Thermochimica Acta 515 (2011) 13–23

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Crystallization and biodegradation of poly(butylene azelate): Comparison with poly(ethylene azelate) and poly(propylene azelate)

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ARTICLE INFO

Article history:
Received 9 September 2010
Received in revised form
30 November 2010
Accepted 12 December 2010
Available online 21 December 2010

Keywords:
Biodegradable
Enzymatic hydrolysis
Crystallization
Melting behavior
Poly(butylene azelate)
Thermal properties

ABSTRACT

Crystallization of the new biodegradable polyester poly(butylene azelate) (PBAz) under isothermal and non-isothermal conditions was studied and compared to that of the two homologues, poly(ethylene azelate) (PEAz) and poly(propylene azelate) (PPAz). Among them, poly(butylene azelate) has the faster and easier crystallization, as it was proved by the low supercoolings and lower activation energy needed for nonisothermal crystallization. The enthalpy of melting of the pure crystalline PBAz and the equilibrium melting point were found 36.3 kJ/mol and 67.5 °C, respectively, compared to 34.2 kJ/mol and 62 °C for PEAz and 31.9 kJ/mol and 72.2 for PPAz. The secondary nucleation theory was applied and crystallization regime transitions I/II and II/III were observed at 30 and 39 °C, respectively. Chemical hydrolysis at 30 °C shows very slow rates. On the other hand the enzymatic degradation rates of PBAz were comparable to those of poly(ε-caprolactone) (PCL) or PEAz. However, PPAz has much faster enzymatic hydrolysis.

1. Introduction

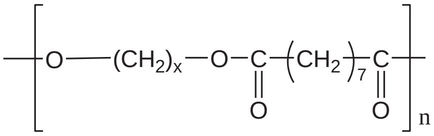
The rapid development of polymer science and engineering and the wide applications of polymeric materials are obviously one of the characteristics of the last century. However, the wide applications of plastics also result in an irreversible buildup of polymer waste in the environment.

Biodegradable plastics were developed to protect the environment from conventional plastic wastes. Several biodegradable plastics are now commercially available, including synthetic polyesters such as poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL) and poly(butylene succinate) (PBSu) and microbial polyesters including polyhydroxyalkanoates (PHA), such as polyhydroxybutyrate (PHB) [1,2].

Applications of biodegradable plastics include packaging materials, bottles, medical implants, fabrics and agricultural mulch films. These polyesters have physical properties, such as melting point (T_m), tensile strength and elongation, similar to those of traditional plastics [3–6]. In addition to physical properties, biodegradability is an important property of these polyesters, since they are used for environmental applications [7–10].

As with other semicrystalline polymers, mechanical properties and degradation rates of biodegradable aliphatic polyesters depend strongly on their chemical structures, but they also depend on their crystal structures, morphology and crystallinity, which in turn are determined directly by the thermal treatment imposed on the polymers during solidification process [7,8]. Therefore, it is very important to investigate the crystallization kinetics and morphology of these biodegradable aliphatic polyesters, to understand the relationship between structural features and crystallization conditions.

Polyesters based on azelaic acid (I) had not been studied till recently. In this work crystallization and enzymatic degradation of poly(butylene azelate) ($x=4$) are studied in comparison with poly(ethylene azelate) (PEAZ) ($x=2$) and poly(propylene azelate) (PPAZ) ($x=3$).



$$\left[-O-(CH_2)_x-O-\underset{\underset{O}{\|}}{C}-(CH_2)_7-\underset{\underset{O}{\|}}{C}- \right]_n$$

x=2 to 4

(I)

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doi:10.1016/j.tca.2010.12.010

2. Experimental

2.1. Materials

The polyesters studied in this work were synthesized from azelaic acid and 1,2-ethanediol or 1,3-propanediol or 1,4-butanediol. Azelaic acid, 1,2-ethanediol and 1,4-butanediol (purum 99%), were purchased from Aldrich Chemical Co. 1,3-Propanediol (CAS Number: 504-63-2, purity: >99.7%) was kindly supplied by Du Pont de Nemours Co. Tetrabutyl titanate catalyst of analytical grade and polyphosphoric acid (PPA) used as heat stabilizer were purchased from Aldrich Chemical Co. All the other materials and solvents which were used for the analytical methods were of analytical grade.

The aliphatic polyesters were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. In brief, the proper amount of azelaic and proper diol in an acid/diol molar ratio 1/1.1 and the catalyst $Ti(OBu)_4$ 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).

In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol azelaic acid), which is believed to prevent side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was slowly increased to 230 °C while stirring speed was increased at 720 rpm. The polycondensation continued for about 60 min.

2.2. Intrinsic viscosity measurement

Intrinsic viscosity measurements were performed using an Ubbelohde viscometer Oc at 25 °C in chloroform, at a solution concentration of 1 wt%.

2.3. Gel permeation chromatography (GPC)

GPC analysis 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. $CHCl_3$ 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.

2.4. Differential scanning calorimetry (DSC)

A Perkin-Elmer, Pyris Diamond differential scanning calorimeter (DSC), calibrated with indium and zinc standards, was used for the study of crystallization and melting of the polyesters. Samples of 5 ± 0.1 mg were used in tests. They were sealed in aluminium pans and heated at a heating rate 20 °C/min to 90 °C, which is about 40 °C above the melting point and quite above the equilibrium melting point of the studied polymers. The samples were held at 90 °C for 3 min in order to erase any thermal history. For isothermal crystallizations the sample was rapidly cooled to 20 °C above the crystallization temperature and finally cooled to that at a rate 50 °C/min, to achieve equilibration of the instrument. The crystallization exothermic peak was then recorded. Heating scans were performed at a rate of 20 °C/min. If some other procedure was followed in specific tests this will be described in the corresponding part.

Isothermal crystallization experiments of PBAz were also performed after self-nucleation of the polyester sample. Self-nucleation measurements were performed in analogy to the procedure described by Müller et al. [11–13].

The protocol used is very similar with that described by Müller et al. [12] and can be summarized as follows: (1) melting of the sample at 90 °C for 3 min in order to erase any previous thermal history; (2) subsequent cooling at a rate of 10 °C/min to 0 °C, which creates a “standard” thermal history; (3) partial melting by heating at 10 °C/min up to a “self-nucleation temperature”, T_s; (4) thermal conditioning at T_s for 5 min. Depending on T_s, the crystalline polyester domains will be completely molten, only self-nucleated or self-nucleated and annealed. If T_s is sufficiently high, no self-nuclei or crystal fragments can remain and the sample is then in the so-called Domain I, the complete melting domain. At intermediate T_s values, the sample is almost completely molten, but some small crystal fragments or crystal memory effects remain, which can act as self-nuclei during a subsequent cooling from T_s, and the sample is said to be in Domain II, the self-nucleation domain. Finally, if T_s is too low, the crystals will only be partially molten, and the remaining crystals will undergo annealing during the 5 min at T_s, while the molten crystals will be self-nucleated during the later cooling, and the sample is in Domain III, the self-nucleation and annealing domain; (5) cooling scan from T_s at 200 °C/min to the crystallization temperature (T_c), where the effects of the previous thermal treatment will be reflected on crystallization; (6) heating scan at 20 °C/min to 90 °C, where the effects of the thermal history will be apparent on the melting signal. Experiments were performed to check that the sample did not crystallize during the cooling to T_c and that a full crystallization exotherm was recorded at T_c.

For non-isothermal crystallization the same melting procedure described above was applied before the cooling scan. Cooling scans were performed at rates 2.5, 5, 7.5, 10, 15 and 20 °C/min. A fresh sample was used in each run. Heating rate was in most tests 20 °C/min. If some other rate was used this will be discussed in the specific section.

2.5. Wide angle X-ray diffractometry (WAXD)

The crystalline structure of the polyesters was investigated by WAXD using a Panalytical X'Pert Pro MPD powder diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm) equipped with an Antoon Paar, TTK-450 hot stage, for measurements at various temperatures. Using the hot stage, the samples were heated to various temperatures in the instrument and thus the WAXD patterns of the polymers were recorded at various temperatures to investigate variations in the crystalline structure.

2.6. Polarizing light microscopy (PLM)

A polarizing light microscope (Nikon, Optiphot-2) equipped with a Linkam THMS 600 heating stage, a Linkam TP 91 control unit and also a Jenoptic ProgRes C10Plus camera with the Capture Pro 2.1 software was used for PLM observations.

2.7. Enzymatic degradation study

Polyesters in the form of films measuring 30 mm × 30 mm × 0.35 mm, prepared by melt pressing using an Otto Weber hydraulic press (Type PW 30) connected with an Omron E5AX temperature controller, were placed in Petri dishes containing phosphate buffer solution (pH 7.2) with 0.09 mg/mL *Rhizopus delemar* lipase and 0.01 mg/mL *Pseudomonas cepacia* lipase. The Petri dishes were then incubated at 30 °C in an oven, while the media were replaced at specified times. After a specific period of incubation, the films were removed from the Petri dishes,

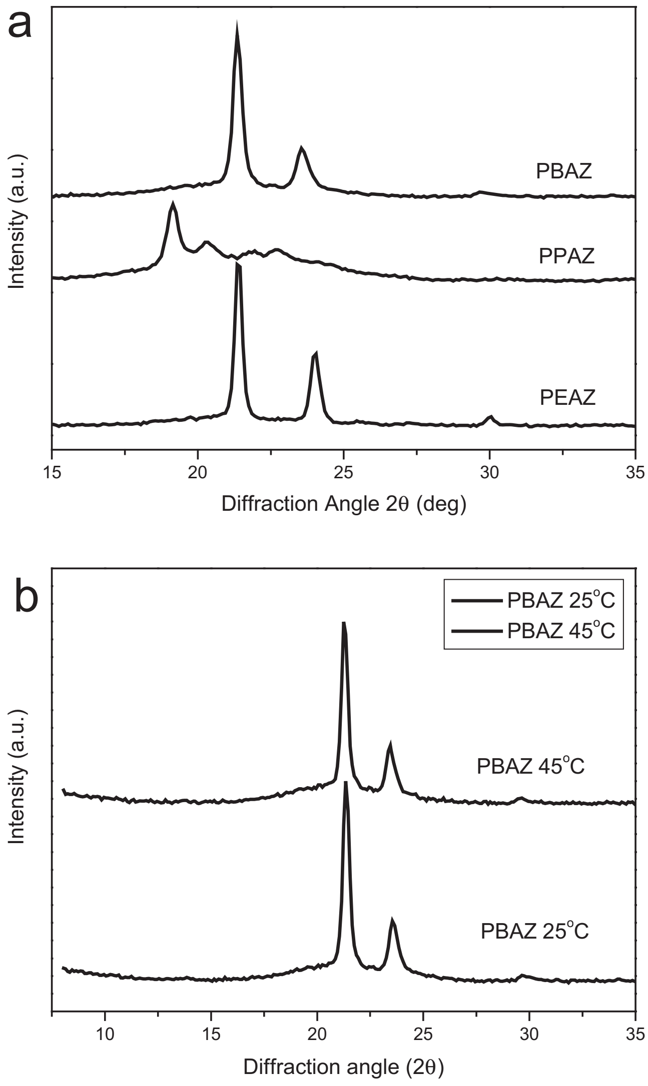

Fig. 1. (a) WAXD patterns of the azelate polyesters, (b) WAXD patterns of PBAz recorded at 25 and 45 °C.

washed with distilled water, and weighed until constant weight was achieved. The degree of biodegradation was estimated from the mass loss. Hydrolysis experiments were also performed in the absence of enzyme.

3. Results and discussion

3.1. Polyester synthesis and characterization

Poly(ethylene azelate) (PEAz), poly(propylene azelate) (PPAz) and poly(butylene azelate) (PBAz) samples were prepared following the two step melt polycondensation method as described in Section 2. The number average molecular weight of the polyester samples was sufficiently high, of about $M_n = 21{,}000$ Da (GPC) for PEAz (with $M_w/M_n = 2.24$, while the intrinsic viscosity measured in chloroform was IV = 0.69 dL/g), $M_n = 25{,}000$ Da ($M_w/M_n = 2.14$ and IV = 0.842 dL/g) for PPAz and $M_n = 24{,}000$ Da ($M_w/M_n = 2.23$ and IV = 0.78 dL/g) for PBAz.

WAXD patterns of crystalline powder of the azelate polyesters were recorded first at room temperature (Fig. 1a) but also after heating to 45 °C. The patterns for PEAZ and PBAZ, meaning the two azelate polyesters with odd total number of ethylene groups in the repeating unit, show some similarity and they are very different from that of PPAZ with an even number of methylene groups in its repeating unit, referring to the peak positions but also to the crystallinity. For PPAZ a significant amount of amorphous material is present in the sample as can be judged from the quite large amorphous halo and the low crystalline reflection peak intensity. Furthermore, there was no change in the WAXD patterns after heating to higher temperature. As can be seen in Fig. 1b the WAXD patterns of PBAZ at elevated temperature (45 °C) compared to those recorded at 25 °C show no substantial differences, meaning that there was no crystal transition during heating but only some partial melting and some crystal perfection process might occur.

3.2. Isothermal crystallization

3.2.1. Isothermal crystallization kinetics

The isothermal crystallization of the polyesters from the melt was studied at various temperatures. Crystallization of polymer melts is usually accompanied by significant heat release, which can be measured by differential scanning calorimetry (DSC). Based on the assumption that the evolution of crystallinity is linearly proportional to the evolution of heat released during the crystallization, the relative degree of crystallinity, $X(t)$, can be obtained according to the following equation:

$$X(t) = \frac{\int_0^t (dH_c/dt)dt}{\int_0^\infty (dH_c/dt)dt} \tag{1}$$

where dH_c denotes the measured enthalpy of crystallization during an infinitesimal time interval dt. The limits t and ∞ are used to denote the elapsed time during the course of crystallization and at the end of the crystallization process, respectively. Subsequently, the relative crystallinity $X(t)$ at time, t, was determined using Eq. (1). Fig. 2a shows the evolution of the relative degree of crystallinity with time during crystallization of PBAZ at various temperatures. From these curves, the half time of crystallization, $t_{1/2}$, was directly determined as the time elapsed from the onset of crystallization to the point where the crystallization is half completed.

Fig. 2b shows the variation of the crystallization half times with crystallization temperature for the three polyesters. It is obvious that $t_{1/2}$ values increased almost exponentially as the crystallization temperature increased. In order to compare the isothermal crystallization rates of the polymeric materials the reciprocal half-time of crystallization, $1/t_{1/2}$ was used. The plots of this variable as function of T_c for the materials are also shown in Fig. 2b (right axis). Obviously, the crystallization rates decrease with increasing temperature. From the plots of Fig. 2b it is evident that PBAZ presents a faster crystallization compared to PEAZ or PPAZ.

Fig. 2c shows the crystallization half-times for the succinate (PESU, PPSU, PBSU), azelate (PEAZ, PPAZ, PBAZ) and sebacate polyesters (PESEB, PPSEB, PBSEB). As can be seen, PESU and PPSU crystallize rather slowly, but PBSU is the one succinate polyester that crystallizes fast. The melting points are high at least for PESU and PBSU and the temperature window of crystallization is wide for PESU and PPSU. Azelate and sebacate polyesters crystallize at lower temperatures. However, it is important to say that the degree of supercooling is not large for these polymers and they show fast crystallization rates.

The crystallization kinetics of PBAZ was investigated using the most common approach is the so-called Avrami method [14–18]. Accordingly, the relative degree of crystallinity, $X(t)$, is related to the crystallization time, t, according to:

$$X(t) = 1 - \exp(-kt^n) \quad \text{or} \quad X(t) = 1 - \exp[-(Kt)^n] \tag{2}$$

where, n is the Avrami exponent which is a function of the nucleation process and k is the growth function, which is dependent on nucleation and crystal growth. Since the units of k are a function

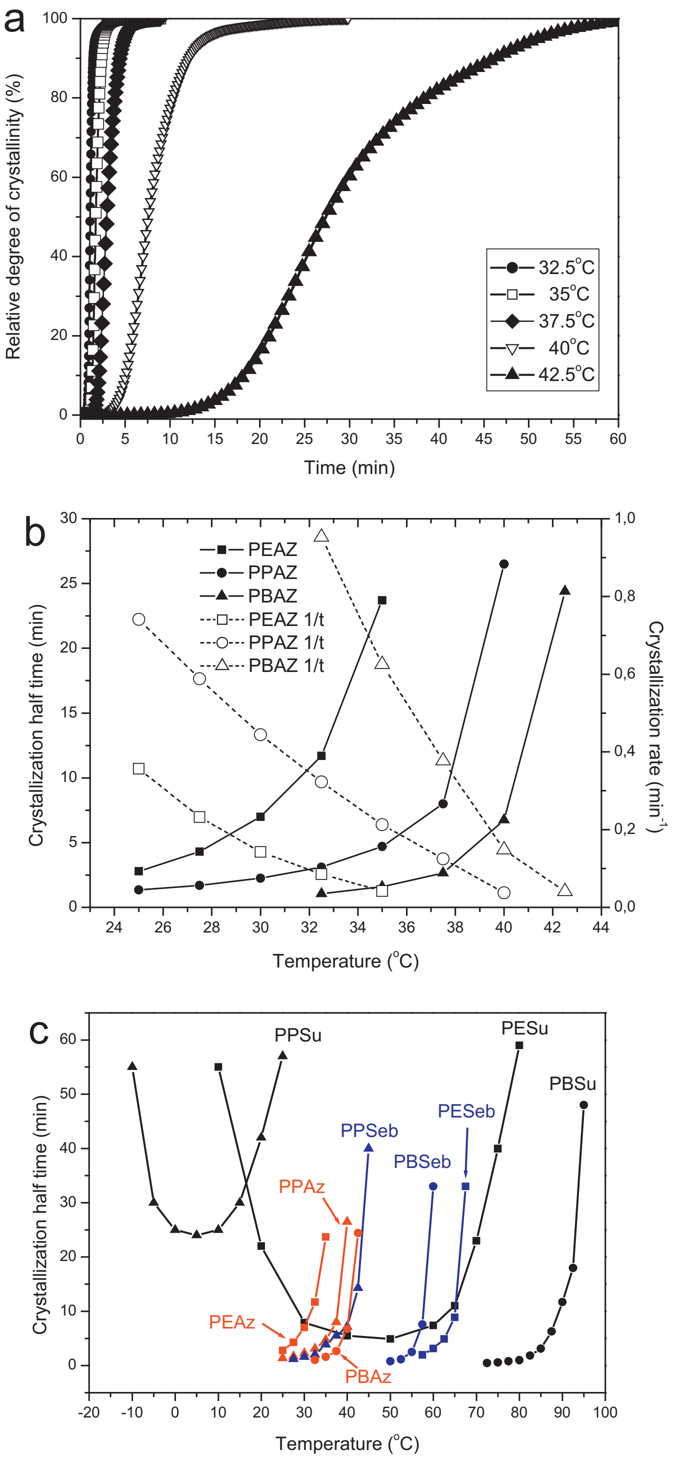

Fig. 2. (a) Evolution of relative degree of crystallinity with time during isothermal crystallization at various temperatures for PBAz, (b) variation of the isothermal crystallization half times ($t_{1/2}$) and the crystallization rates ($1/t_{1/2}$) with crystallization temperature for the three azelate polyesters and (c) comparison of the isothermal crystallization half times of the succinate, azelate and sebacate polyesters.

of n, Eq. (2) can be written in the composite-Avrami form using K instead of k (where $k = K^n$) [14–16]. The values of n, k and K, can be calculated from fitting to experimental data using the double logarithmic form of Eq. (2):

$$\log\{-\ln[1-X(t)]\} = \log k + n \log t \tag{3}$$

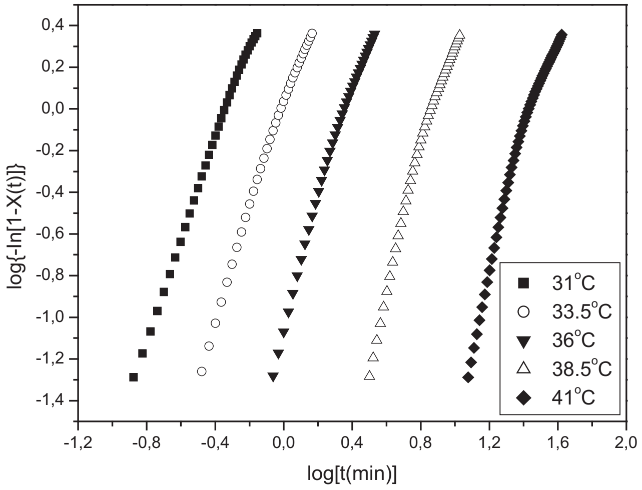

Fig. 3. Avrami plots for the isothermal crystallization of PBAz.

Table 1
Results of the Avrami analysis of the isothermal crystallization of PBAZ.

Temperature (°C)	n	k (min^{-n})	K (min^{-1})
31.0	2.46	2.333	1.411
33.5	2.74	1.007	1.003
36	3.12	0.349	0.714
38.5	3.64	0.047	0.431
41.0	3.71	0.005	0.243

Plots of $\log\{-\ln[1-X(t)]\}$ vs. $\log t$ were constructed for PBAZ and are shown in Fig. 3 (Table 1)

In these plots an initial linear part is observed, which was used for the estimation of the parameters n and k. The deviation, which is observed after this first linear part in the Avrami plots, is often attributed to secondary crystallization. From the slope and the intersection of the Avrami plots, values of n and k, respectively, were calculated and the results are summarized in Table 2. In the same table, the values of K calculated from the respective values of n and k, are included. It is known that the value of n strongly depends on both the mechanism of nucleation and the morphology of crystal growth, and that ideally n would be an integer [14]. The n values found in the case of PBAZ were in the vicinity of 2.5–3.5 for the crystallization temperatures from 31 °C to 41 °C and they should possibly be related to three-dimensional growth. The Avrami parameters k and K are indicative of the crystallization rate. Both of the parameters decrease with increasing temperature.

The melting traces of the crystallized samples were recorded on heating at 20 °C/min. Fig. 4 shows such melting traces of PBAz. The crystallization temperatures are indicated in the figure. As can be seen the melting peak temperature of PBAz samples increased with crystallization temperature.

Table 2
Results of the Avrami analysis of the non-isothermal crystallization of PBAz.

Cooling rate (°C/min)	n	Z_t (min^{-n})	K_{Avrami} (min^{-1})
20	4.53	8.449	1.602
15	5.26	6.456	1.426
10	5.59	3.193	1.231
7.5	6.00	1.806	1.104
5	5.44	0.992	0.999
2.5	4.63	0.393	0.817

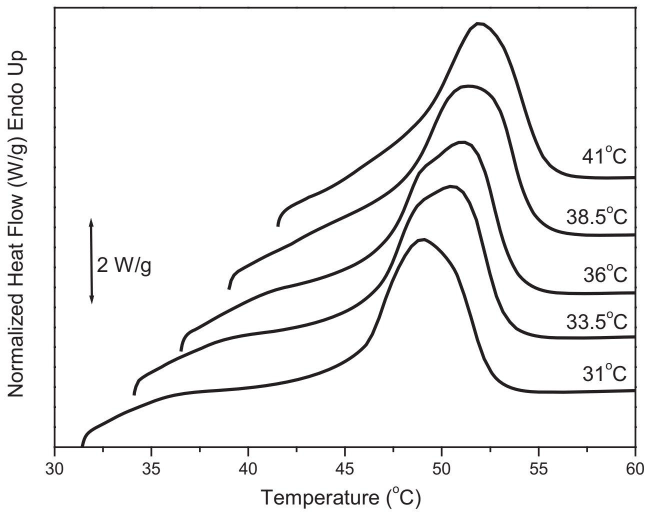

Fig. 4. DSC heating scans showing the melting behavior of PBAz samples crystallized at various temperatures.

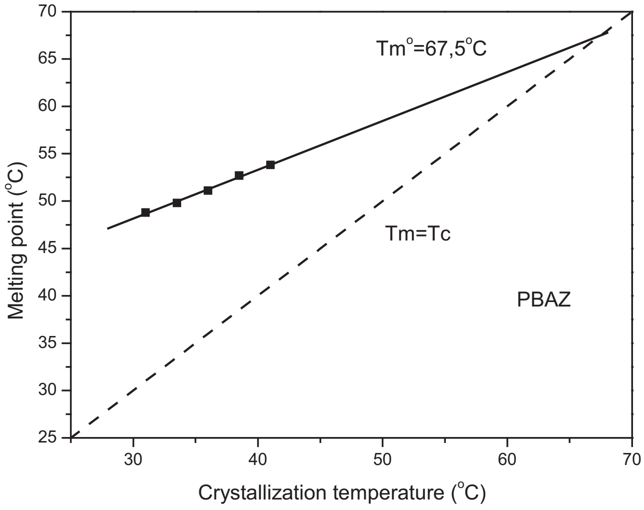

Fig. 5. Hoffman–Weeks plot for the estimation of the equilibrium melting point of PBAz.

3.2.2. Determination of the equilibrium melting temperature and heat of fusion

Equilibrium melting temperature ($T_m{}^o$) is one the most important parameters characterizing a polymer. Study of crystallization of polymers demands knowledge of $T_m{}^o$ which by definition is the melting temperature of lamellar crystals with an infinite thickness. Extrapolative methods are used to estimate equilibrium melting temperature ($T_m{}^o$). The Hoffman–Weeks (H–W) method has been commonly used and accepted to estimate $T_m{}^o$ [19]. In this procedure, the measured T_ms of specimens crystallized at different crystallization temperatures (T_cs) are plotted against T_c and a linear extrapolation to the line $T_m = T_c$, and the intercept gives $T_m{}^o$. In the Hoffman–Weeks equation:

$$T_m = T_m^o\left(1 - \frac{1}{r}\right) + \frac{T_c}{r} \tag{4}$$

T_m is the observed melting temperature of a crystal formed at a temperature T_c, r is the thickening coefficient equal to $l_c/l_g{}^*$ where l_c is the thickness of the grown crystal and $l_g{}^*$ is the initial thickness of a chain-folded lamellar crystal [19]. The prerequisite for the application of this theory is the isothermal thickening process of lamellar crystals at a specific crystallization temperature and the dependence of the thickening coefficient on the crystallization temperature.

The Hoffman–Weeks plot for PBAz constructed using the melting peak temperatures against the crystallization temperature, as well as the $T_m = T_c$ line is shown in Fig. 5. The extrapolated value corresponding to $T_m{}^o$ was found to be $T_m{}^o = 67.5\,^\circ$C. The respective values were $T_m{}^o = 62\,^\circ$C for PEAz and $T_m{}^o = 72.2\,^\circ$C for PPAz [20,21].

In an attempt to estimate the heat of fusion of the pure crystalline PBAz and to compare with the two others a series of samples of different crystallinities were prepared and the respective WAXD patterns were recorded. Fig. 6 shows the calculation procedure for estimating the respective areas for the amorphous and crystalline material in the WAXD patterns of the as received polyester samples. Then the degree of crystallinity values were calculated using the relative areas under the crystalline peaks, A_c, and the amorphous background, A_{am}, using the following equation after Hay et al. [22]:

$$X_c = \left(1 + \frac{A_{am}}{A_c}\right)^{-1} \tag{5}$$

From Fig. 6 it is obvious that the as received samples had high degree of crystallinity, of about 51% for PBAz or even higher (55%) for PEAz, while it was significantly suppressed in case of PPAz (27%). The particular samples crystallized during slow cooling in the reactor and also during storing at room temperature for 20 days before study. Using the calculated degree of crystallinity values for a series of samples of different crystallinities and the values of heat of fusion obtained from the respective DSC heating traces of the samples, the values for the enthalpy of fusion of the 100% crystalline polyester were found $\Delta H_m{}^o = 160 \pm 10$ J/g for PEAz, $\Delta H_m{}^o = 140 \pm 10$ J/g for PPAz and $\Delta H_m{}^o = 150 \pm 10$ J/g for PBAZ. Considering the molecular weight of the repeating units for PEAz the value of $\Delta H_m{}^o = 160$ J/g corresponds to 34.2 kJ/mol, that of 140 J/g for PPAz corresponds to 31.9 kJ/mol and that of 150 J/g for PBAz corresponds to 36.3 kJ/mol. Given the equilibrium melting point $T_m{}^o$ and enthalpy of fusion $\Delta H_m{}^o$ values reported above and using the equation for the Gibbs free energy

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

for $\Delta G = 0$, the entropy of fusion was found to be $\Delta S_m{}^o = 102.2$ J/(mol K) for PEAz, $\Delta S_m{}^o = 92.5$ J/(mol K) for PPAz and $\Delta S_m{}^o = 106.6$ J/(mol K) for PBAz.

Fig. 6d shows the variation of the equilibrium melting points and the heat of fusion with the number of methylene units (x) in the diol segment of the succinate, azelate and sebacate polyesters. The values are obviously $x = 2$ for poly(ethylene alkane dicarboxylate)s, $x = 3$ for poly(propylene alkane dicarboxylate)s and $x = 4$ for poly(butylene alkane dicarboxylate)s. As it can be seen, the odd-even effect is more pronounced in the case of succinates. As there is a small total number of methylene units, this effect is rather expected to be significant. In case of azelates, there is odd number of methylene units in the diacid segment and the effect is the opposite, meaning that poly(propylene azelate) shows higher melting point than poly(ethylene azelate) or poly(butylene azelate).

3.2.3. Application of the secondary nucleation theory

It has been suggested that the kinetic data of isothermal polymer crystallization can be analyzed using the spherulitic growth rate in the context of the Lauritzen–Hoffman secondary nucleation theory [23,24].

Accordingly, the growth rate G is given as a function of the crystallization temperature, T_c by the following bi-exponential equation:

$$G = G_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{T_c(\Delta T)f}\right] \tag{7}$$

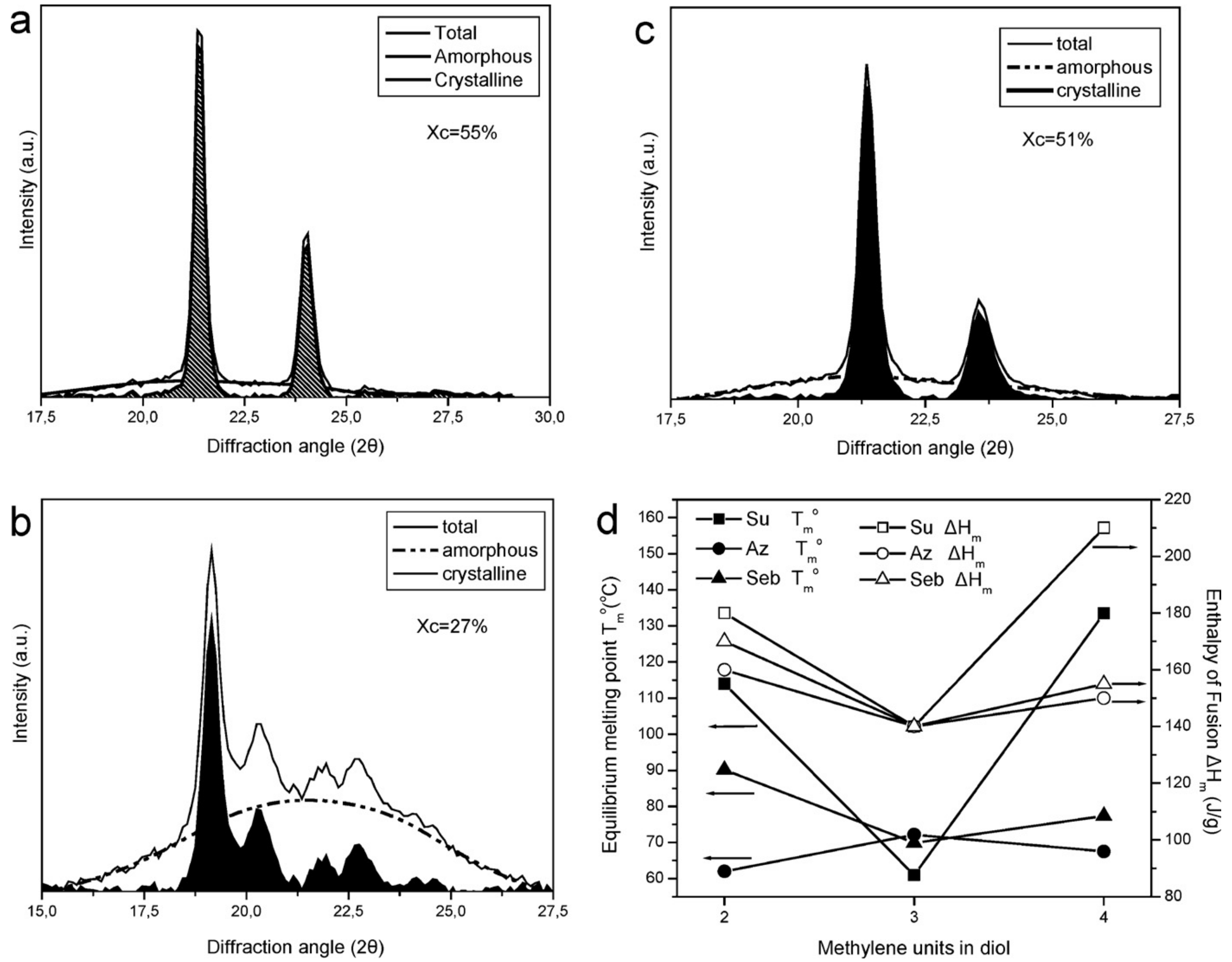

Fig. 6. Calculation of the crystalline portion of the (a) PEAz, (b) PPAz, (c) PBAz samples and (d) variation of the equilibrium melting point and the enthalpy of fusion with number of methylene units in the diol segment of the polyesters.

where, G_0 is the pre-exponential factor, the first exponential term contains the contribution of diffusion process to the growth rate, while the second exponential term is the contribution of the nucleation process; U^* denotes the activation energy which characterizes molecular diffusion across the interfacial boundary between melt and crystals, usually set equal to 1500 cal/mol and this was the case in this work and T_∞ is the temperature below which diffusion stops, usually equal to $T_\infty = T_g - 30\,\mathrm{K}$; K_g is a nucleation constant and ΔT denotes the degree of undercooling ($\Delta T = T_m{}^o - T_c$); f is a correction factor which is close to unity at high temperatures and is given as $f = 2T_c/(T_m{}^o + T_c)$; the equilibrium melting temperature, $T_m{}^o$ was set equal to 67.5 °C for PBAZ, while the glass transition temperature was assumed equal to −66 °C, since this value was concluded from DSC measurements of quenched samples. In most cases some crystallinity was always present in the samples, even after quenching, increasing a little the T_g. The value −66 °C seemed to be limiting for amorphous PBAz.

The nucleation parameter, K_g, is usually calculated from Eq. (7) using the double logarithmic transformation:

$$\ln(G) + \frac{U^*}{R(T_c - T_\infty)} = \ln(G_0) - \frac{K_g}{T_c(\Delta T)f} \tag{8}$$

Plotting the left-hand side of Eq. (8) with respect to $1/(T_c(\Delta T)f)$ a straight line should appear having a slope equal to K_g. Critical break points, identified by the change in the slope of the line, when appear in such a plot, have been attributed to regime transitions accompanied by morphological changes of the crystals formed (i.e. change from axialite-like to banded spherulite and non-banded spherulite morphology).

Usually for the study of the crystallization habits and the measurement of the spherulite growth rates polarized light microscopy is used. For the polyesters of this work in general diffuse structures as a result of mixed birefringence were observed during isothermal crystallization at various temperatures. Mixed birefringence has been also reported in early works for these polyesters [25]. In such a case of mixed birefringence, accurate measurement of the spherulite radius is extremely difficult.

Instead of using PLM measurements, several authors have treated the isothermal crystallization rate data obtained by DSC, according to the Lauritzen–Hoffmann analysis (Eq. (8)) [26–29]. The basic assumption used for the evaluation of G was that the spherulite growth rate is inversely proportional to the crystallization half-time, $G \approx 1/t_{1/2}$ [26]. This approximation although it is purely empirical has been widely used in the literature [26–29]. Also, DSC measures the overall crystallization rate, which reflects the rate of a complex process since both nucleation and crystal growth take place.

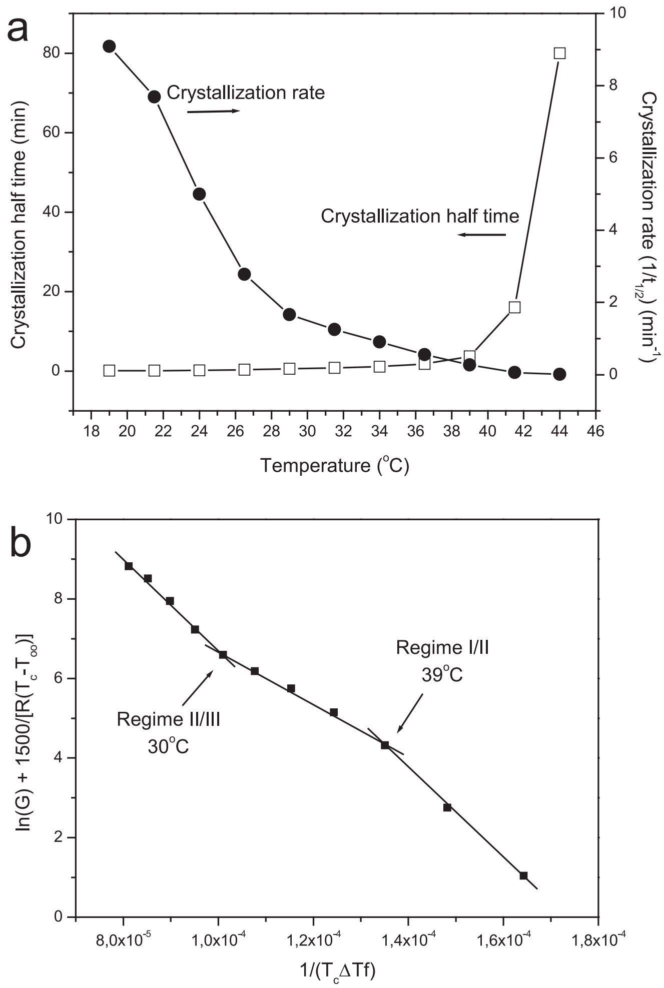

Fig. 7. (a) Dependence of crystallization rates measured from DSC crystallization tests after self nucleation on crystallization temperature and (b) Lauritzen–Hoffman plots for PBAz.

Müller et al. have proposed a new method involving self nucleation before isothermal crystallization to distinguish crystal growth from nucleation [12,13]. According to the procedure of Müller, the inverse of isothermal crystallization half time after self nucleation of the sample is strictly associated with the crystal growth and thus such data can be used instead of spherulite growth rates in the calculations following the secondary nucleation theory [12,13]. In previous papers the application of this new method gave very satisfactory results, as the final values obtained for the parameter K_g were very close to those obtained using data from PLM measurements [28,29]. Thus, the self nucleation method of Müller et al. was applied in this work as an alternative to obtain crystallization rate data for PBAz.

Fig. 7a shows the dependence on temperature of the crystal growth rates measured from DSC crystallization tests after self nucleation.

These values were used in the calculations which resulted in the data used for the construction of the plot of Fig. 7b. As one can see there are two critical break points, which can obviously be attributed to the crystallization regime transitions. However, clear change in morphology evidencing the regime II/III transition could not be observed from PLM as the corresponding critical break point appears at about 30 °C, which is a low temperature to study with PLM. For the regime I/II transition the breakpoint was observed at about 39 °C.

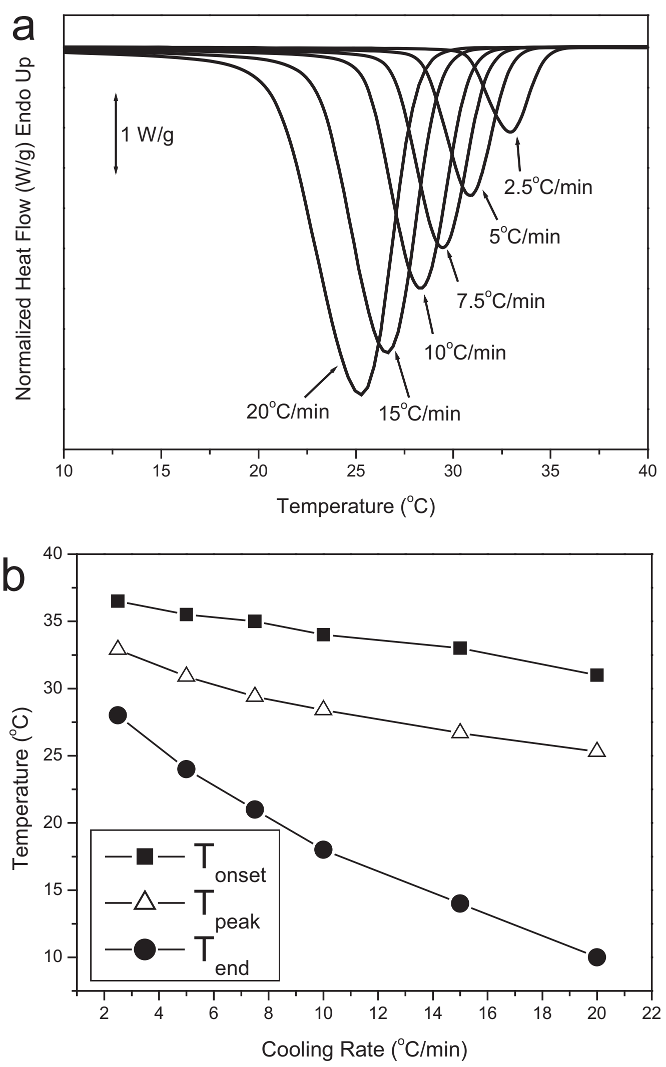

Fig. 8. (a) Exothermic crystallization peaks observed during cooling of PBAz in the DSC at different cooling rates and (b) variation of the onset temperature (T_{onset}), peak temperature (T_{peak}) and temperature at the end of the crystallization peak (T_{end}) with cooling rate.

From the slopes of the lines it was concluded that $K_{gI} = 111{,}822\,K^2$, $K_{gII} = 61{,}536\,K^2$ and $K_{gIII} = 116{,}094\,K^2$. This means that the ratios K_{gI}/K_{gII} and K_{gII}/K_{gIII} have values equal to $K_{gI}/K_{gII} = 1.82$ and $K_{gIII}/K_{gII} = 1.89$, respectively, quite close to the expected value 2. The K_g values are lower than those for poly(butylene succinate) (PBSu) and also lower than those for PEAZ and PPAZ as a result of a more flexible chain due to the increased number of methylene groups in the acid moiety [6].

3.3. Non-isothermal crystallization

3.3.1. DSC non-isothermal crystallization study

From dynamic crystallization experiments, data for the crystallization exotherms as a function of temperature can be obtained, at each cooling rate, as one can see in Fig. 8a for the crystallization on cooling of PBAz.

The variations of the temperature when crystallization begins, T_{onset}, and ends, T_{end}, and the peak temperature, T_{peak}, are shown in Fig. 8b. As it was expected, with increasing cooling rate all the aforementioned characteristic temperature values decreased, meaning that the higher the cooling rate the later the crystallization process started and completed. As it was expected, the crystallization

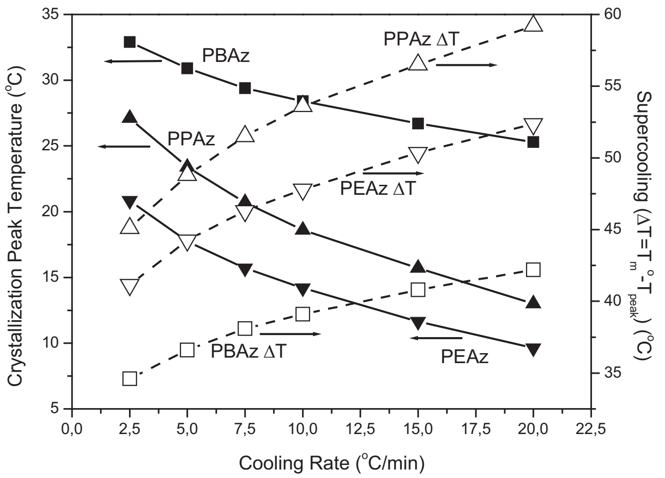

Fig. 9. Variation of crystallization peak temperature or supercooling with cooling rate for PEAz, PPAz and PBAz.

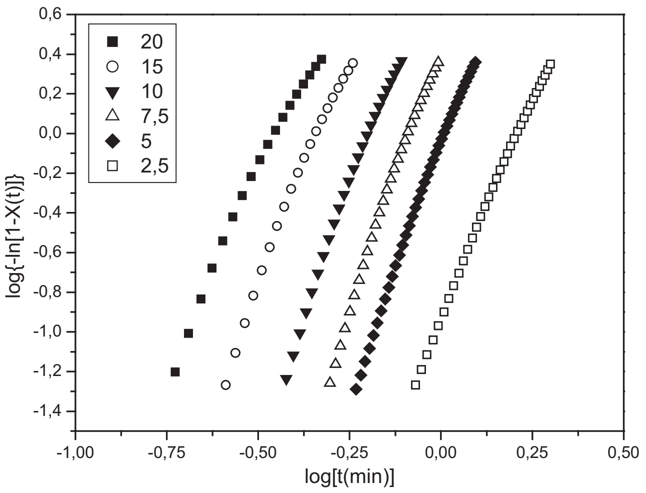

Fig. 10. Avrami plots for non-isothermal crystallization of PBAz.

exotherm becomes broader and it shifts to lower temperatures with increasing cooling rate. Fig. 8b shows that this broadening is because the decrease in T_{end} is greater than the respective in T_{onset}.

The heat corresponding to the crystallization peak ranged from 57.1 for a cooling rate 20 °C/min to 58.2 J/g for a cooling rate 2.5 °C/min, meaning a negligible drop with increasing cooling rate. Using a value of $\Delta H_m{}^o = 150$ J/g for the enthalpy of fusion of the 100% crystalline PBAz polyester, the crystallinity of the samples after crystallization during cooling was found to be about 39%.

Fig. 9 shows the plots of the crystallization peak temperature and the respective supercooling as a function of the cooling rate for PEAz, PPAz and PBAz. For PBAz the lower supercooling is needed, which means that crystallization is easier. In contrast for PPAz the higher supercooling is needed. This is in accordance with the findings for the isothermal crystallization rates and the degree of crystallinity usually obtained by the polyesters.

From the data for the crystallization exotherms as a function of temperature dH_c/dT the relative crystallinity as a function of temperature $X(T)$ can be calculated as follows:

$$X(T) = \frac{\int_{T_o}^{T_c} (dH_c/dT)dT}{\int_{T_o}^{T_\infty} (dH_c/dT)dT} \tag{9}$$

where T_o denotes the initial crystallization temperature and T_c, T_∞ the crystallization temperature at time t and after the completion of the crystallization process, respectively.

The crystallization temperature T_c, can be converted to crystallization time, t, with the well-known relationship for non-isothermal crystallization processes that is strictly valid when the sample experiences the same thermal history as designed by the DSC furnace [30]:

$$t = \frac{(T_c - T_o)}{\beta} \tag{10}$$

where β is the constant cooling rate.

To quantitatively describe the evolution of the crystallinity during nonisothermal crystallization, a number of models have been proposed in the literature [31]. The most common approaches is that based on the modified Avrami equation.

3.3.2. Modified Avrami method

According to the modified Avrami method, the relative degree of crystallinity, X, can be calculated from [31]:

$$X = 1 - \exp(-Z_t t^n) \quad \text{or} \quad X = 1 - \exp\left[-(K_{\text{Avrami}} t)^n\right] \tag{11}$$

where Z_t and n denote the growth rate constant and the Avrami exponent, respectively. Since the units of Z_t are a function of n, Eq. (11) can be written in the composite-Avrami form using K_{Avrami} instead of Z_t (where $Z_t = K_{\text{Avrami}}{}^n$) [32].

Again Z_t and n can be calculated by fitting the experimental data to an equation similar to Eq. (11). In Fig. 10 plots of $\log\{-\ln(1-X)\}$ vs. $\log(t)$ are shown for PBAZ. As it can be seen straight lines are obtained in each cooling rate and from the slope and intercept of each line n and $\log Z_t$ are calculated. The resulting values for the parameters n, Z_t and K_{Avrami} are presented in Table 2.

3.3.3. Effective activation energy of non-isothermal crystallization

For a non-isothermal crystallization process, it is interesting to evaluate the effective activation energy, ΔE, as this is a crucial parameter for the process. Several mathematical procedures have been proposed in the literature for the calculation of ΔE, considering the variation of the peak temperature with the cooling rate, α, like the Kissinger's method which has been widely applied in evaluating the overall effective activation energy [31]. However, these methods have been formulated for heating experiments (i.e. positive values of β). Vyazovkin [33,34] has demonstrated that dropping the negative sign for β is a mathematically invalid procedure that generally makes the Kissinger equation inapplicable to the processes that occur on cooling. Moreover, the use of this invalid procedure may result in erroneous values of the effective energy barrier, ΔE. The use of multiple heating rate methods such as isoconversional methods is recommended [35]. An isoconversional method can in principle be applied to non-isothermal crystallizations for evaluating the dependence of the effective activation energy on conversion and temperature. The differential isoconversional method of Friedman and the advanced integral isoconversional method of Vyazovkin are the most appropriate [36,37].

In this investigation the method of Friedman was used. According to the differential isoconversional method of Friedman, different effective activation energies are calculated for every degree of crystallinity from [36]:

$$\ln\left(\frac{dX}{dt}\right)_{X,i} = \text{Const} - \frac{\Delta E_X}{RT_{X,i}} \tag{12}$$

where dX/dt is the instantaneous crystallization rate as a function of time at a given conversion X, ΔE_X is the effective activation

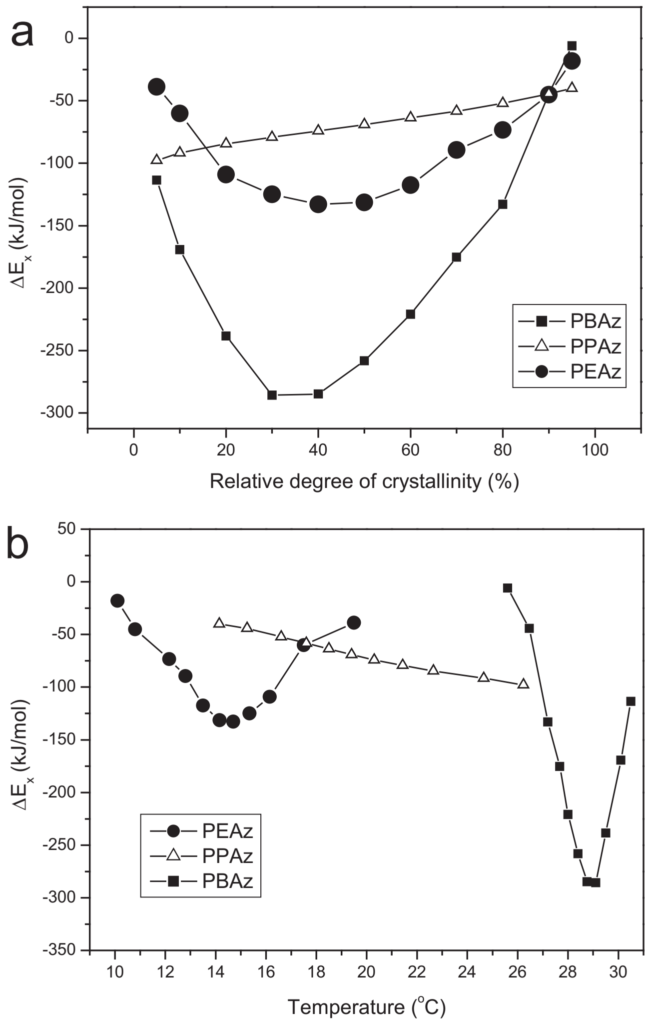

Fig. 11. Dependence of the effective activation energy on (a) the relative degree of crystallinity and (b) the crystallization temperature.

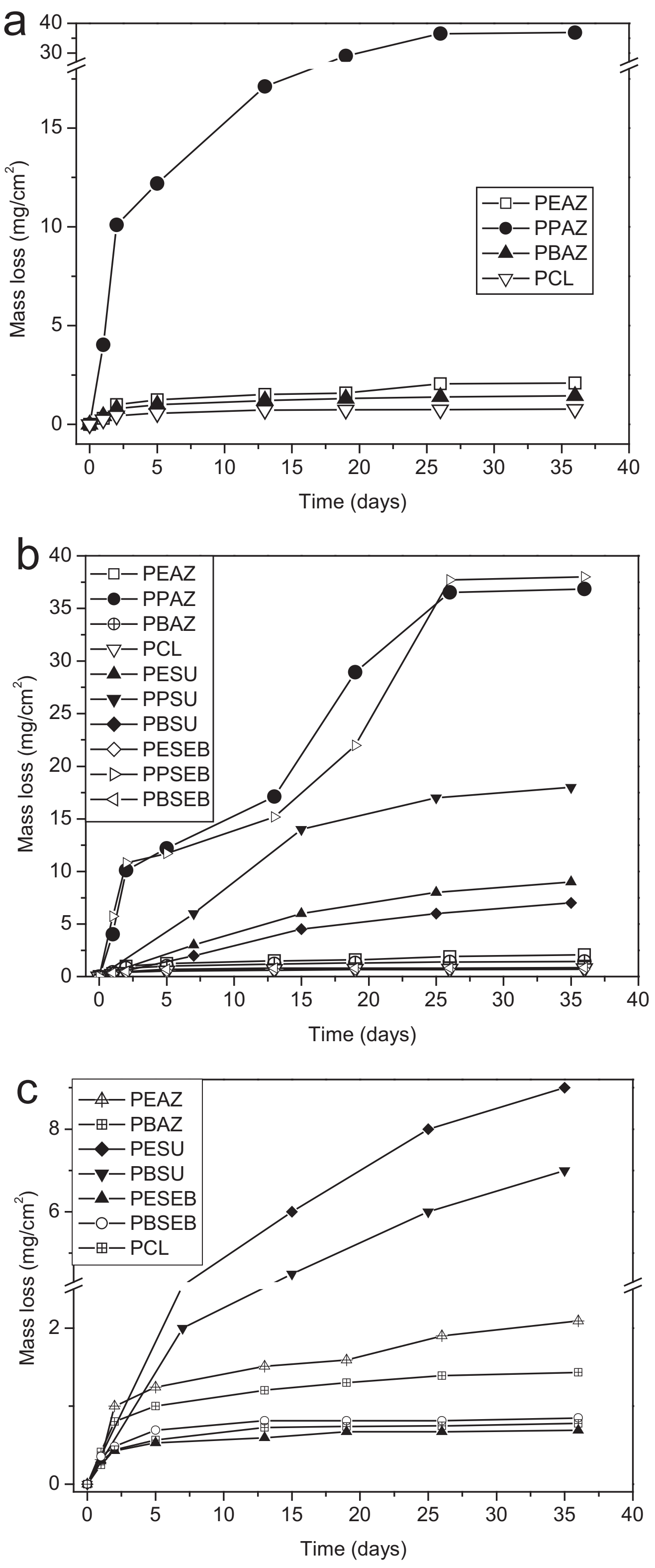

Fig. 12. (a) Mass loss as a function of time of enzymatic hydrolysis for PEAz, PPAz, PBAz and PCL, (b) comparison of the mass loss for the azelates, succinates and sebacates and (c) enlargement of b to show details.

energy at a given conversion X, $T_{X,i}$ is the set of temperatures related to a given conversion X at different cooling rates, β_i and the subscript i refers to every individual cooling rate used.

According to this method, the $X(t)$ function obtained from the integration of the experimentally measured crystallization rates is initially differentiated with respect to time to obtain the instantaneous crystallization rate, dX/dt. Furthermore, by selecting appropriate degrees of crystallinity (i.e. from 5% to 95%) the values of dX/dt at a specific X are correlated to the corresponding crystallization temperature at this X, i.e. T_X. Then by plotting the left hand side of Eq. (12) with respect to $1/T_X$ a straight line must be obtained with a slope equal to $\Delta E_X/R$. The effective activation energy, thus obtained was subsequently plotted as a function of the relative degree of crystallinity, as one can see in Fig. 11a. The effective activation energy shows a minimum (or maximum at absolute values) in the vicinity of $X = 35\%$ for PBAz and at about 45% for PEAz. The increase of the effective activation energy for high values of degree of conversion might be attributed to the spherulite impingement, which means a change in the mechanism of crystallization from primary alone to primary and mainly secondary after impingement. In contrast for PPAz there is an almost linear behavior. However, it should be noted that PPAz always shows about half of the crystallinity of the other two azelates in its samples. Fig. 11b shows the variation of the effective activation energy with temperature. At lower values the preexisting crystallinity plays negative role, meaning reducing chain mobility and thus increasing effective activation energy.

3.4. Biodegradation

First chemical hydrolysis of the azelate polyesters without enzymes was tested at 30 °C. As PCL is well-known biodegradable polyester, enzymatic hydrolysis of PCL was also tested at the same experimental conditions, for comparison. The observed hydrolysis rates of all the polymers in the absence of enzyme however were very slow. Thus, it was assumed that chemical hydrolysis of the polyesters of this work at 30 °C shows negligible rates. On the other hand, as Fig. 12a shows, a significant mass loss with time was observed during the enzymatic hydrolysis of the polyesters at 30 °C. As was reported in Section 2 in this study a mixture of *R. delemar* and *P. cepacia* lipases was used in enzymatic hydrolysis experiments. The plots of Fig. 12a show that PEAz and PBAz have a little faster enzymatic hydrolysis rates than PCL, but PPAz is the polyester which shows really fast enzymatic hydrolysis.

Among the factors affecting the enzymatic hydrolysis rates, the most important are the chemical structure of the polyester, meaning the distance between the ester bonds and probable stereochemical hindrance for the attachment of the enzyme on the hydrolyzing groups, the hydrophilic/hydrophobic balance within the main chain, the molecular weight, with polyesters of low molecular weight to hydrolyze faster, the degree of crystallinity, with amorphous material to hydrolyze easier while crystalline phase is much less affected and the melting point, with polymers of low melting point close to the hydrolysis temperature to show faster degradation [7,8,38,39].

In the case of the polyesters of this work, the fact that PPAz hydrolyzes much faster than the rest should be attributed mainly to the lower crystallinity, which in the tested specimens was about 50–55% for PEAz and PBAz and 60% for PCL, but much lower, i.e. about 27% for PPAz. Furthermore, the molecular weight of PCL was about 60,000 Da compared to 25,000 Da for the azelate polyesters. This also might be partly responsible for the slower enzymatic degradation of PCL observed here. The melting points of the azelate polyesters are about 55 °C, while that of PCL is about 60 °C, not much higher.

After all, it is concluded that the enzymatic degradation rates of PEAz and PBAz are rather comparable to those of PCL, but the enzymatic hydrolysis rates of PPAz are really fast.

To have a more complete picture, Fig. 12b shows comparatively the mass loss during degradation of the succinate, azelate, sebacate polysters and PCL. Fig. 12c is an enlargement of the plots for the more slowly degrading polymers of Fig. 12b. Obviously poly(propylene alkane-dicarboxylate)s degrade much faster in all cases. PESu and PBSu also show rather fast enzymatic hydrolysis. The general conclusion that can be derived is that highly crystalline samples degrade slowly.

4. Conclusions

The crystallization of poly(butylene azelate) was found to be faster than those of poly(ethylene azelate) and poly(propylene azelate). The WAXD pattern of PBAz seems similar to that of PEAz, which also has an even number of methylene groups in the diol segment, but quite different to that of PPAz with and odd number of methylene groups in the diol segment. The equilibrium melting point was found 67.5 °C and the enthalpy of melting of the pure crystalline polyester was found 36.3 kJ/mol. The usual degree of crystallinity for PBAz samples was about 50%, about the same with PEAz, while PPAz usually has a much lower crystallinity in its crystallized samples, of about 27%. Analysis of the crystallization rates applying the secondary nucleation theory showed that PBAz has two crystallization regime transitions from regime I to II at 39 °C and from II to III at 30 °C. The enzymatic hydrolysis of the polyester shows comparable rates to those of PCL, in contrast to poly(propylene azelate), which shows much faster biodegradation rates.

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