NUKLEONIKA 2010;55(1):57–64

Biodegradable polyester blend and copolyesters studied by positron annihilation and other methods

Maria Dębowska,
Jadwiga Rudzińska-Girulska,
Małgorzata Serwadczak,
Adam Kiersnowski,
Jacek Pigłowski

Abstract. Two polyesters, i.e. an aromatic one: poly(butylene terephthalate) – PBT and an aliphatic one: poly(ε-caprolactone) – PCL were mixed in melt to obtain a biodegradable product. DSC, ^{1}H NMR, SEM, WAXS, SAXS, BOD and PALS measurements were performed to study the homopolymers as well as their physical blend and copolyesters. The latter were obtained due to the transesterification reaction. *Ortho*-positronium (*o*-Ps) annihilation lifetimes were used to create the distributions of free volume. The progressive changes in probability density function of free volume, i.e. increase in large free volume holes contribution to the total free volume, appearing when going from the homopolymers to the blend and then to the copolyesters reflect the influence of: the addition of aliphatic polyester, the weight fraction of it in the composition and transesterification. The higher contribution of larger free volume holes corresponds well with the reduced crystallinity of compositions revealed in X-ray diffraction and the worsening of the regularity of structure of the macromolecules involved in formation of crystals, deduced from the ^{1}H NMR.

Key words: mixing of polymers • polyesters • transesterification • positron annihilation • positronium • free volume

M. Dębowska✉, J. Rudzińska-Girulska
Institute of Experimental Physics,
University of Wrocław,
9 M. Borna Sq., 50-204 Wrocław, Poland,
Tel.: +48 71 375 9350, Fax: +48 71 328 7365,
E-mail: debowska@ifd.uni.wroc.pl

M. Serwadczak, A. Kiersnowski, J. Pigłowski
Polymer Engineering and Technology Division,
Faculty of Chemistry,
Wrocław University of Technology,
27 Wybrzeże Wyspiańskiego Str.,
50-370 Wrocław, Poland

Received: 26 June 2009
Accepted: 26 August 2009

Introduction

Mixing of polymers is an attractive alternative to synthesis of a new material. One can obtain a targeted product, tailored to meet specific needs by mixing suitable components in the proper way. Dominance of plastics in packaging nowadays, followed by a rapid rise of waste in the natural environment, brought about the development of research on biodegradable materials of good mechanical properties. Biodegradable polymer blends are usually composed of a durable component mixed with a biodegradable one. Obtaining of the good recipe for mixing is possible if the relationship between the microstructure of polymers and their macroscopic properties is known.

In the theory of mixing of polymers the free volume effects are included. The free volume influences transport and mechanical properties as well as relaxation behaviour of polymers. In the past, greater than weighted mean values of density and viscosity of blends, compared to the constituent homopolymers, have been explained in terms of free volume and specific interactions [15]. Free volume approach has been also applied in modelling of the phenomenon of polymer/polymer solubility with use of molecular dynamic [15].

It is generally accepted that the positron annihilation lifetime spectroscopy (PALS) is a good tool to study the free volume in polymers, in spite of the limitations of the method. It prevails, for instance, over the reverse gas chromatography and ^{129}Xe NMR spectroscopy [17]. PALS is in particular very useful in studies of changes of the free volume when such phenomena as mixing, rise of temperature or phase separation take place [3, 5].

Blends of polyesters are interesting from two main reasons: industrial applications and for academic interest. Miscibility reported for certain pairs of polyesters occurred to be influenced by transesterification [13]. It was shown that transesterification between PBT and poly(tetramethylene succinate) – PTMS (an aliphatic polyester) may lead to a random copolymer [11]. Blending of biodegradable PTMS with PBT (a polyester of good mechanical properties) was proposed in order to obtain a biodegradable blend [8]. Results of extensive studies of transesterification, taking place when mixing PBT with PTMS are given in [12].

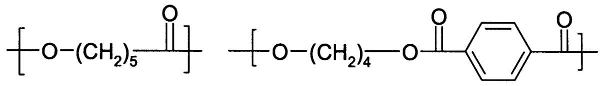
A PALS technique has been applied to some polyesters, their blends and copolyesters to study free volume [15, 19] and the effect of crystallinity on chain mobility and free volume [18], the effect of copolymer composition on free volume and gas permeability [6] and the influence of gamma irradiation on different polyesters [2, 9].

Materials

Poly(ε-caprolactone) (M_n = 42500 g/mol) with a melt flow index of 1.9 g/10 min (at 250°C and 2.16 kg), density 1.145 g/cm^3 was purchased from Aldrich Chemical Company, Inc. Poly(butylene terephthalate) with a melt flow index 16 g/10 min (at 250°C and 2.16 kg), density 1.30 g/cm^3 was supplied by DuPont Engineering Polymers under trade name Crastin® 6130 NC010. The corresponding repeating units of PCL and PBT are as in Scheme 1.

The samples based on poly(butylene terephthalate) and poly(ε-caprolactone) were prepared by melt-blending of the components in a twin screw corotating extruder at 240°C. The mixing time was fixed at 15 min. The mixer was rinsed with nitrogen to prevent degradation of the polymers during processing. Two samples (PBT/PCL 40/60 0.5% Sn and PBT/PCL 60/40 0.5% Sn) were synthesized by reactive extrusion of the polymers in the twin screw extruder in the same conditions as given above. The mixing of the latter samples was carried out in the presence of 0.5 wt.% of dibutyltin dilaurate, $Sn(Bu)_2(Lau)_2$ (Sigma-Aldrich) as a transesterification catalyst. The weight ratio of PBT to PCL was fixed at 40/60 and 60/40.

Symbols of all samples under study as well as their composition are given in Table 1.



Scheme 1. Repeating units of PCL (left) and PBT (right).

Table 1. Content and symbols of samples

Sample	Catalyst (wt.%)	PBT (wt.%)	PCL (wt.%)
PBT/PCL 40/60	0	40	60
PBT/PCL 40/60 0.5%Sn	0.5	40	60
PBT/PCL 60/40	0	60	40
PBT/PCL 60/40 0.5%Sn	0.5	60	40

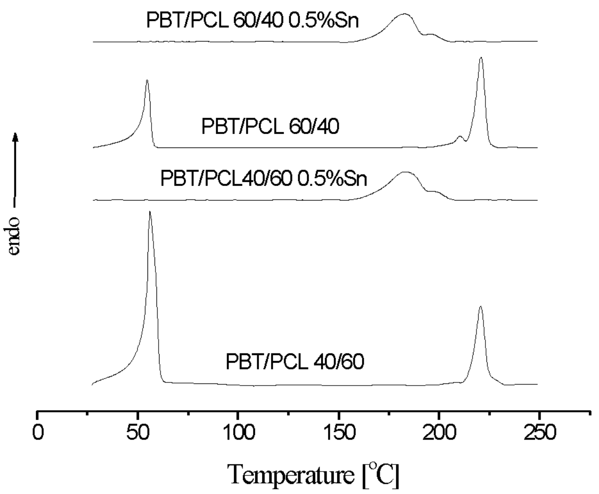


Fig. 1. Melting peaks of the second heating scan of DSC for the PBT/PCL blend and copolyesters.

Differential scanning calorimetry (DSC) measurements

Thermal properties of the samples were analyzed by differential scanning calorimetry (DSC) using a Mettler Toledo DSC821^e instrument. The samples were heated at the scanning rate of 10 K/min from 26 to 260°C, then cooled down to 25°C and reheated to 260°C. The heats of fusion were estimated from appropriate peaks, recorded during the second scan. The endotherms from the second scan are given in Fig. 1.

Heterogeneity of the samples PBT/PCL 40/60 and PBT/PCL 60/40 may be deduced from two separate melting peaks corresponding to neat polyesters and proving that the components in the samples are immiscible. The catalyst of transesterification – $Sn(Bu)_2(Lau)_2$, used on mixing, improved compatibility of constituents as it is seen from the melting curves for the samples PBT/PCL 40/60 0.5% Sn and PBT/PCL 60/40 0.5% Sn. One melting peak there, placed between the melting points of PBT and PCL, is a proof of homogeneity of the samples.

^{1}H nuclear magnetic resonance (^{1}H NMR) measurements

The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance DRX 300 MHz NMR spectrometer using deuterated chloroform and trifluoroacetic acid (3:7 v/v) as a mixing solvent. Each spectrum was registered in time of 10 min with the typical sequence: pulse – 10 μs, break – 4.5 μs, acquisition – 2.65 μs. In calibration of the spectra the peak coming from the trimethylosilane, present in $CDCl_3$, was used. Its position was set as 0 ppm.

Figure 2 presents the ^{1}H NMR spectrum of the PBT/PCL 60/40 sample, as an example. The molar ratios in the PBT/PCL samples were estimated using signals at 8.1 and 1.6 ppm coming from the protons of the benzene ring in PBT and the protons from the methylene units in PCL. The compositions of all the samples are in good agreement with those expected from the compositions in feed (Table 2).

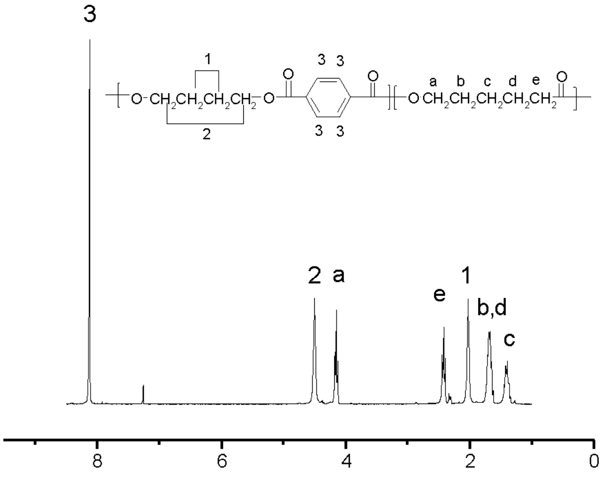


Fig. 2. The ^{1}H NMR spectrum for the PBT/PCL 60/40 blend.

Table 2. Composition of PBT/PCL samples

Sample	Composition in feed (biodegradable mer mol%)	Composition determined from ^{1}H NMR spectra (biodegradable mer mol%)
PBT/PCL 40/60	73.99	73.54
PBT/PCL 40/60 0.5%Sn		73.54
PBT/PCL 60/40	55.83	56.20
PBT/PCL 60/40 0.5%Sn		56.14

The ^{1}H NMR spectroscopy was used to recognize the details of the polymer chain structure in the studied samples obtained by mixing in melt. In the ^{1}H NMR spectra of the samples PBT/PCL 40/60 0.5% Sn, PBT/PCL 60/40 0.5% Sn and PBT/PCL 40/60 sample, except for the nuclear resonances of PBT and PCL, there are several new peaks confirming the existence of new heterolinkages inside the backbones of them, resulting from the transesterification. The crucial parts of the ^{1}H NMR spectra, taken into account in monitoring of the occurrence of transesterification reaction, are shown in Fig. 3. The tetramethylene proton resonances, which are located at 4.1–4.6 ppm, are split into multiplets owing to the various possible environments for the tetramethylene unit confirming a new copolymer formation. The exemplary signals marked by letters ‘f’, ‘g’, ‘h’ in the spectrum for the sample PBT/PCL 40/60 0.5% Sn correspond to the chemical shifts 4.43, 4.37 and 4.24 ppm. The signal marked as ‘f” (TC) and ‘g’ (TC) originate from the methylene protons (respectively, number 2 and 1 in Fig. 2) of the PBT mer when the latter is adjacent to the PCL mer. The ‘h’ signal (CT) corresponds to the methylene protons from –O-CH$_2$– in the PCL mer when it is adjacent to the aromatic ring of the PBT mer. The capital letter ‘C’ was used to denote the poly(ε-caprolactone) unit and ‘T’ to mark the poly(butylene terephthalate) unit. The results shown in Fig. 3 revealed the presence of comonomers composed of terephthalate and caprolactone units in the samples, obtained by reactive mixing in presence of the catalyst. In the case of the PBT/PCL 40/60 sample, obtained without catalyst, occurrence of the transreaction is also evident. The transesterification of the sample was promoted only by mixing.

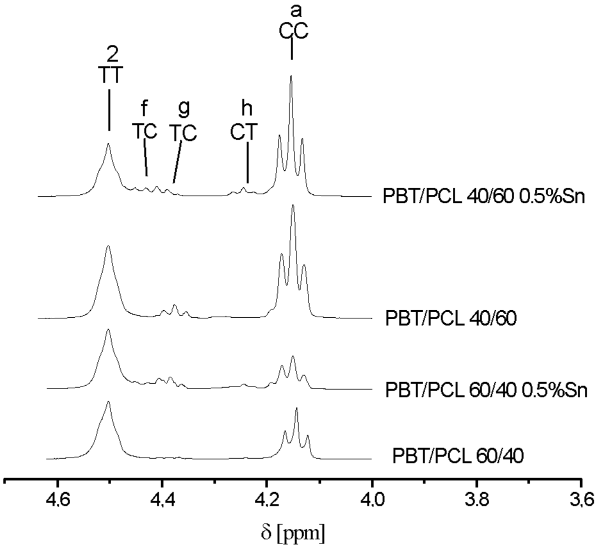


Fig. 3. The essential parts of the ^{1}H NMR spectra relevant to confirming the occurrence of copolyesterification in the samples PBT/PCL 40/60, PBT/PCL 40/60 0.5% Sn and PBT/PCL 60/40 0.5% Sn.

Microscopic studies

Similar conclusions, as in case of the DSC results, can be drawn from the polarizing microscopy and SEM studies. Polarizing microscopy was used to study morphology of the obtained samples. Images were obtained in a polarized light with the use of a microscope Olympus BX-51, equipped with a digital camera Olympus CC12. Thin layers of the studied samples were obtained from the solution (chloroform and trifluoroacetic acid 3:7 v/v) by the method of spin-coating. The percentage

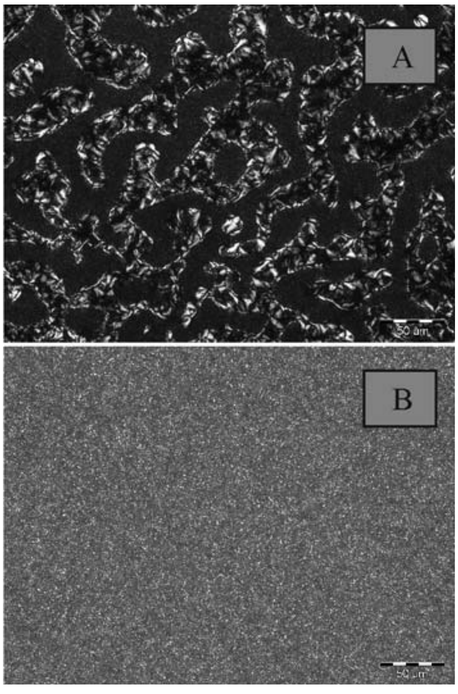


Fig. 4. The results from the polarizing microscopy for the samples PBT/PCL 40/60 (A) and PBT/PCL 40/60 0.5% Sn (B), magnification ×40.

concentration of a polymer in the solution was equal to 5 wt.%. The formation of layers took place according to three programmed stages: 600 rpm for 20 s, 1000 rpm for 25 s and 3000 rpm for 25 s. Exemplary images taken in the polarized light are given in Fig. 4.

It is seen that the sample PBT/PCL 40/60 is heterogeneous (Fig. 4A) and immiscible while in the case of the sample PBT/PCL 40/60 0.5% Sn (Fig. 4B) the homogeneity and miscibility are clearly seen. Similar in character the result is for the pair of the samples PBT/PCL 60/40 and PBT/PCL 60/40 0.5% Sn.

Scanning electron microscopy was used to study the topography of the surface of sample fractures. A fracture was formed in liquid nitrogen after making a notch. Then gold was placed on the surface by sputtering. The images of the fractures were obtained with the use of an electron microscope JEOL JMS-5800LV. The exemplary data are given in Fig. 5.

The agglomeration of PCL in the matrix of PBT is seen in the case of the sample PBT/PCL 40/60 (Fig. 5A), while in the sample PBT/PCL 40/60 0.5% Sn no agglomeration is present. The latter confirms the conclusion that the transesterification resulted in homogeneity and miscibility of samples. The same is the SEM result for the pair: PBT/PCL 60/40 and PBT/PCL 60/400.5% Sn.

X-ray diffraction studies

The aim of the studies was to estimate the influence of polymer mixing and copolymerization on the supramolecular structure of the PBT/PCL samples. A WAXS technique was used to find the mass crystallinity (X_C^{WAXS}) and compare unit cells of samples. A SAXS technique was applied to reveal the lamellar structure of the samples.

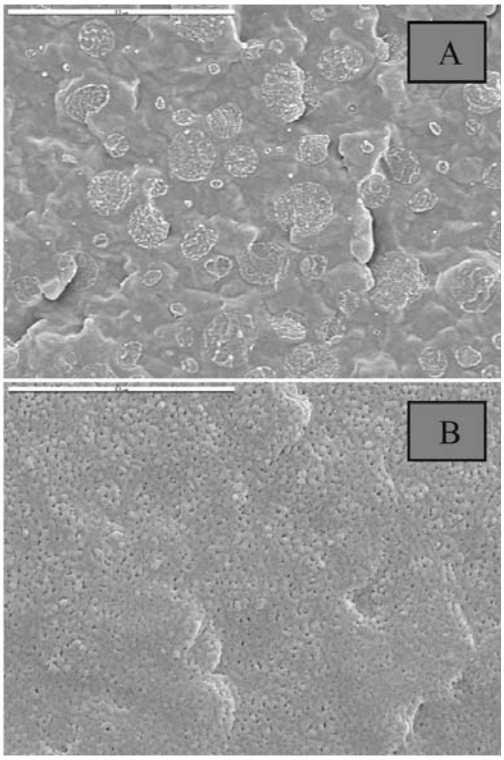


Fig. 5. The SEM results for the samples PBT/PCL 40/60 (A) and PBT/PCL 40/60 0.5% Sn (B), magnification ×3000.

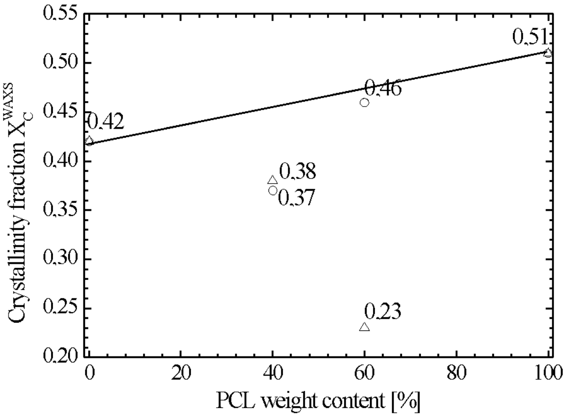


Fig. 6. Comparison of the crystallinity fractions in the PBT/PCL samples vs. the content of the aliphatic polyester PCL: PBT/PCL 40/60 and PBT/PCL 60/40 – circles; PBT/PCL 40/60 0.5% Sn and PBT/PCL 60/40 0.5% Sn – triangles. The line corresponds to the law of addition.

Wide angle X-ray scattering (WAXS) measurements were carried out on a Bragg-Brentano URD 6 diffractometer, with a sealed X-ray tube with the copper anode powered by a Seifert generator set at 40 kV and 30 mA. Small angle X-ray scattering (SAXS) measurements were accomplished using an evacuated Kratky camera (Hecus-M'Braun, CuKα, 40 kV, 30 mA). The samples for both WAXS and SAXS experiments were annealed for 24 h at 80°C. The crystalline fractions (X_C^{WAXS}) were evaluated from the WAXS powder diffraction profiles by the ratio between the crystalline diffraction area and the total area of the diffraction profile. The crystalline diffraction area has been obtained from the total area of the diffraction profile by subtracting the amorphous halo. Comparison of crystallinity between the studied samples is given in Fig. 6.

As it is seen, both the mixing and especially the reactive mixing (transesterification promoted by a catalyst) resulted in reduction of the crystallinity in relation to the linear law of additivity (dashed line). The highest reduction occurred for the sample PBT/PCL 40/60 0.5% Sn (X_C^{WAXS}) = 0.23.

Exemplary pair of SAXS curves is presented in Fig. 7. In Table 3 the characteristics of the lamellar structure of the studied samples are given.

Because of this, high errors are coupled with the values of the characteristics of the lamellar system for them.

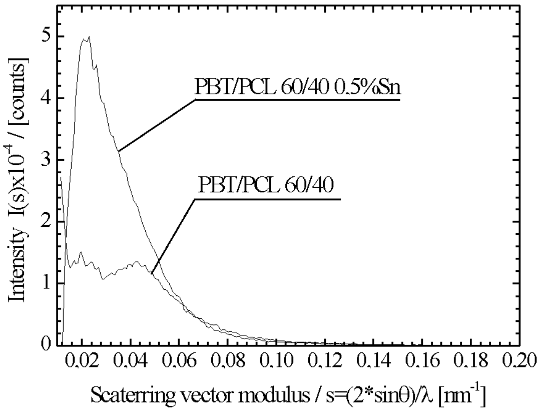


Fig. 7. The influence of the catalyst of transesterification, seen in the pair of the desmeared SAXS profiles, for the samples obtained by mixing with (copolyester) and without the catalyst (blend).

Table 3. Lamellar structure of the studied samples

Sample	Long period* d_{ac} (nm)	Crystallite thickness l_c (nm)	Thickness of the amorphous layer l_a (nm)	Volume fraction of crystallinity Φ_C^{SAXS}
PBT	17.3	6.6	10.7	0.38
PCL	14.2	6.3	7.9	0.44
PBT/PCL 60/40	27.6 / 15.1**	–	–	–
PBT/PCL 40/60	30.8 / 17.1**	–	–	–
PBT/PCL 60/40 0.5%Sn	34.0	11.2	22.8	0.33
PBT/PCL 40/60 0.5%Sn	26.7	5.1	21.6	0.19

* – from the first maximum of the correlation function.

** – in the samples marked by stars two independent lamellar systems occurred of different d_{ac}.

The conclusions on the basis of the X-ray diffraction data are as follows:

1. Results from WAXS and SAXS indicate that in the samples PBT/PCL 60/40, and PBT/PCL 40/60 the individual components of them do not cocrystallize and two separate lamellar systems are formed with different values of d_{ac}, l_c and l_a. The pair PBT/PCL is immiscible.
2. In the samples of copolyesters: PBT/PCL 60/40 0.5% Sn and PBT/PCL 40/60 0.5% Sn only single lamellar system exists.
3. In the copolyesters, mentioned above, the triclinic system, characteristic of PBT, is retained. Little shifts of characteristic peaks prove that some changes of unit cell parameters take place. It indicates that the level of fragmentation occurring during the process of copolyesterification is higher in the case of PCL in comparison to PBT.
4. The reduction of crystallinity in PBT/PCL samples takes place in relation to the linear additivity law. The reason of the reduction is the worsening of the regularity of structure of the macromolecules involved in formation of crystals. The highest reduction happens for the sample PBT/PCL 40/60 0.5% Sn.

Biodegradability of samples

In the research on biodegradability of the samples the biochemical oxygen demand (BOD) was checked. The biochemical oxygen demand is a measure of the quantity of oxygen uptaken by microorganisms, required for the oxidation of the substrate polymer [14]. In the studies BOD was determined by a respirometric manometric method test, with use of the Oxi Top Control system [10]. A polymer film of dimensions 10 × 10 × 0.05 mm was used for tests with *Rhodococcus*, *Acinetobacter* strains and *fungi Cerrena* (7 days at 25°C).

The respirometric test is based on an automatic pressure measurement in a closed bottle at constant temperature. The microorganisms consume oxygen by degrading the organic matter and the formed CO_2 gas is removed by means of an absorber (sodium hydroxide pellets). The overall result is a pressure decrease in the bottle. The BOD value is calculated automatically using the ideal gas law, modified for conditions in a closed space, and expressed in milligrams of the consumed oxygen per one milligram of a polymer film, added to the bottle (mg of O_2/1 mg of a polymer film) [10].

The biodegradability of the investigated samples was calculated by subtracting the biochemical oxygen demand of a control blank from that of the tested sample and dividing the resulting value by the theoretical oxygen demand (ThOD) of the latter.

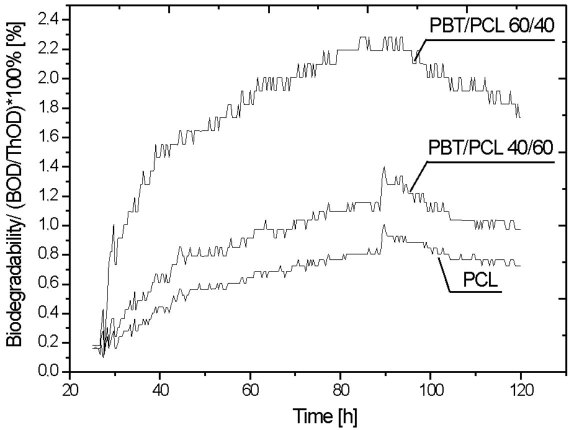


Fig. 8. The biodegradability of PCL and PBT/PCL 40/60 and PBT/PCL 60/40.

The control blank for the respirometric test was prepared identically, excepting the addition of the polymer film. The ThOD values, corresponding to the complete oxidation of the tested films, were calculated from the stoichiometric amount of oxygen, required to oxidize a compound of general formula $C_nH_aO_b$ to the final products as CO_2 and H_2O [1]: $C_nH_aO_b + [n + (a/4) - (b/2)]\ O_2 \rightarrow nCO_2 + a/2\ H_2O$. This equation shows that the complete oxidation of 1 mole of the organic compound $C_nH_aO_b$ would consume $[n + (a/4) - (b/2)]$ moles of O_2. This number, divided by the compound molecular weight and multiplied by the molecular weight of oxygen, represents the oxygen consumption in the BOD units, i.e. in milligrams of O_2 per one milligram of the polymer. The results are presented in Figs. 8 and 9.

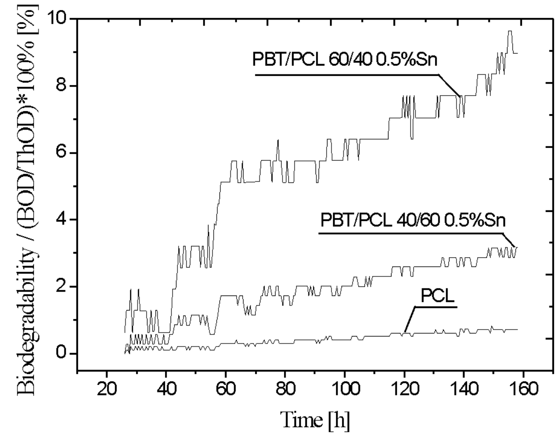


Fig. 9. The biodegradability of PCL and PBT/PCL copolyesters.

Table 4. Characteristics of the distributions of τ_3, R_{FV} and V_{FV} for PBT/PCL samples in the temperature region 290–340 K, obtained in the frame of the model MOD_125_31_LOG, used in the analysis of the positron annihilation lifetime spectra

Sample	$<tau_3>$ (ns)	$<tau_3>$ dispersion (ns)	$<R_{FV}>$ (nm)	$<R_{FV}>$ dispersion (nm)	$<V_{FV}>$ (nm^3)	$<V_{FV}>$ dispersion (nm^3)
PBT	1.67–1.94	0.38	0.25–0.28	0.04	0.07–0.10	0.03–0.04
PBT/PCL 60/40	1.76–2.23	0.53	0.26–0.30	0.05–0.04	0.08–0.12	0.05
PBT/PCL 60/40 0.5% Sn	2.17–2.66	0.51	0.30–0.34	0.04	0.12–0.17	0.05–0.06
PBT/PCL 40/60	2.09–2.44	0.62	0.29–0.31	0.05	0.11–0.14	0.06
PBT/PCL 40/60 0.5% Sn	2.30–2.70	0.49	0.31–0.34	0.04	0.13–0.17	0.05
PCL	2.31–2.76	0.58	0.31–0.34	0.05–0.04	0.13–0.18	0.06

It is seen that all the samples PBT/PCL are biodegradable. However, in the case of the samples obtained by reactive mixing (with use of the catalyst), BDO is considerably higher.

Measurements of positron annihilation lifetime spectra (PALS)

The measurements were performed with the use of a "fast-fast" type spectrometer in a vacuum chamber (10^{-5} Pa) in the range of temperature from 288 to 340 K (with a step of 5 K). Because of the need of space between the scintillation counters to place the chamber, the effectiveness of counting rate was reduced and the accumulation of ca. 1.5×10^6 counts took about 24 h. The presence of the chamber between the counters influenced also the time resolution of the spectrometer and resulted in ca. 300 ps FWHM (full width at half maximum) of the time resolution curve. The sandwich "samples-source" included two slices of the studied sample of the thickness equal to 2 mm and the diameter of 17 mm and the source ^{22}Na (between Kapton thin foils) of activity about 1 MBq.

For analysis of the measured spectra, the program by Kansy was used [7]. In the model of analysis of the lifetime spectra there was assumed that:

1. The shortest-lived component of τ_1 = 125 ps corresponds to the annihilation events of *para*-positronium (*p*-Ps). The component intensity is I_1.
2. There is a lognormal distribution of the lifetimes τ_2, corresponding to the free annihilation of positrons in small open, free spaces in crystallites. The distribution is characterized by the averaged value $<\tau_2>$ and its standard deviation σ_2. The component intensity is I_2.

There is a lognormal distribution of the longest lifetimes τ_3, corresponding to the annihilation of *o*-Ps in free volume holes. The distribution is characterized by the averaged value $<\tau_3>$ and its standard deviation σ_3. The component intensity is I_3. The ratio $I_3/I_1 = 3$.

The same model of analysis is consequently used by Dlubek *et al.* [3] in their papers on free volume in polymers. The model, in the case of our data, is a perfect match to the experimental data. A very good concordance of experimental spectra with the used model was achieved in the case of all of our data ($\chi^2 < 1.1$). The model is further in the text called as "MOD_125_31_LOG".

From the measured positron lifetime spectra, the distributions of the longest lifetime τ_3 in the temperature region of the measurements were reconstructed. From the distributions of τ_3, one can obtain the probability density functions of the radius R_{FV} and volume V_{FV} of free volume (FV) holes, $y(V_{FV})$, using the semi-empirical model of *o*-Ps trapping and annihilation in FV holes, and the relationship between τ_3 and the radius R_{FV} of a spherical FV hole, given by Tao [16] and Eldrup [4]. Free volume in our studies corresponds to empty holes in the samples, i.e. the space not occupied by macromolecules, in which the *o*-Ps atom is formed, localized and annihilated by pick-off. The spherical shape of the FV hole, assumed in the frequently used model, is of course an simplification. In spite of it the model works well when studying systematic and controlled changes of FV in examined samples [17].

In Table 4 one can find the characteristic values of the obtained distributions, i.e. $<\tau_3>$, $<R_{FV}>$, $<V_{FV}>$ the averaged values of τ_3, R_{FV} and V_{FV}, as well as their standard deviations ("dispersions").

It is clear from Table 4 that there is a considerable difference between the $<\tau_3>$ values for PBT and PCL, which makes it possible the study of the system PBT/PCL. There is a rise of the averaged values of τ_3, R_{FV} and V_{FV} ($<\tau_3>$, $<R_{FV}>$, $<V_{FV}>$) when the temperature increases. Their progressive increase occurs also when PCL – the aliphatic polyester is added to the aromatic one – PBT . The greater increase is observed when much more amount of PCL is added to PBT. The effect is intensified by addition of the catalyst of the transesterification to the samples.

Below the free volume distributions $y(V)$, obtained for all the samples PBT/PCL and the temperature 290 K, are given in Figs. 10 and 11 to show the influence of both the PCL content and the catalyst on FV distributions. The condition $\int_0^\infty y(V)dV = 1$ is fulfilled for the distributions. The values of $y(V)$ are given in nm^{-3}.

It is evident that both the addition of PCL as well as the addition of the catalyst cause the higher contribution of larger free volume holes (CLFVH) to the total free volume, seen by *o*-Ps. For comparison the CLFVH values, corresponding to the contribution of the free volume of the holes greater than 0.046 nm^3, were calculated for all the studied samples (Table 5). The value of 0.046 nm^3 corresponds to the position of the maximum of the free volume distribution for the sample PBT/PCL 60/40.

Final remarks

Because one can find detailed conclusions in each section where results of particular method of research were presented, below only a résumé is given.

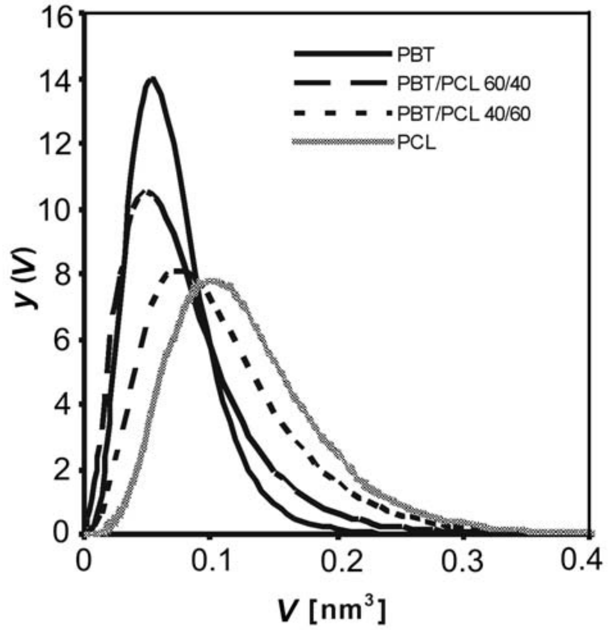


Fig. 10. The probability density functions of the free volume for the PBT/PCL samples at 290 K, created in the frame of the model MOD_125_31_LOG – the influence of the content of samples.

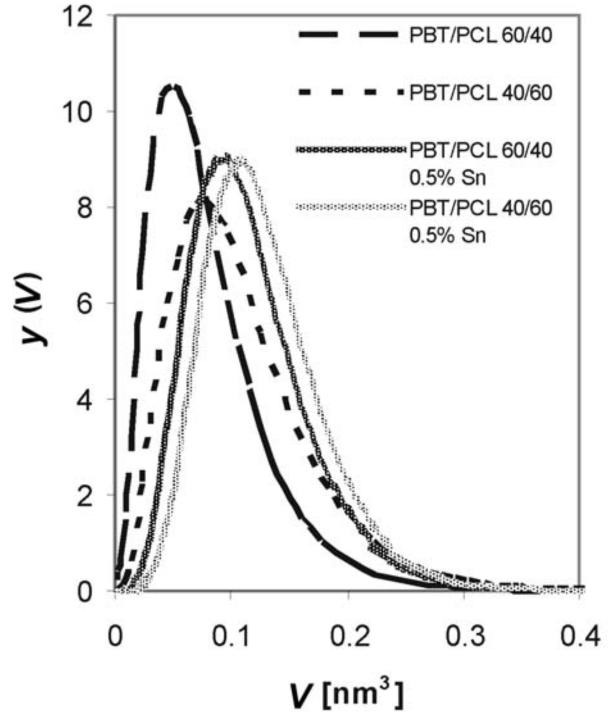


Fig. 11. The probability density functions of the free volume for the PBT/PCL samples at 290 K, created in the frame of the model MOD_125_31_LOG – the influence of the catalyst.

- By mixing two polyesters: PBT and PCL four samples were obtained which can be categorized into two groups: blends (sample PBT/PCL 60/40) and copolyesters (samples: PBT/PCL 40/60, PBT/PCL 40/60 0.5% Sn, PBT/PCL 60/40 0.5% Sn) if as a criterion of identity the transesterification is accepted (see Fig. 3).
- All the samples obtained by mixing (standard and reactive way) are biodegradable and their BOD values are higher than those for PCL. Greater susceptibility to biodegradability is observed for samples with higher content of PBT. In the case of the samples obtained by reactive mixing the BOD values are higher in comparison to the corresponding samples (of the same content), obtained in the standard way of mixing (Figs. 8 and 9).

Table 5. Values of CLFVH for the PBT/PCL samples, obtained in the frame of the model MOD_125_31_LOG

Sample	CLFVH (%)
PBT	75
PBT/PCL 60/40	73
PBT/PCL 40/60	89
PBT/PCL 60/40 0.5% Sn	96
PBT/PCL 40/60 0.5% Sn	98
PCL	97

- The DSC and microscopy studies revealed immiscibility of the samples PBT/PCL 60/40 and PBT/PCL 40/60 (see Figs. 1, 4, 5).
- Results of WAXS and SAXS measurements indicate that the weight proportion 40:60 of PBT:PCL used in the reactive mixing is exceptional and results in the least crystallinity, very thick amorphous layer and the thinnest crystallite thickness (see Fig. 6 and Table 3).
- In the obtained free volume distributions the influence of both the content and the presence of the catalyst of the transesterification is seen (see Figs. 10 and 11).
- The increase in the contribution of the large free volume holes (CLFVH) to the total free volume in the samples is significant in the samples in which the transesterification occurred: PBT/PCL 40/60, PBT/PCL 60/40 0.5% Sn, PBT/PCL 40/60 0.5% Sn (see Table 5). In case of the two latter samples, obtained by reactive mixing, the contribution is close to the corresponding value of CLFVH for the aliphatic copolyester PCL.
- The nearly equal contribution of the large holes (CLFVH) to the total free volume in the two latter samples, differing so much in morphology and the total crystallinity (Table 3, Fig. 6), is the reason of our supposition that there is an additional factor that influences the free volume in the studied samples. It is the transesterification reaction in general, its extent and probably the sequence distribution of units in the studied copolyesters. The sequence distributions of units is often assumed as the key factor in determining behavior of copolymers. Preliminary estimation indicates that the extent of transesterification in the two samples is similar.
- It is worthy of mentioning that the role of changes in distributions of free volume holes and especially the contribution of large free volume holes to the total free volume of a sample is significant to diffusion and permeability of the penetrant molecules in polymers.
- Any linkage between biodegradability and free volume (seen by *o*-Ps) that could be expected, because of the relationship of them both with a content of an amorphous phase in polymer samples, has been probably blurred in the case of our studies as a result of the summary effect of many agents influencing

biodegradability and free volume in the studied samples. The reduced crystallinity of samples, obtained in the reactive way (samples PBT 40/60 0.5% Sn and PBT 60/40 0.5% Sn), promotes both the biochemical oxygen demand (higher BOD values, Figs. 8 and 9) as well as the contribution of the larger free volume holes (higher CLFVH values). However, the BOD values are higher in the sample with a greater content of PBT, while the CLFVH values significantly increase with the rise of PCL content.

Acknowledgment. This work was partly supported by Grant N508 031 32/2347 from Polish Ministry of Science and Higher Education. The authors (M.D. and J.R.-G.) gratefully acknowledge the technical assistance of Eng. Jan Beliczyński at PALS measurements.

References

1. Baker JR, Milke W, Michelcic JR (1999) Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals. Water Res 33:327–334
2. Buttafava A, Consolati G, Mariani M, Quasso F, Ravasio U (2005) Effects induced by gamma irradiation of different polyesters studied by viscometry, thermal analysis and positron annihilation spectroscopy. Polym Degrad Stab 89:133–139
3. Dlubek G (2008) Positron annihilation spectroscopy. In: Seidel A (ed) Encyclopedia of polymer science and technology. John Wiley & Sons, Hoboken
4. Eldrup M, Lightbody D, Sherwood JN (1981) The temperature dependence of positron lifetimes in solid pivalic acid. J Chem Phys 63:51–58
5. Faupel F, Kanzow J, Günther-Schade K, Nagel C, Sperr P, Kögel G (2004) Positron annihilation spectroscopy in polymers. Mater Sci Forum 445;6:219–223
6. Hill AJ, Weinhold S, Stack GM, Tant MR (1996) Effect of copolymer composition on free volume and gas permeability in poly(ethyleneterephthalate)-poly(1,4 cyclohexylenedimethylene terephthalate) copolyesters. Eur Polym J 32:843–849
7. Kansy J (1996) Microcomputer program for analysis of positron annihilation lifetime spectra. Nucl Instrum Methods Phys Res A 374:235–244
8. Kim YJ, Park OO (1999) Miscibilities and rheological properties of poly(butylenes succinate)-poly(butylenes terephthalate). J Appl Polym Sci 72:945–951
9. Mariani M, Ravasio U, Varoli V, Consolati G, Faucitano A, Buttafava A (2007) Gamma irradiation of polyester films. Radiat Phys Chem 76:1385–1389
10. OxiTop instruction manual (2006) Wissenschaftlich-Technische Werkstätten GmbH, Weilheim
11. Park SS, Chae H, Im SS (1998) Transesterification and crystallization behavior of poly(butylenes succinate)/poly(butylenes terephthalate. J Polym Sci, Part B: Polym Chem 36:146–156
12. Pisula W, Pigłowski J, Kummerlöwe C (2006) Preparation and characterization of copolyesters of PTMS and PBT. Polimery 51:341–350
13. Porter RS, Wang LH (1992) Compatibility and transesterification in binary polymer blends. Polymer 33:2019–2030
14. Sawyer CN, McCarty PL (1978) Chemistry for environmental engineering. McGraw Hill Book, New York
15. Simon GP, Zipper MD, Hill AJ (1994) On the analysis of positron annihilation lifetime spectroscopy data in semicrystalline miscible polymer blend system. J Appl Polym Sci 52:1191–1202
16. Tao SJ (1972) Positronium annihilation in molecular substances. J Chem Phys 56:5499–5510
17. Yampolski YuP (2007) Metody izucheniya svobodnogo objema. Uspekhii Khimii 76:66–87
18. Zipper MD, Simon GP, Cherry P, Hill A J (1994) The effect of crystallinity on chain mobility and free volume in the amorphous regions of a miscible polycarbonate/polyester blend. J Polym Sci, Part B: Polym Phys 32:1237–1247
19. Zipper MD, Simon GP, Tant MR, Small JD, Stack GM, Hill AJ (1995) A free volume study of miscible polyester blends. Polym Int 36:127–136