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Synthesis, characterization, and properties of poly(ethylene terephthalate)/poly(1,4-butylene succinate) block copolymers

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Abstract

Reactive blending at 290 °C of a series of mixtures of poly(ethylene terephthalate) (PET) and poly(1,4-butylene succinate) (PBS) led to the formation of block PET/PBS copolyesters. The block lengths of the resulting copolymers decreased with the severity of the treatment. Copolyesters with PET/PBS molar compositions of 90/10, 80/20, 70/30, and 50/50 were prepared by this method and their composition and microstructure were characterized by ^{1}H and ^{13}C NMR, respectively. The T_g, T_m, and crystallinity of the copolymers decreased as the content in PBS and the degree of randomness increased. The elastic modulus and tensile strength of the copolymers decreased with the content of PBS, whereas, on the contrary, the elongation at break increased. The PET/PBS copolymers exhibited a pronounced hydrolytic degradability, which increased with the content in 1,4-butylene succinic units. Hydrolysis mainly occurred on the aliphatic ester groups.

Keywords: Poly(ethylene terephthalate) (PET); Poly(1,4-butylene succinate) (PBS); Polyester

1. Introduction

Aromatic polyesters are materials displaying an excellent pattern of physical properties. Since they are strongly resistant to hydrolysis, as well as to bacterial and fungal attack, they usually remain unaltered in the environment. On the contrary, aliphatic polyesters are biodegradable products that can be degraded under relatively mild conditions, but these materials have poor thermal and mechanical properties. The combination of aromatic and aliphatic units in the same polyester chain has been envisaged for a long time as an attractive approach to obtain novel products encompassing biodegradability and high performance properties.

A fair variety of random copolymers made of a mixture of terephthalic acid and several aliphatic diacids with different diols has been prepared by melt polycondensation, and their structure and properties have been examined in more or less detail [1–9]. Furthermore, reactive blending of already existing homopolyesters has proven to be a successful and inexpensive tool to produce new aliphatic/aromatic copolyesters with intermediate properties. In fact, this technique has been recently used for the preparation of poly(1,4-butylene succinate)/poly(1,4-butylene terephthalate), poly(1,4-butylene adipate-*co*-succinate)/poly(1,4-butylene terephthalate), and poly(1,4-butylene glutarate-*co*-adipate-*co*-succinate)/poly(1,4-butylene terephthalate) copolyesters [10–13].

The investigation reported on potential degradable aliphatic/aromatic copolyesters prepared by reactive blending of poly(ethylene terephthalate) (PET) with a degradable aliphatic polyester is however scarce. To our knowledge, poly(ε-caprolactone)/PET [14–19], poly(succinic anhydride-*co*-ethylene oxide)/PET [20], poly(ethylene adipate)/PET [21,22], and poly(glycolic acid) and poly(lactic acid)/PET copolymers [23], are the only accounts encountered in the accessible literature. In this work, we wish to report on the preparation of copolyesters made of terephthalic and succinic acid and ethylene and 1,4-butylene glycol. These copolyesters are obtained by heating a mixture of PET and poly(1,4-butylene succinate) (PBS) in the molten state. PET is a thermoplastic of exceptional importance for its large number of applications in a wide variety of industrial and technological fields. PBS is one of the most accessible biodegradable polymers, which has been extensively studied for its potential use as a future conventional plastic. In this study, the microstructure of the resulting PET/PBS copolyesters is fully characterized, and their thermal,

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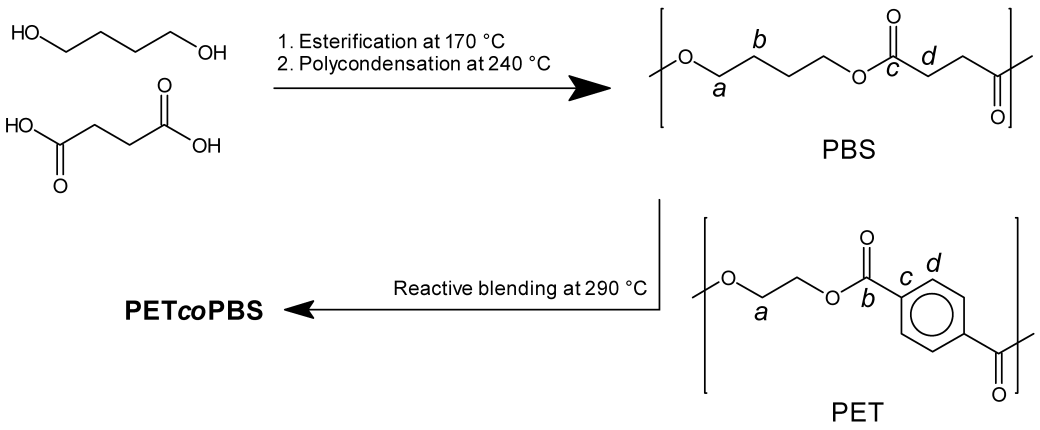

Scheme 1.

mechanical, and hydrolytic degradation properties are evaluated with reference to the two parent homopolymers.

2. Experimental section

2.1. Synthesis of PBS and PET/PBS copolyesters

Succinic acid, 1,4-butanediol, and tetrabutyl titanate were commercial reagent-grade products, which were used without further purification. The PET homopolymer used in this work was kindly provided by Catalana de Polímers, S.L. (El Prat de Llobregat, Barcelona, Spain). The solvents used for purification and/or characterization were all either technical-grade or high-purity grade and used as received.

The block copolymers described in this work were prepared according to the synthetic route depicted in Scheme 1. The PBS homopolyester was obtained by a two-step procedure including esterification and subsequent polycondensation reactions. Succinic acid (10.0 g, 84.68 mmol) and 1,4-butanediol (16.79 g, 186.30 mmol) were charged to a 100 ml, three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The esterification reaction was carried out at 170 °C under a nitrogen flow for a period of 6 h with continuous removal of the released water. The polycondensation reaction was performed at 240 °C under a 0.5–1 mbar vacuum using tetrabutyl titanate as a catalyst. The high viscous liquid formed was cooled down to room temperature and the atmospheric pressure was restored with a nitrogen flow to prevent degradation. The solid mass was dissolved in chloroform and the polymer was precipitated with cold diethyl ether, collected by filtration, and extensively washed with cold methanol and diethyl ether. The sample was dried under a reduced pressure at 60 °C for 72 h.

For reactive blending, the PET/PBS mixtures were melt-mixed in a 50 ml, three-necked, round-bottom flask equipped with a mechanical stirrer and a distillation column under a nitrogen flow at 290 °C. First, the PET homopolymer was introduced and allowed to melt completely while stirring in an inert atmosphere. The desired amount of PBS was then added and the mixture was homogenized for a period of 5 min before the actual reaction time was recorded. Samples were taken from the reaction mixture along the course of the reaction to analyze in detail the change in the microstructure of the resulting copolymers. A physical equimolar PET/PBS blend was prepared by dissolving the two respective homopolymers in a chloroform/TFA mixture (8/1 (v/v)), followed by subsequent coprecipitation with cold diethyl ether. This physical blend was dried in vacuo at 60 °C for 72 h.

2.2. Measurements

Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 °C operating at 300.1 and 75.5 MHz, respectively. The polyesters were dissolved in a 8/1 (v/v) mixture of deuterated chloroform ($CDCl_3$) and trifluoroacetic acid (TFA), and the spectra were internally referenced to tetramethylsilane. Sixty-four scans for ^{1}H NMR and 1,000–10,000 scans for ^{13}C NMR were acquired with 32K and 62K data points and delay times of 1 and 2 s, respectively. Quantitative ^{1}H NMR spectra were recorded with pulse widths of 6 μs (60°) and delay times of 20 s. For ^{13}C NMR spectra, the pulse and spectral widths were 4.3 μs (90°) and 18 kHz, respectively. The intrinsic viscosity $[\eta]$ of the polymers was measured from dichloroacetic acid solutions with an Ubbelohde viscometer thermostated at 25 ± 0.1 °C. Gel permeation chromatography (GPC) measurements were performed on a Waters GPC system equipped with a refractive index detector. The eluent was 1,1,1,3,3,3-hexafluoro-2-propanol. Two 7.8 × 300 mm Styragel columns packed with divinylbenzene cross-linked polystyrene (pore size = 10^3 and 10^4 Å) in series were used for the analysis with the aforementioned eluent at a flow rate of 0.5 ml min^{-1} at 35 °C. The molecular weights and the molecular weight distributions were calculated against monodisperse polystyrene standards with the Maxima 820 software. Although

M_n and M_w values determined by PS-calibrated-GPC are only indicative, they may be used for comparative purposes.

The thermal properties of the polyesters were evaluated by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC Pyris 1. A heating rate of 20 or 30 °C min^{-1} was applied and polymer samples of 4–6 mg were heated and cooled under a nitrogen flow of 20 ml min^{-1}. Indium and zinc were used as the calibration standards. Thermogravimetric analysis (TGA) was conducted with a Perkin–Elmer TGA-6 thermobalance at a heating rate of 10 °C min^{-1}. Densities were measured by the flotation method at 20 °C using heptane/tetrachloromethane mixtures. Tensile testing was performed on rectangular specimens (55 × 5 mm) cut from amorphous, isotropic films having a thickness of about 200 μm. The tensile tests were conducted at room temperature on a Zwick BZ2.5/TN1S universal tensile testing apparatus operating at a constant cross-head speed of 10 mm min^{-1} using a 0.5N pre-load and a grip-to-grip separation of 20 mm. All reported tensile data represent an average of at least six independent measurements. Powder X-ray diffraction patterns were obtained on flat photographic films with a modified Statton camera using nickel-filtered Cu Kα radiation with a wavelength of 1.5418 Å and these patterns were calibrated with molybdenum sulfide.

Table 1
Composition, molecular weight, and microstructure of PET, PBS, and PET/PBS copolyesters

Polymer	Composition[a]	$[\eta]$[b]	M_n[c]	PD[c]	Density[d]	n_{ET}/n_{BS}[e]	R[f]
PET	100	0.63	13,300	2.5	1.34	–	–
PBS	100	1.12	29,100	2.7	1.26	–	–
Copolyester[g]							
90/10–30	89.6/10.4	0.65	14,600	2.6	1.32	37.7/5.9	0.19
90/10–60	90.4/9.6	0.74	17,800	2.8	1.33	16.5/2.0	0.57
80/20–30	80.7/19.3	0.66	13,100	3.0	1.31	7.6/3.8	0.39
80/20–60	81.0/19.0	0.78	19,500	2.9	1.30	5.1/1.8	0.76
70/30–30	71.2/28.8	0.78	19,600	2.7	1.29	7.1/3.6	0.42
70/30–60	71.0/29.0	0.94	24,800	2.9	1.28	5.4/2.5	0.59
50/50–30	50.5/49.5	0.82	15,200	3.0	1.16	3.3/4.1	0.55
50/50–60	51.4/48.6	0.97	23,400	3.5	1.17	2.2/2.5	0.85

[a] PET/PBS molar ratio of the resulting copolyesters.
[b] Intrinsic viscosity (dl g^{-1}).
[c] Number-average molecular weight and the copolymer polydispersity.
[d] Density (g ml^{-1}).
[e] The number-average sequence lengths of the ethylene terephthalate (ET) and 1,4-butylene succinate (BS) blocks were calculated as mentioned in the text.
[f] The degree of randomness was calculated as described in the text.
[g] The copolyesters were coded by the initial PET/PBS molar ratio and their blending time (in min).

2.3. Hydrolytic degradation

Films of PET, PBS, and PET/PBS copolymers with a thickness of 225–275 μm, were prepared via casting at room temperature from a 10% (w/v) 1,1,1,3,3,3-hexafluoro-2-propanol/chloroform (1/5 (v/v)) solution on a silanized Petri dish. The films were cut into 12 mm diameter, 60–90 mg weight disks, which were dried in vacuo at 50 °C for 72 hours before incubation. Incubation was carried out in 50 ml of distilled water at 37 °C in a temperature-controlled oven. After incubation, the samples were rinsed thoroughly in distilled water and dried in vacuo to constant weight. Sample weighting, viscometric measurements, DSC, and ^1H

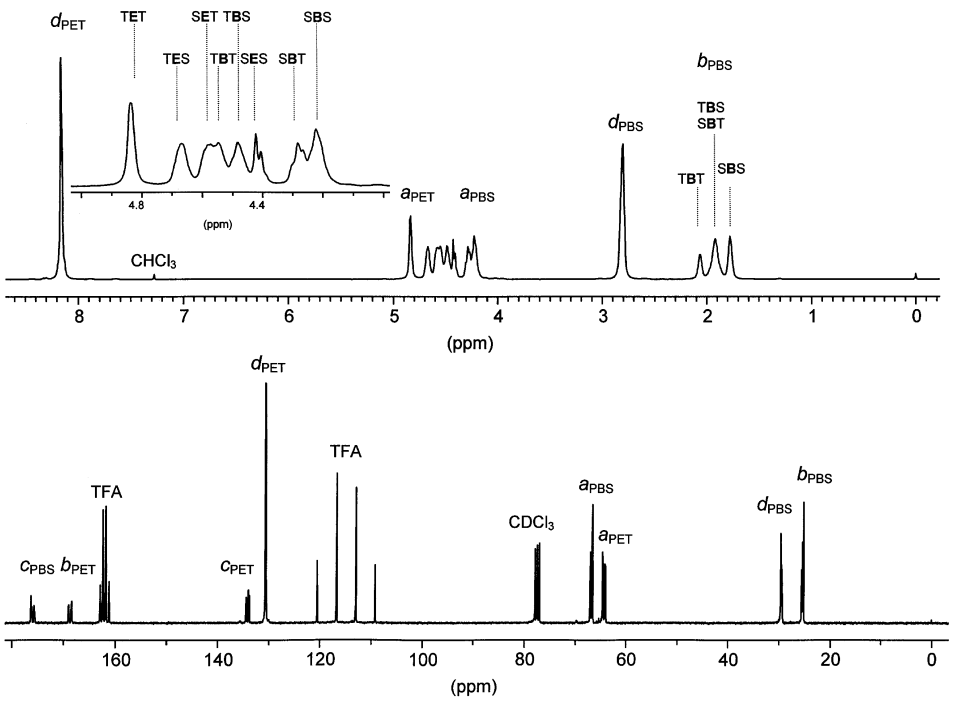

Fig. 1. 300.1 MHz ^1H NMR spectra (top) and 75.5 MHz ^{13}C NMR (bottom) spectra of the PET/PBS (50/50) blend after 60 min of reactive blending.

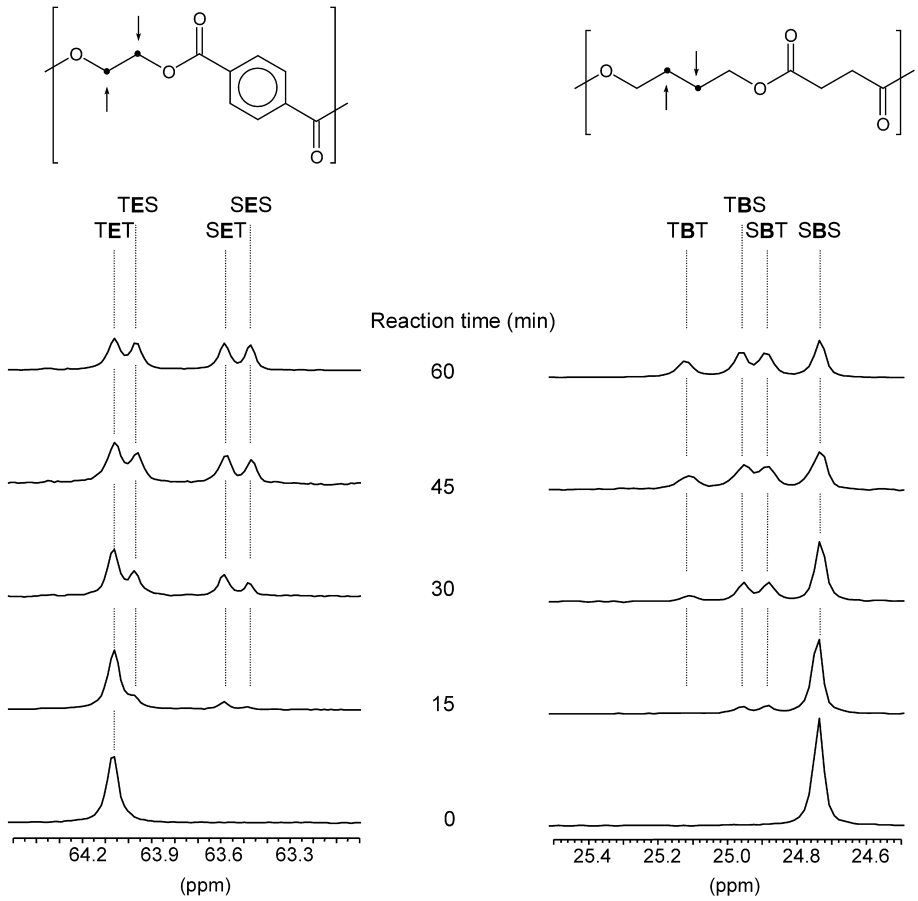

Fig. 2. 75.5 MHz ^{13}C NMR spectra of the physical equimolar PET/PBS blend and of this blend after the indicated reactive blending time. Methylene carbon signals of the ethylene glycol unit (left) and methylene carbon signals of the 1,4-butylene glycol unit (right) are shown.

NMR spectroscopy were used to follow the evolution of the hydrolytic degradation.

3. Results and discussion

3.1. Reactive blending of PET/PBS mixtures

PBS could be successfully synthesized as described in the experimental part. The polyester had an intrinsic viscosity of 1.12 dl g^{-1} and a number- (M_n) and weight-average (M_w) molecular weight of 29,100 and 79,100 g mol^{-1}, respectively. The characteristics of the PET and PBS homopolymers, and the series of copolyesters prepared at different reaction times from initial PET/PBS molar feed ratios of 90/10, 80/20, 70/30, and 50/50 are listed in Table 1. All copolyesters had an intrinsic viscosity and molecular weights between those of PET and PBS, with the polydispersity ranging from 2.5 to 3.5. Higher intrinsic viscosities were obtained for blends with a higher content in PBS. Interestingly, it was also observed that the molecular weights increased with the treatment most likely due to chain-extension promoted by the occurrence of end-group reactions.

3.2. Composition and microstructure

The composition and microstructure of the copolyesters resulting from the reactive blending of the PET/PBS blends were determined by ^{1}H and ^{13}C NMR spectroscopy, respectively. The ^{1}H NMR spectrum of the untreated, physical PET/PBS blend showed resonance signals at 4.84 and 8.16 ppm, which were attributed to the methylene and the terephthalic protons of PET, respectively. Furthermore, the observed resonance signals at 1.77 and 4.22 ppm were assigned to the methylene protons of the 1,4-butylene glycolic units of PBS, whereas the signal arising at 2.79 ppm was attributed to the methylene protons of the succinic acid units of PBS. Thus, the spectrum of the physical mixture was concluded to be the simple addition of the PET and PBS spectra.

The ^{1}H NMR spectrum recorded for the PET/PBS (50/50) blend after 60 min of heating is shown in Fig. 1. New signals appeared at 1.91 and 2.05 ppm, and in the 4.2–4.8 ppm region. With the progress of reactive blending, these new signals gradually increased, and this can be taken as a first indication of the occurrence of transesterification reactions taken place upon reactive blending of PET and PBS. In the ^{13}C NMR spectra of the physical blends, signals

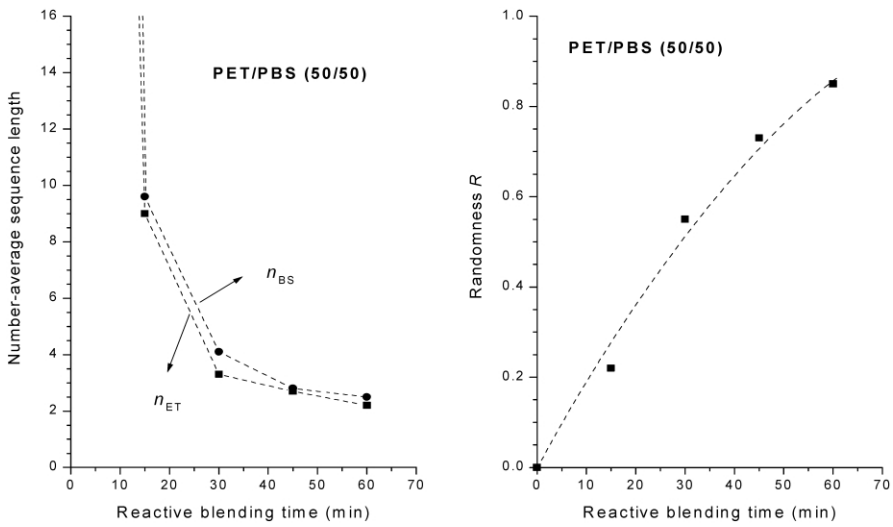

Fig. 3. The change of the number-average sequence lengths (left) and the degree of randomness (right) upon reactive blending for the PET/PBS (50/50) blend.

arising at 25.2 and 66.7 ppm (methylene carbons of 1,4-butylene glycol), 29.6 ppm (methylene carbons of succinic acid), 64.6 ppm (methylene carbons of ethylene glycol), 130.7 ppm (protonated terephthalic carbons), 134.0 ppm (non-protonated terephthalic carbons), 168.5 ppm (carbonyl of terephthalic acid), and 176.3 ppm (carbonyl of succinic acid) were observed. Besides these signals, new signals were detected for the melt-mixed blends due to the occurrence of transesterification reactions.

For a correct assignment of the new signals appearing in the ^{1}H and ^{13}C NMR spectra of PET/PBS copolyesters, spectra were compared for different reaction times and for different initial compositions and compared with those obtained from PET and PBS. Definite support was obtained from the correlation data provided by two-dimensional NMR HETCOR spectra. The composition of the resulting copolymers could be directly determined by ^{1}H NMR spectroscopy using the relative integrated value of the signals arising from the methylene protons of the ethylene glycol and the succinic acid, respectively. The initial blend compositions remained essentially unchanged, although a small loss of 1,4-butylene succinic units was observed after 60 min of treatment. This is probably due to incipient degradation of PBS with the formation of volatile products.

It is generally accepted that upon reactive blending of two condensation homopolymers, the occurrence of transesterification reactions leads to the formation of block copolymers, with the blocks gradually decreasing in length with the extent of the treatment. The evolution of the microstructure of the copolyesters obtained by reactive blending of PET and PBS was followed in detail for the copolyester PET/PBS (50/50). The resonance signals arising from the methylene carbons of the ethylene (E) and 1,4-butylene glycol (B) units were used to follow the progress of the transesterification reactions. As can be seen in Fig. 2, new resonance signals could be detected upon reactive blending with their relative intensities increasing with the advance of the process. As expected, reactive blending of PET and PBS was found to generate TES (and equivalent SET), SES, SBT (and equivalent TBS), and TBT dyads, where T stands for terephthalic and S for succinic units, respectively, in addition to the TET and SBS sequences present in the initial homopolymers. The relative intensities of the dyad peaks for the melt-mixed blends were used to calculate the number-average sequence lengths and the degree of randomness of the resulting copolyesters according to the following Eqs.:

$$n_{ET} = \frac{N_{TET} + \left(\frac{N_{TES}}{2}\right)}{\left(\frac{N_{TES}}{2}\right)} \qquad n_{BS} = \frac{N_{SBS} + \left(\frac{N_{SBT}}{2}\right)}{\left(\frac{N_{SBT}}{2}\right)}$$

$$R = \frac{1}{n_{ET}} + \frac{1}{n_{BS}}$$

Fig. 3 represents the variation in the number-average sequence lengths and the degree of randomness upon reactive blending. It is shown that the sequence lengths of the ethylene terephthalic (n_{ET}) and 1,4-butylene succinic (n_{BS}) units decreased with the advance of the reactive process and that the randomness of the copolymer gradually increased. It was concluded therefore that the microstructure of the melt-mixed PET/PBS blends evolved from a blocked microstructure to an almost completely randomized copolymer, due to the occurrence of extensive transesterification reactions between the two homopolymer counterparts.

3.3. Thermal and mechanical properties of the copolyesters

In the first place the thermal stability of the copolyesters was evaluated by studying the thermal degradation of PET/PBS (50/50) with reference to the parent homopolymers by TGA under both non-isothermal and isothermal

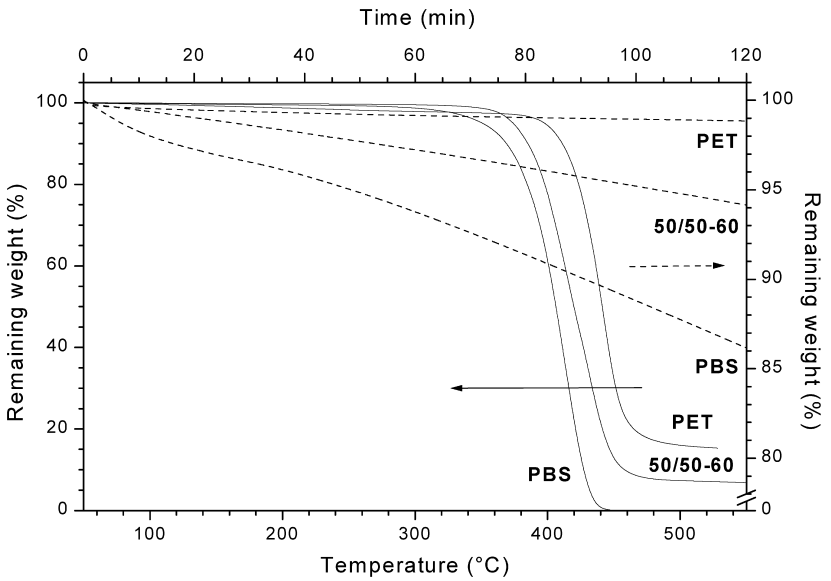

Fig. 4. Non-isothermal (solid line) and isothermal (dashed line) TGA traces of PET, PBS, and PET/PBS (50/50) melt-mixed for 60 min.

conditions. The TGA traces obtained in this study are shown in Fig. 4. The PBS homopolymer started to degrade around 300 °C, whereas PET appeared to be more stable with an onset degradation temperature at around 380 °C. Isothermal heating at 290 °C reflected that PBS degraded significantly at this temperature, whereas PET remained essentially unaltered. This provides an explanation for the slight loss in PBS found for the copolyesters prepared by prolonged reactive blending. The thermal stability of the equimolar PET/PBS copolyester melt-mixed for 60 min was found to be intermediate between those of the neat homopolymers, in both kinds of experiments.

The DSC data of the PET/PBS copolyesters examined in this work are collected in Table 2. A T_g around 40 °C is reported in the literature for the PBS [4] homopolymer. In this work, to evaluate the T_g, DSC heating traces were registered at a heating rate of 30 °C min^{-1} from samples molten at 290 °C and subsequently quenched in liquid N_2. The T_g for the equimolar physical mixture of PET and PBS was found around 78 °C, evidencing that the two homopolymer phases separated upon solidification. After reactive blending, the copolyesters (50/50) showed a single T_g below 0 °C, which evidenced the monophasic nature of this sample. On the other hand, the copolyesters enriched in PET showed the T_g of the PET-rich phase, whereas that of the PBS-rich phase was undetectable, which might be due to

Table 2
Thermal and tensile properties of PET, PBS, and PET/PBS copolyesters

Polymer	Thermal properties							Tensile properties[a]		
	T_g[b] (°C)	T_m[c] (I) (°C)	ΔH_m[c] (I) (J g^{-1})	T_c[c] (°C)	ΔH_c[c] (J g^{-1})	T_m[c] (II) (°C)	ΔH_m[c] (II) (J g^{-1})	E (MPa)	σ_{max} (MPa)	ε_{break}(%)
PET	78	246	31	170	27	245	22	1440 (165)	37 (5)	80 (30)
PBS	−40[d]	113	110	65	61	113[e]	71[e]	465 (65)	31 (7)	425 (140)
Copolyester										
90/10–30	63	239	35	160	28	235	24	1425 (95)	41 (6)	190 (45)
90/10–60	57	221	27	148	24	224	20	1380 (125)	39 (7)	230 (65)
80/20–30	54	215	23	151	22	212	18	835 (70)	34 (4)	455 (40)
80/20–60	36	177	9	–	–	–	–	915 (95)	36 (5)	505 (75)
70/30–30	42	194	12	109	14	187	11	450 (105)	31 (6)	815 (60)
70/30–60	32	176	5	–	–	–	–	620 (85)	33 (7)	920 (55)
50/50–30	−2	–	–	–	–	–	–	–	–	–
50/50–60	−1	–	–	–	–	–	–	–	–	–

[a] The standard deviations are given in parenthesis.
[b] The glass-transition temperature (T_g) was taken as the inflection point of the heating DSC traces of amorphous samples recorded at a heating rate of 30 °C min^{-1}.
[c] The melting (T_m) and crystallization (T_c) temperatures and melting (ΔH_m) and crystallization (ΔH_c) enthalpies were registered by DSC at a heating/cooling rate of 20 °C min^{-1}. (I): first heating; (II): second heating.
[d] Ref. [4].
[e] Additional cold-crystallization was detected at 94 °C with a ΔH_{cc} of 10 J g^{-1}.

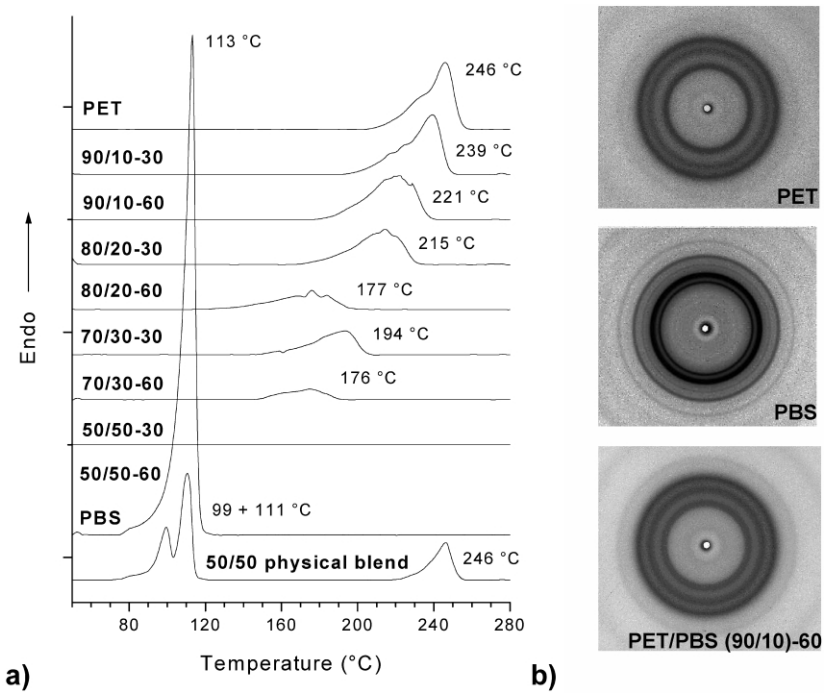

Fig. 5. (a) DSC traces of PET, PBS, the equimolar physical PET/PBS blend, and the melt-mixed PET/PBS blends. (b) Powder X-ray diffraction patterns of PET, PBS, and the PET/PBS (90/10) blend after 60 min of reactive blending.

compositional effects. Furthermore, the T_g of the PET-rich phase decreased with the advance of reactive blending due to increasing randomization and consequent miscibility of the blend mixture, and with the content in PBS.

The heating DSC scans of the cast films of the melt-mixed blends, along with those of the parent PET and PBS homopolymers were recorded at 20 °C min^{-1} and are shown in Fig. 5(a). The heating trace of PET and PBS shows a melting endotherm at 246 and 113 °C, respectively, the enthalpy of the latter corresponding to a highly semicrystalline material. The equimolar, physical mixture of PET and PBS before reactive blending shows melting endotherms reminiscent of those recorded separately for the PET and PBS homopolymers. Conversely, the thermograms obtained from the PET/PBS blends after reactive blending for 30 and 60 min displayed a single melting behavior and revealed

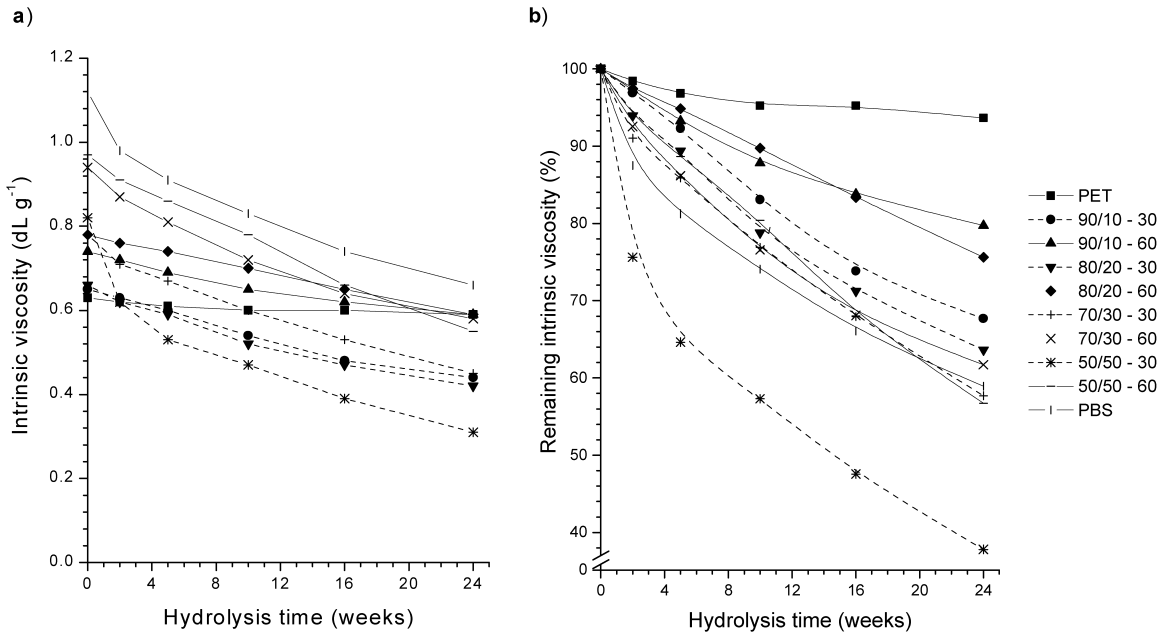

Fig. 6. Changes in the intrinsic viscosity (a) and the remaining intrinsic viscosity (b) *vs* incubation time for polyesters and copolyesters subjected to hydrolytic degradation at 37 °C.

Table 3
Hydrolytic degradation of PET, PBS, and the PET/PBS copolyesters

Polymer	RW[a] (%)		$[\eta]$ (dl g^{-1})			T_m (°C)			ΔH_m (J g^{-1})			[BS][b]	
	I	III	I	II	III	I	II	III	I	II	III	I	III
PET	100	97	0.63	0.59	0.48	246	247	249	30	40	42	0	0
PBS	100	83	1.12	0.66	0.13	113	115	112	109	113	135	100	100
Copolyester													
90/10–30	100	95	0.65	0.44	0.27	239	238	246	35	41	48	10.4	6.2
90/10–60	100	96	0.74	0.59	0.41	221	224	233	27	38	39	9.6	8.0
80/20–30	100	93	0.66	0.42	0.17	215	217	230	22	28	35	19.3	13.8
80/20–60	100	96	0.78	0.59	0.38	177	184	195	9	15	13	19.0	16.2
70/30–30	100	86	0.78	0.45	0.18	194	195	214	12	15	21	28.8	18.2
70/30–60	100	90	0.94	0.58	0.32	176	178	198	5	8	11	29.0	22.0
50/50–30	100	64	0.82	0.31	0.10	–	–	–	–	–	–	49.5	29.2
50/50–60	100	73	0.97	0.55	0.13	–	–	117	–	–	7	48.6	35.7

Degradation conditions: (I) initial polymer films; (II) 24 weeks of hydrolytic degradation at 37 °C; (III) samples degraded as for II were subjected to an additional degradation for one month at 80 °C.

[a] Remaining weight. No weight loss occurred for the samples degraded under condition (II).

[b] PBS content in the copolymer in mol%. No change in the copolyesters composition occurred under condition (II).

that for a given composition the ability to crystallize decreased with the advance of the transesterification reactions. Copolyesters containing equimolar amounts of PET and PBS were unable to crystallize. As can be seen in Fig. 5(b), powder wide-angle X-ray diffraction revealed that the structure adopted by the semicrystalline copolyesters is the characteristic triclinic crystalline structure of PET. No signs of crystalline PBS blocks were detected, most likely because the number-average sequence length of the 1,4-butylene succinic units is too short to form stable crystallites. The decrease in melting temperature and enthalpy with the content in PBS evidenced the depressing effect of the incorporation of BS units into the PET chain on the crystallite perfection and crystallinity. The inability of the equimolar PET/PBS copolyesters to crystallize can be attributed to the fact that for this composition, the transesterification reactions decreased the length of both PET and PBS blocks to less than four residues.

The tensile properties, such as the Young's modulus (E), the maximum tensile stress (σ_{max}), and the elongation at break (ε_{break}), were determined for amorphous, non-oriented PET, PBS, and melt-mixed blends, and the results are listed in Table 2. Unfortunately, the tensile properties of the melt-mixed equimolar PET/PBS blends could not be evaluated, since no adequate specimens could be prepared. It was observed that the E modulus and σ_{max} decreased with the content of PBS, whereas at the same time the ε_{break} considerably increased. No considerable differences in the tensile properties were observed for the copolyesters prepared at different melt-mixing times. The fact that the ε_{break} of PBS was lower than that of the 80/20 and 70/30 blends is thought to be due to the presence of a small amount of crystallinity in the PBS samples, as crystallization of this polyester cannot be completely repressed, even when rapid melt-quenching is applied.

3.4. Hydrolytic degradation

The hydrolytic degradation of the melt-mixed PET/PBS blends was performed at 37 °C. It was observed that the films became brittle upon incubation, although no significant weight loss occurred during the degradation experiments. Conversely, the intrinsic viscosity of all the samples steadily decreased from the beginning and evolved according to the plot showed in Fig. 6. It was found that the blends that were melt-mixed for 30 min degraded faster than the ones melt-mixed for 60 min. Reactive blending randomized the copolymer and gave rise to smaller PBS blocks, which difficult the degradability of these moieties. It was also apparent that the degradation increased with the content of PBS, when the hydrolytic degradation of polymer blends with the same degree of randomness was compared. The fact that the PET/PBS (50/50) blend treated for 30 min degraded faster than PBS, can be explained by the amorphous state of these copolyester samples, whereas the PBS film was semicrystalline.

In order to accelerate the hydrolytic degradation and to study in more detail the hydrolysis process, the incubation temperature was elevated to 80 °C for one additional month after six months of degradation at 37 °C. As can be seen in Table 3, all samples showed a significant weight loss and a strong decrease in the intrinsic viscosity, which increased with the content in PBS. Nevertheless, the tendencies observed during the hydrolytic degradation conducted at 37 °C remained unchanged. Furthermore, amorphous PET samples were also submitted to degradation, and they were found to degrade slightly faster than the semicrystalline PET samples. The amorphous samples remained highly amorphous with the advance of incubation time, even at 80 °C.

Changes in the thermal properties occurring upon hydrolytic degradation are listed in Table 3, which

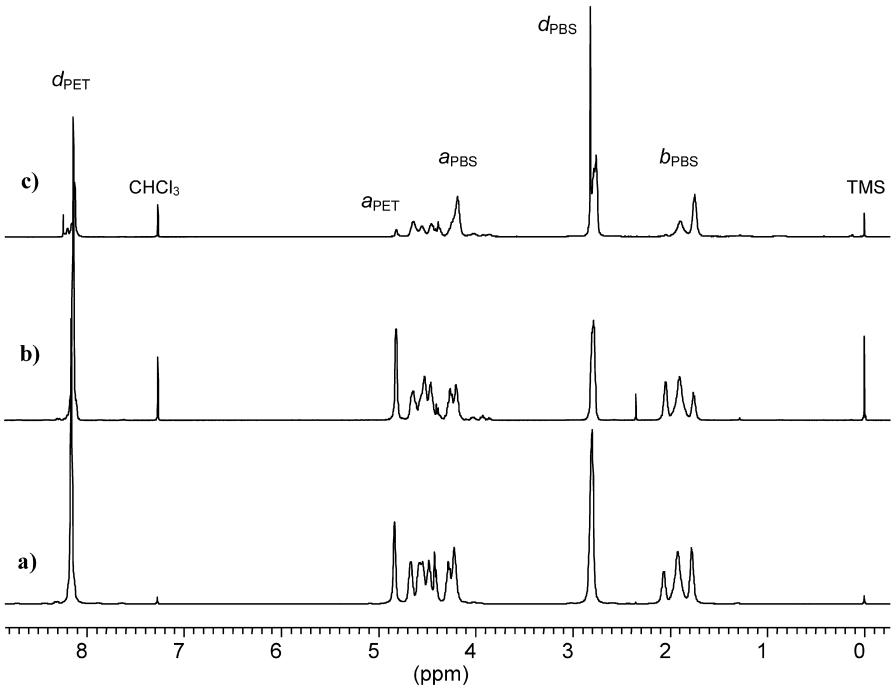

Fig. 7. ^{1}H NMR spectra of the copolymer PET/PBS (50/50)-60 subjected to hydrolytic degradation at 80 °C. (a) initial disc, (b) residual disc, and (c) the residue left by the mother solution after evaporation to dryness.

compares the melting temperatures and enthalpies of the initial samples with the samples incubated for six months at 37 °C, and the samples subjected to a subsequent degradation for one month at 80 °C. In general it could be observed that the T_m and crystallinity of the samples increased with degradation, which should be taken as an indication that the hydrolysis preferentially took place in the amorphous phase.

^{1}H NMR analysis of the degraded samples revealed that the copolyester composition changed considerably during the hydrolytic degradation. Fig. 7 shows the ^{1}H NMR spectra of the initial and degraded PET/PBS (50/50)-60 copolyester sample, as well as the spectrum of the degradation products recovered by evaporation to dryness of the mother solution. These spectra revealed that the content of the BS units of the incubated samples largely decreased upon degradation, as the peaks arising from the PBS blocks decreased in intensity with respect to those assigned to the PET blocks. The spectra of the residue left by evaporation of the mother solution confirmed that the degradation products consisted mostly of PBS blocks. These results are a clear indication that the PBS blocks are responsible for the degradability observed for these copolyesters.

4. Concluding remarks

Reactive blending of poly(ethylene terephthalate) (PET) and poly(1,4-butylene succinate) (PBS) mixtures conducted at 290 °C led to block PET/PBS copolyesters differing in composition and microstructure. The block lengths decreased with the advance of the treatment and the copolymers finally attained an almost random microstructure. The melting temperature and enthalpy of the copolymers decreased with the content of PBS and the degree of randomness. Powder X-ray diffraction revealed that the crystalline structure of PET is preserved for the semicrystalline copolyesters, whereas no signs of the crystalline phase entirely made of the aliphatic counterpart was observed. The tensile strength of amorphous, non-oriented copolymer samples decreased with the content in PBS, whereas the elongation at break increased. The PET/PBS copolymers underwent significant hydrolytic degradation at 37 °C, which increased with the content in 1,4-butylene succinic units, but decreased with the degree of randomization. Hydrolysis was found to occur mainly on the aliphatic ester groups.

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