steps [23]. The first step takes place between 300 and 380 °C (β-hydrogen bond scission) and is characterized by the departure of water, CO_2 and 5-hexenoic acid (random chain cleavage via cis-elimination) followed by unzipping (up to 400 °C) and the additional formation of ε-CL. PPAd degrades in one step with maximum degradation temperature at 400 °C. Such aliphatic polyesters are degrading via β- and α-hydrogen bond scission of macromolecular chains, forming low molecular weight volatile products such as CO_2, H_2O, aldehydes, ketones, alcohols, acids and allyl compounds [24,25]. As can be followed from derivative mass curves, the temperature of the maximum decomposition rates for PCL/PPAd 70/30 w/w and PCL/PPAd 35/65 w/w was almost the same with that of PCL (Fig. 5). This is an indication that independently from molar ratio in copolymers, PCL parts, which are the most stable at higher temperatures, cause a further stabilization on copolymers thermal decomposition. The influence of PPAd on these samples can be seen mainly in the first area of the mass loss where a small overlapped peak is shown. This peak seems to be affected from the quantity of PPAd in the samples, but its effect, even in the copolymer with 65 wt% PPAd, is rather small. It seems that at the first area of 250–350 °C, a random chain scission occurs upwards in both sequences, and at higher temperatures, cyclization and elimination of ε-CL byproducts may take place. When PPAd is linked to PCL, this results in the delay of the evaporation of PPAd short blocks (because they are linked to more stable PCL) and mass loss in TGA analyses of copolymers takes place at higher temperatures. This can explain the retarded (by reference to neat PPAd) mass loss observed, which cannot be assigned to a real "stabilization". However, this is an indication that maybe the degradation mechanism in these copolymers is different and more complicated than that of neat polymers.

In order to comprehensively analyse the mass loss upon heating mechanisms of the studied copolymers, it is important for the kinetic parameters (activation energy, E, and pre-exponential factor, A) and the conversion function $f(\alpha)$ to be evaluated. The relationship between kinetic parameters and degree of conversion (α) can be found by using the mass loss curves in TG dynamic thermograms that were recorded at different heating rates such as 5, 10, 15 and 20 °C/min.

The activation energy, E, of mass loss upon heating can be calculated by the isoconversional Ozawa, Flynn and Wall (OFW) [26–28] and Friedman [29] methods. These are "model free" methods which assume that the conversion function $f(\alpha)$ does not change with the alteration of the heating rate for all values of α. OFW method involves the measuring of the temperatures corresponding to fixed values of α from experiments at different heating rates β. Therefore, plotting $\ln(\beta)$ against $1/T$ in the form of

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

should give straight lines with slope directly proportional to the activation energy ($-E/R$), where T is the absolute temperature and R is the gas constant. If the determined activation energy is the same for the various values of α, 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 [28].

Friedman proposed the application of the logarithm of the conversion rate $\mathrm{d}\alpha/\mathrm{d}T$ as a function of the reciprocal temperature, in the form of:

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

It is obvious from the above equation that if the function $f(\alpha)$ is constant for a particular value of α, then the sum $\ln(f(\alpha)) + \ln A/\beta$ is also constant. By plotting $\ln(\mathrm{d}\alpha/\mathrm{d}T)_i$ against $1/T_i$, the value of the $-E/R$ for a given value of α can be directly obtained.

The results of both methods are presented in Figs. 6 and 7 and present great similarities. Both methods revealed the same trend of activation energies for the whole conversion range studied. However, comparing the results of the application of the two methods, we observed that the values calculated by the Friedman method were slightly higher than those of the Ozawa method. 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 the 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 α. That error can be estimated by comparison with the Friedman results [30].

In Figs. 6 and 7 the dependence of the activation energy on the degree of conversion α for all the studied samples is presented. As can be seen, the calculated values of the activation energy of PCL/PPAd 70/30 w/w and PCL/PPAd 35/65 w/w in the area of $\alpha > 0.2$

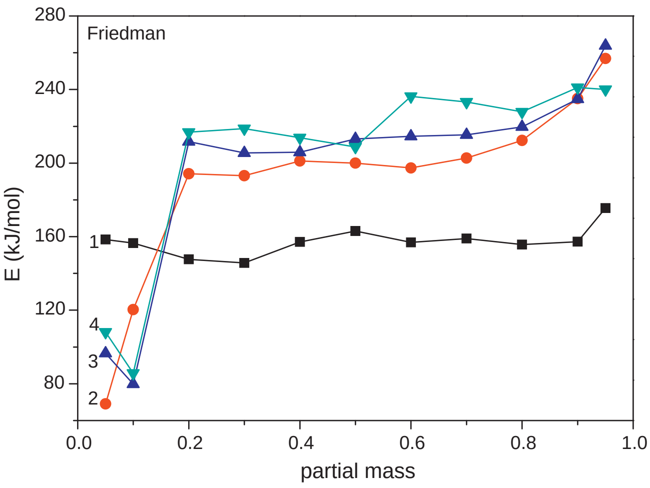

Fig. 7. The dependence of the activation energy on the degree of conversion (partial mass loss) resulted from Friedman's method. The lines are guide to the eye. 1: PPAd, 2: PCL, 3: PCL/PPAd 70/30 w/w, 4: PCL/PPAd 35/65 w/w.

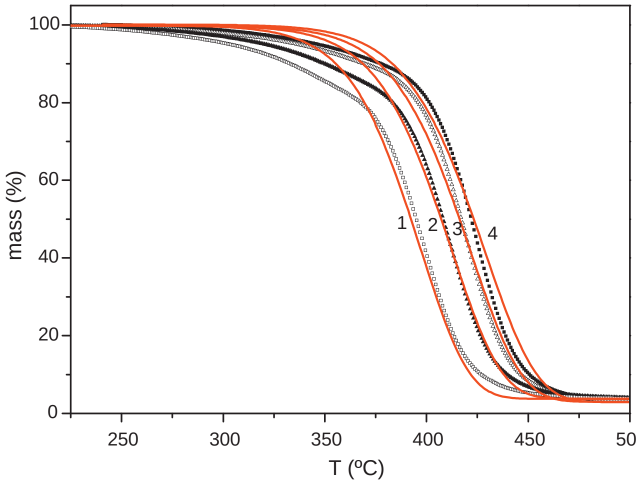

Fig. 8. Fitting and experimental data of PCL/PPAd 70/30 w/w for the reaction mechanism Fn and different heating rates β. 1: 5, 2: 10, 3: 15 and 4: 20 °C/min.

are higher than that of PCL and much higher from the corresponding of PPAd. It seems that the activation energy of PCL/PPAd 70/30 w/w and PCL/PPAd 35/65 w/w is affected mainly from PCL part. The dependence of E on α for these samples presents the same trend as for PCL. Comparing the results for PCL, PCL/PPAd 70/30 w/w and PCL/PPAd 35/65 w/w it can be seen that this dependence of E on α can be divided into two main distinct regions. In the first region for values of α up to 0.2, E presents a large increase as proved by both of the used methods and in the second one ($\alpha > 0.2$), E presents a plateau or a slight increase depending on the method. The dependence for PPAd is different and an almost stable value for E can be assumed for entire area of α. This dependence of E on α for PCL/PPAd copolymers as well as neat PCL is an indication of a complex reaction with the participation of at least two different mechanisms. Although the "two mechanisms" — as a result of the increasing E with α — is a rather typical phenomenon for many polymers [31,32] it is based on the multistep TG curve. However, we were led to this conclusion for the studied samples (PCL/PPAd 70/30 w/w and PCL/PPAd 35/65 w/w) as a result of the studies of both, multistep TG and the dependence of E on α.

In order to determine the nature of the mechanism or mechanisms of mass loss upon heating through the comparison of the experimental and theoretical data, it is initially considered that the mass loss of the studied samples can be described only by a single mechanism, without presuming the exact mechanism. If the results of the identification with the help of this single mechanism could not be considered as satisfactory then, knowing this mechanism ($f(\alpha)$), the kinetic parameters and the conversion function of the other mechanism can be determined, in order to obtain a better agreement between experimental and theoretical data. To determine the conversion function $f(\alpha)$ we used a method referred to as the "model fitting method" [33,34]. This method, does not assume the knowledge of E and $f(\alpha)$ in advance, and was applied simultaneously on the experimental data taken at the heating rates $\beta = 5$, 10, 15 and 20 °C/min. It was shown that the "model fitting method" applied to multiple heating rate data gives activation energies similar to the values estimated by the isoconversional methods [35].

For the fitting, sixteen different kinetic models were used. In Fig. 8 the results of fitting for PCL/PPAd 70/30 w/w as an example. The two best forms of the conversion functions obtained by fitting are: the mechanism of autocatalysis n^{th}-order (Cn) for which $f(\alpha) = (1-\alpha)^n(1+K_{\text{cat}}X)$ where K_{cat} is a constant, X the decomposed parts of polymer and the n^{th}-order (Fn). It is obvious that the fitting cannot be accepted. The results of the fitting were more or less the same for the other studied samples.

Due to the quality of the fitting for the kinetic description of the studied samples two mechanisms were used. For the determination of the two different mechanisms the followings were assumed: (a) the two mechanisms follow each other, (b) the unknown mechanism corresponds to the first stage of mass loss. An improvement of fitting is observed and the agreement of experimental and theoretical results (Fig. 9) is remarkable, verifying that the polymer is decomposed by two different mechanisms during its mass loss upon heating.

The kinetic model of the first decomposition mechanism is autocatalysis n^{th}-order (reaction model Cn) or n^{th}-order (reaction model Fn) with the same quality of the fitting. In this stage of identification for the best possible results, we had the parameters (E, A, and n) of both the examined mechanisms recalculated and the correlation coefficient was 0.9998. The results of the dependence of the activation energy on the degree of conversion, α, are in well agreement with mass loss. The first decomposition mechanism is attributed to small mass loss, while the second decomposition mechanism is attributed to the main mass loss and is also autocatalysis nth-order.

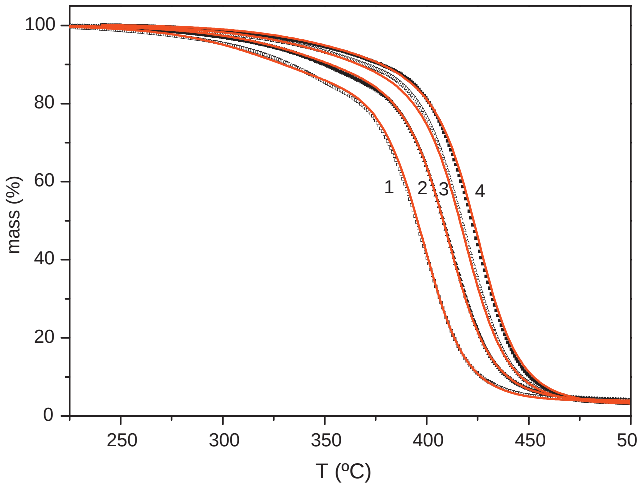

Fig. 9. Fitting and experimental data of PCL/PPAd 70/30 w/w for two reaction mechanisms (Fn–Cn) and different heating rates β. 1: 5, 2: 10, 3: 15 and 4: 20 °C/min.

Table 3

Calculated values of activation energy, pre-exponential factor and exponent n for all studied samples.

	First mechanism			Second mechanism		
	log *A*	*E* (kJ/mol)	*n*	log *A*	*E* (kJ/mol)	*n*
PCL	3.0	64.3	0.6	12.7	197.5	1.8
PCL/PPAd 70/30	4.6	82.4	0.8	14.2	215.8	1.8
PCL PPAd 35/65	5.3	92.8	0.6	14.4	220.1	1.8
PPAd	7.7	117.3	0.78	10.0	157.3	0.7

The results of the fitting with the mechanisms Fn–Cn are presented at Table 3. The differences of the calculated values for the mechanisms Cn–Cn are negligible and for this reason are not presented.

The calculated values of the activation energy present the same trend as those obtained by the isoconversional calculations. Furthermore, it seems that the different polymers as well as their parts (PCL or PPAd) in copolymers have different effects on activation energies of each mechanism.

The activation energy of the first mechanism in neat PPAd is 117.3 kJ/mol and the corresponding for neat PCL is 64.3 kJ/mol. These differences can be attributed to the formation of different byproducts during thermal decomposition of these aliphatic polyesters. In copolymers the activation energy of the first mechanism is increased as the quantity of the PPAd increased and thus PPAd content has the highest effect on this decomposition mechanism. In the first area of mass loss, *E* is equal 82.4 kJ/mol for PCL/PPAd 70/30 w/w and 92.8 kJ/mol for PCL/PPAd 35/65 w/w. These values are lower from the corresponding of PPAd, but much higher from that of PCL. The trend for the second area is different. Neat PCL has an activation energy 197.5 kJ/mol which is higher from the corresponding activation energy of PPAd (157.3 kJ/mol). The values of *E* for PCL/PPAd copolymers are larger from the corresponding values of PCL and PPAd. This was unexpected and it seems that PCL caused a further stabilization to the copolymers.

As mentioned above, at low temperatures, thermal degradation of PPAd takes place by random chain scission [14,24,25] while in PCL by random degradation and elimination of 5-hexenoic acid [23,36–38]. In the case of PPAd as was verified from the decomposition of similar aliphatic polyesters i.e. poly(propylene succinate), poly(propylene glutarate) and poly(propylene suberate) [24,25], at low temperatures α-hydrogen bond scission takes place at higher extent, while at higher temperatures β-hydrogen bond scission is the dominant mechanism. PCL, at low temperatures decomposes mainly via β-hydrogen bond scission. In each case different degradation byproducts are formed and as was found from TG curves (Figs. 4 and 5) their evaporation takes place at different temperatures. In the case of PCL the evaporation of 5-hexenoic acid should be immediate, while in the case of PPAd the random chain scission takes place and is followed by evaporation of formed byproducts at higher temperatures. This results in different activation energies calculated for each polyester. In the case of copolymers, which have higher activation energy at low temperatures than neat PCL, it can be said that the chemical links between PPAd and PCL blocks have higher thermal stability, compared with the internal links of PCL blocks. It seems that in the case of random scission the formation and evaporation of 5-hexenoic acid is diffusion dependant and thus, will depend on the chain lengths of PCL and PPAd in the copolymers. From the ^{13}C-NMR spectra it was found that the block length of PPAd increases by increasing its molar ratio in the copolymers and the opposite happens for PCL blocks. It is possible that in copolymer with higher PPAd content and thus lower PCL blocks, lower amount of 5-hexenoic acid had been formed and since its evaporation is diffusion depended, its mass loss is occurs at higher temperatures.

In the second decomposition step, in the case of PCL the formation of ε-caprolactone (ε-CL) (cyclic monomer) is dominate as the result of an unzipping depolymerization process [24,36–38]. ε-CL has higher molecular ion compared with 5-hexenoic acid and thus the activation energy increases compared with the first step. In the case of PPAd at high temperatures β-hydrogen bond scission is the dominant mechanism while α-hydrogen bond scission takes place in lower extent. Dicarboxylic acids, allyl and diallyl compounds are mainly produced. Since the activation energies of PCL/PPAd copolymers are even higher than neat PCL it seems that both polymeric blocks (PPAd and PCL) have a synergistic effect. Consequently, at higher temperatures, where autocatalysis takes place it seems that the copolymers are decomposing with a more complicated mechanism than neat copolymers. The unzipping mechanism of PCL as well as the α- and mainly the β-hydrogen bond scission that takes place in PPAd, are all affected from the existence of the other monomer parts in macromolecular chain. This results in the further thermal stabilization of the copolymers. The exact mechanism cannot be determined by using TGA and other techniques must be used such as GC–MS, TGA–FTIR, etc. However, this is beyond the scope of the present study.

4. Conclusions

The prepared poly(ε-caprolactone-b-propylene adipate) copolymers consisted from low and high PPAd content such as 30 and 65 wt%. As found by NMR spectroscopy the theoretical feeding of monomers during polymerization is identical with the calculated, revealing the applicability of the used method to prepare such copolymers. From ^{13}C-NMR spectra and the estimation of randomness β it was verified that block copolymers were formed and their PPAd and PCL block length depends from their molar ratio.

Thermal properties of the prepared copolymers such as T_{g}, T_{m} and heat of fusion ranged between those of neat copolymers. Some differences that were observed in melting points of the copolymer containing 65 wt% PPAd could be attributed to the formation of crystals with lower perfection.

From TGA data it was found that PCL has higher thermal stability than PPAd, while their copolymers have almost identical thermal stability with PCL. This is an indication that independently from the molar ratio in copolymers, PCL parts, cause a further stabilization on copolymers mass loss upon heating. Thus, it can be said that the chemical links between PPAd and PCL blocks have higher stability from the internal links of PCL blocks.

Mass loss upon heating was found to be described by two mechanisms that follow each other. The first mechanism is attributed to small mass loss, while the second mechanism is attributed to main mass loss as in autocatalysis n^{th}-order (reaction model Cn or Fn). From the activation energies of both mechanisms and mainly of the second mechanism, which take place at higher decomposition temperatures, it is verified that the mechanism of mass loss upon heating in copolymers maybe different from the corresponding of neat polymers.

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