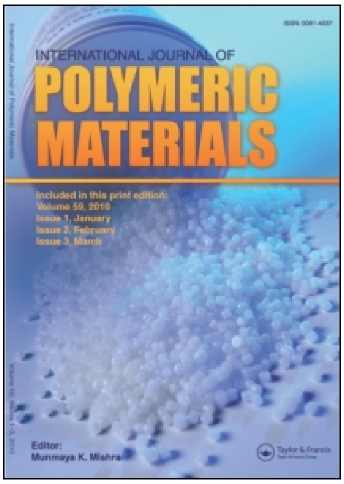

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Blends of Poly(hydroxybutyrate) and Poly(ethylene succinate) Prepared in the Presence of Samarium

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Blends of the commercial biodegradable polymer poly(hydroxybutyrate) (PHB) with the oligomeric polyester poly(ethylene succinate) (PES) were prepared by melt processing in the presence of $Sm(acac)_3$*. The occurrence of transesterification reactions during blend processing using the samarium catalyst was investigated.* ^1H *NMR analyses showed no evidence of transreactions, even using high content of catalyst (4 wt%), long reaction times and high temperatures (200°C). Under the drastic reaction conditions employed, chain degradation characterized by a significant decrease in the molecular weight (MW) of PHB has taken place. PHB/PES blends form immiscible systems in which the PHB crystallizes as large spherulites, but its crystallization is significantly influenced by the presence of PES, which does not crystallize at conditions in which the poly(hydroxyalkanoate) is crystallized.*

Keywords: blends, degradation, PHB, poly(ethylene succinate), transesterification

INTRODUCTION

Recently, the demand for biodegradable polymers as a solution to problems concerning environmental and biomedical applications has grown. Biologically produced polyesters such as poly(hydroxyalkanoates), in particular poly(hydroxybutyrate) (PHB) have attracted

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significant industrial attention as biodegradable and biocompatible thermoplastics [1–5]. PHB is a thermoplastic polyester that can be applied similarly to many conventional petrochemical-derived plastics currently in use [6–8]. It presents a melting point at about 180°C and degree of crystallinity around 70%. The polyester has also attracted much attention as an environmentally degradable plastic to be used for agricultural, marine and medical applications [9]. However, it has a narrow processing window and, depending on the molecular weight, the material is significantly brittle [10–14].

An interesting way of modifying the properties of a polyester is by blending it with another polyester. In this case the miscibility between the polyesters can be highly increased by using metal catalysts which promote transesterification reactions, generating copolymers. Several transition metal complexes have been described as good catalysts for polyesters transreactions [15,16].

Thus, the combination of biodegradability, better processability and desired physical properties can, in principle, be achieved by blending PHB with another biodegradable polyester, especially if they can undergo chemical reactions in the molten state [12,15,17,18]. However, PHB is thermally unstable at high temperatures and a drastic reduction of molecular weight can occur during processing at temperatures above 200°C [12,19,20].

In the present work, blends of PHB with a synthetic semicrystalline polyester poly(ethylene succinate) (PES) were investigated aiming to produce changes in the structure of the individual components during the preparation of the blend. PES is an aliphatic biodegradable polyester with a well-defined melting temperature around 105°C and glass transition at about -1°C [13,21]. As described for other blends, in principle these polyesters could react during melt processing, generating copolymers containing units of each homopolymer that constitutes the blend [13,22].

EXPERIMENTAL

Materials

PHB (Biocycle) in the form of grains was supplied by PHB Industrial (Brazil) and used as received. PES was synthesized by a two-step bulk condensation polymerization of succinic acid and excess of ethylene glycol following a general technique described in the literature [23]. In a first step, transesterification was carried out using manganese acetylacetonate as catalyst with removal of water from the reaction medium. In a second step, phosphoric acid and antimony trioxide were added and ethylene glycol was removed by bubbling nitrogen at 200°C for 2 h. PES was obtained as a brittle white solid with molecular weight M_w of 3,800 determined by GPC.

Blend Preparation

Blends of commercial PHB with PES were prepared in a Haake Rheocord 9000 internal mixer at 170°C and 60 rpm. The ratio PHB/PES = 60/40 (weight base) was used. Blends were processed for 5, 10, 20 and 40 min. Samarium acetylacetonate ($Sm(acac)_3$) was used as catalyst to promote transreactions in the amount of 1 and 4 wt%.

In order to avoid the influence of the catalyst on the ^1H NMR analysis, blend samples were purified by extracting the blends with acetone or precipitating a dichloromethane polymer solution with ethanol.

Thermal Treatment

With the aim to submit PHB/PES blends to more drastic reacting conditions, a blend processed in a Haake in the shorter time was thermally treated for longer times and higher temperatures than those used for blending. A small amount of the blend (2 g) was placed in a closed glass tube under nitrogen and heated in a silicone oil bath at the desired time and temperature. The samples were treated at 170°C for 2, 4, 6 and 16 h and 200°C for 2 h.

Blend Characterization

The blends were characterized by hydrogen nuclear magnetic resonance (^1H NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and optical microscopy (OM).

^1H NMR spectra of the samples were recorded on a Varian Mercury 300 spectrometer, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard to measure chemical shifts. GPC was performed in a Waters system using $CHCl_3$ as solvent, and a set of phenomenex columns and monodisperse polystyrene as calibration standard.

The spherulite sizes and their size distribution in the homopolymers and some of the blends were evaluated with an Olympus BX 50 optical microscope with polarized light, using hot-pressed 0.12 mm films.

The thermal behavior of the samples was examined using a Perkin Elmer model DSC-7. The analysis was carried out under nitrogen atmosphere in the range 40–200°C in the following sequence: 1) first heating at 10°C/min; 2) cooling at 10°C/min; and 3) second heating at 10°C/min. The melting temperature and enthalpy were calculated from the maximum and the area of the endothermic peak, respectively. The degree of crystallinity (X_c) was calculated by: $X_c = \Delta H_m/\Delta H^\circ_m$, where ΔH_m is melting enthalpy and ΔH°_m is the melting enthalpy of the 100% crystalline polymer [2], considered 146 J/g for PHB [23].

PHB and PES were analyzed by thermogravimetric analysis (TGA) using a TA Instrument Q500 Thermal Analyser from 25 to 700°C under nitrogen flow at the rate of 10°C/min.

RESULTS AND DISCUSSION

Structure of Polymers After Processing

Figure 1 shows the ^1H NMR spectra of PHB, PES and a PHB/PES blend obtained without any catalyst. The spectrum of the blend indicated that no transesterification reactions seem to have occurred when the blend is prepared in the absence of additional catalyst (PES contains residual $Mn(acac)_2$ and Sb_2O_3 catalyst), since only characteristic peaks of the homopolymers were detected. Chemical shifts of PHB

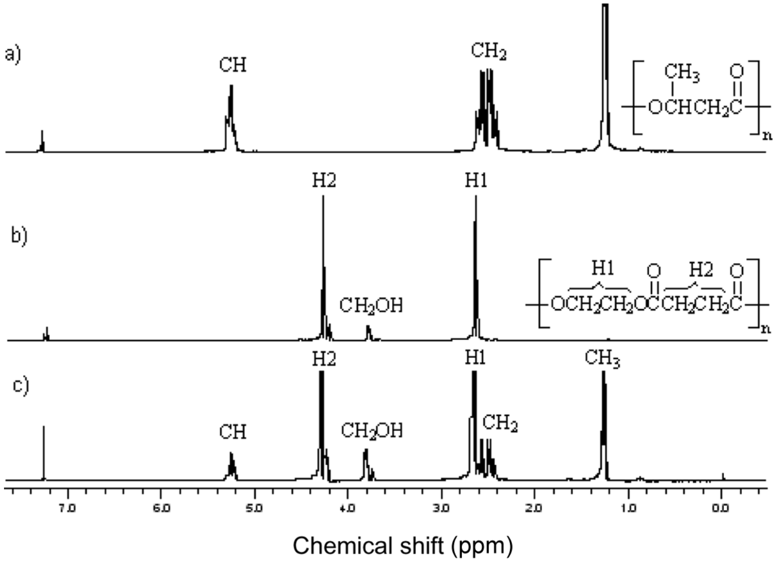

FIGURE 1 ^1H NMR spectra of a) PHB, b) PES and c) PHB/PES blend prepared without catalyst at 170°C for 20 min.

TABLE 1 ^{1}H NMR Chemical Shifts for PHB and PEST

		δ (ppm)		
Polymer	Hydrogen type	Experimental	Literature	Ref.
PES	H1	2.65	2.58	[25]
	$-CH_2OH^a$	3.79–3.82	3.55–3.75	
	H2	4.22–4.29	4.22	
PHB	CH	5.22–5.28	5.16–5.35	[19,20]
	CH_2	2.42–2.64	2.48–2.59	
	CH_3	1.26–1.28	1.24–1.30	

[a] PES end groups.

and PES obtained from ^{1}H NMR analyses are presented in Table 1 [19,20,25].

The spectrum of the blend processed with 4 wt% of Sm(acac)3 for 20 min is presented Figure 2. With addition of the Sm catalyst, no change is also seen, although one new peak at 1.64 ppm is evident. This peak was assigned to the presence of residual water.

From the ^{1}H NMR spectra of the blends, the OCH_2CH_2/CH ratio which is obtained by integration of intensities of PES methylenes and PHB methyne was calculated (Table 2), supplying information on of the content of PES and PHB in the blend after the processing and purification.

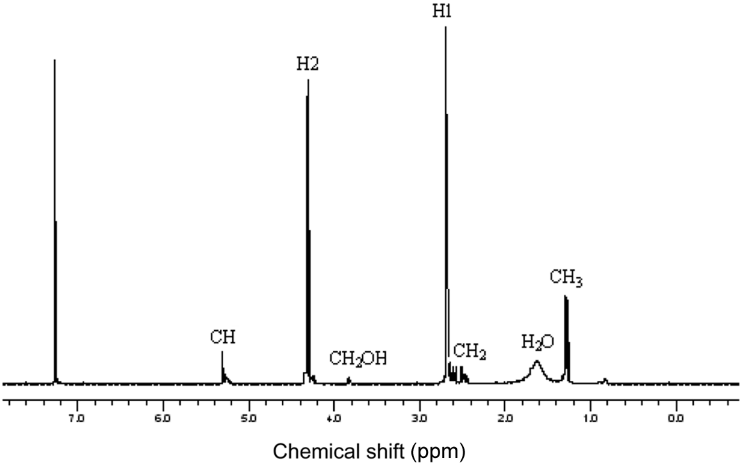

FIGURE 2 ^{1}H NMR spectrum of PHB/PES blend prepared in presence of 4 wt% of catalyst at 170°C for 20 min.

TABLE 2 OCH_2CH_2O/CH Ratio for PHB/PES Blends Prepared without and with $Sm(acac)_3$ Catalyst

Processing time (min)	$Sm(acac)_3$ (wt%)	(OCH_2CH_2O/CH) Ratio
20	0	5.10
20	1	5.10
5		5.77
10	4	4.35
20		3.24
40		0.06

Processing temperature: 170°C.

The blend with 4 wt% of $Sm(acac)_3$processed for 5 min presents a value of OCH_2CH_2O/CH ratio = 5.77, indicating that for that processing condition the content of PES in the blend is the higher one. When the same blend was processed at times between 5 and 40 min, a decrease in the OCH_2CH_2O/CH ratio was observed. The result suggested that with the increase in the processing time, a large fraction of PES was removed from the blend during the purification method (acetone extraction). The higher solubility of PES may have occurred due to the decrease in the molecular weight as the result of degradation processes.

In order to verify if a more drastic reaction condition would promote transesterification between the polyesters, additional thermal treatment of the blend prepared in the mixer at 170°C for 5 min was carried out. The thermal treatment was performed at 170°C for times up to 16 h and at higher temperature (200°C). To avoid the extraction of PES from the blend observed when purification was carried out by extraction with acetone, the purification of these thermal-treated

TABLE 3 OCH_2CH_2O/CH Ratio for PHB/PES Blends Prepared with 4 wt% $Sm(acac)_3$ at 170°C for 5 min Followed by Thermal Treatment at Different Conditions

Processing temperature (°C)	Time of thermal treatment (h)	(OCH_2CH_2O/CH) Ratio
	2	0.50
170	4	0.91
	6	1.18
	16	1.93
200	2	2.10

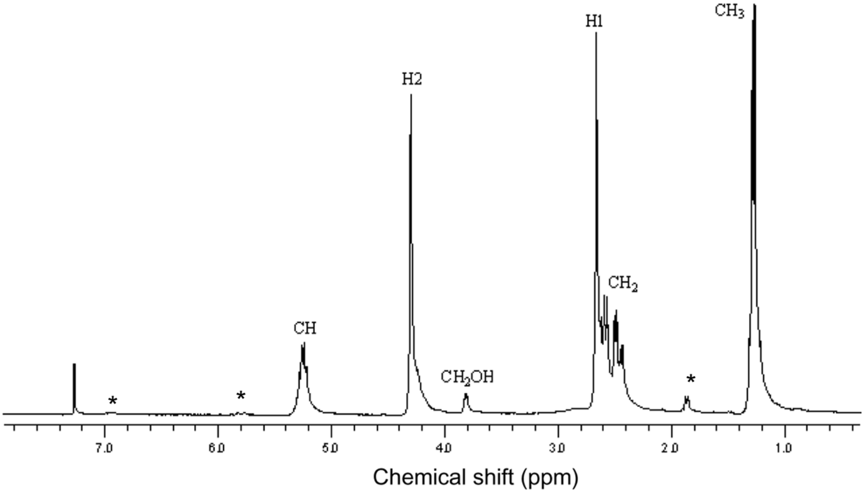

FIGURE 3 ^{1}H NMR spectra of PHB/PES blend prepared in a mixer (4 wt% of catalyst) at 170°C for 5 min and thermal treated at 170°C for additional 16 h (*Signals at 1.8; 5.8 and 6.9 ppm are associated with PHB thermal degradation [20]).

samples was done by precipitating chloroform solution of the blend in ethanol. The results are shown in Table 3.

^{1}H NMR spectra also suggested that no transesterification reaction took place, even at the drastic reaction condition used. Figure 3 shows the spectrum of the blend thermal treated at 170°C for 16 h. Besides the signals of the individual polymers, it presents new low-intensity signals at 1.8; 5.8 and 6.9 ppm. According to the literature those signals are associated with thermal degradation of PHB [20]. Thus, the increase of OCH_2CH_2O/CH ratio with the increase of processing time can be related to degradation of PHB. The peaks are broadened probably due the presence of residual catalyst.

TGA analyses were carried out for PHB and PES in order to have insight on the degradation behavior of both polymer constituents of the blend. The results confirmed that PES is more thermally resistant than PHB which is thermally unstable at temperatures above 170°C. For these PHB and PES samples, it was found an onset temperature of 204 and 279°C, a maximum degradation temperature of 268 and 373°C, and a weight loss at 250°C of 16.8 and 1.7%, respectively.

In principle, being a polyester, PHB may form miscible blends via transesterification with other main chain polyesters when blended by melt processing, particularly in the presence of efficient transesterification catalysts. Miscible polyester blends involving polymers such as poly(ethylene terephthalate) and poly(butylene terephthalate) or polycarbonate obtained when Sm(acac)$_3$ was used as a catalyst were reported in the literature [15,24]. Such a possibility, however, seems to be limited in the case of PHB/PES blends, since the melting points of these polymers are well below that of PET, PBT and PC and they suffer severe degradation under the conditions in which the aromatic polyesters were processed.

Changes in the Molecular Weight

From the GPC analysis, information on the molecular weight of the individual homopolymers in the blends were obtained. Table 4 presents the results of GPC.

Blend samples submitted to long heating times and/or high temperature showed only one peak, shifted to lower elution volumes, indicating the decrease in the molecular weight of PHB and probable overlap of curves. The table also shows that PHB has higher molecular weight than PES which is an oligomer with M_w 3,800. As expected, the molecular weight of both polymers decreased when they were processed. PHB M_w significantly decreased as the processing time and

TABLE 4 Molecular Weights and Polydispersity of PHB and PES in the Blends

PHB/ PES	Sm(acac)$_3$ (wt%)	T_p[a] (°C)	T[b] (min)	V_e (mL)	M_n	M_w	M_p	M_w/M_n
100/0	–	–[c]	–[c]	18.3	176,000	722,400	784,300	4.1
0/100	–	–[c]	–[c]	25.6	2,600	3,800	3,400	1.4
60/40	–	170	20	19.7	95,900	218,100	197,700	2.3
	1	170	20	19.2	108,000	282,500	198,200	2.6
	4	170	5	18.9	141,700	483,800	396,900	3.4
			10	19.2	122,300	420,600	326,300	3.4
			20	19.8	99,500	255,000	187,100	2.6
			40	20.3	36,300	131,000	118,700	3.6
			120	24.0	4,500	9,800	8,200	2.2
			240	24.1	3,600	7,500	7,800	2.1
			360	24.2	3,400	6,600	7,400	1.9
			960	24.3	3,000	5,600	7,000	1.9
		200	120	24.4	2,900	5,300	5,700	1.8

[a] T_p: processing temperature.

[b] Processing or thermal treatment time.

[c] Nonprocessed sample.

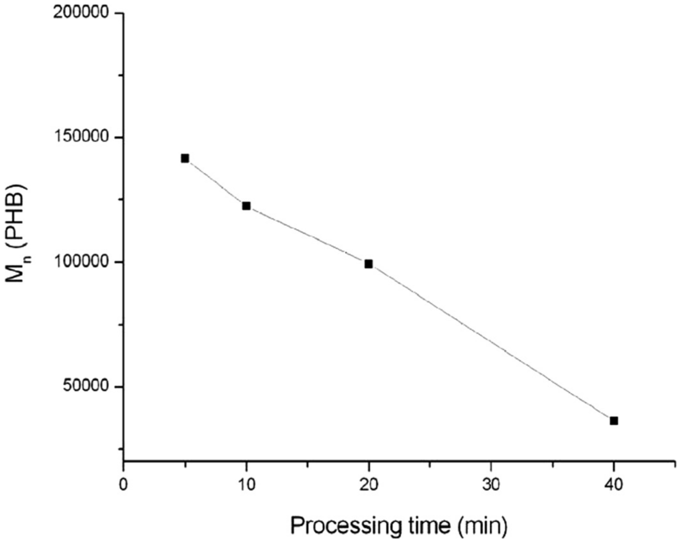

FIGURE 4 Number average molecular weight of PHB *versus* processing time of PHB/PES blends at 170°C.

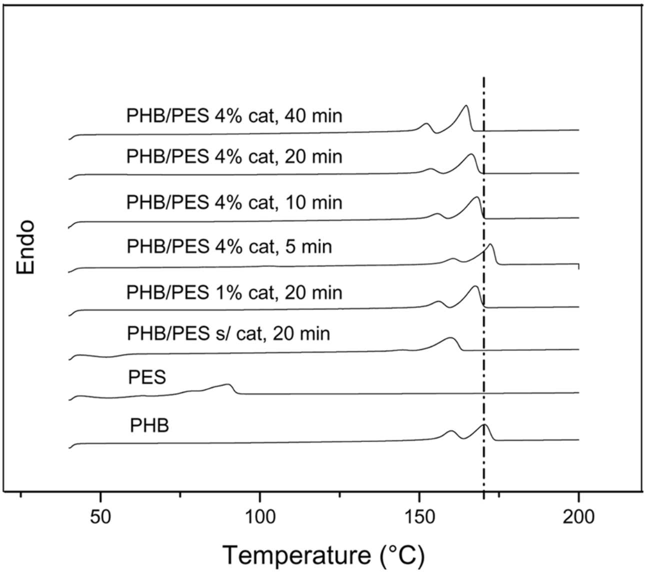

FIGURE 5 DSC thermal curve of second heating of PHB/PES blends processed at 170°C and different times without and with catalyst (1 and 4 wt%).

TABLE 5 Thermal Properties and Degree of Crystallinity of PHB/PES blends[a)]

PHB/PES	$Sm(acac)_3$ (%)	t_p (min)	T_c (°C)	T_m (°C)	ΔH_m(J/g)	X_c (%)
100/0	–	–[b)]	82,6	170.4	86.8	59.5
0/100	–	–[b)]	–	89.8	82.6	–
60/40	–	20	68,9	168.7	83.5	57.2
	1	20	68,3	167.5	82.6	56.8
	4	5	72,5	169.0	81.2	55.8
		10	69,1	168.1	80.3	55.2
		20	68,1	166.3	75.2	51.7
		40	69,5	164.7	63.9	43.9

[a] Processing temperature: 170°C, t_p = processing time, Tc = crystallization temperature, X_c = degree of crystallinity, ΔH_m = melting enthalpy.

[b] Sample not processed.

catalyst concentration was increased. The results suggest that the catalyst used is promoting the degradation reaction of PHB instead of exchange reaction between the two polyesters. The influence of processing time on the number average molecular weight of PHB in the blends is shown on Figure 4.

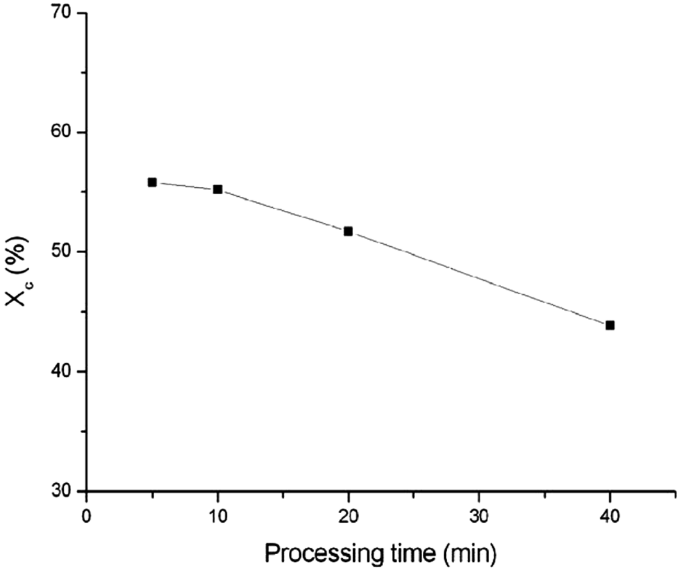

FIGURE 6 Degree of crystallinity *versus* processing time.

Thermal Behavior

Changes of thermal transitions of the blends were investigation by DSC. Figure 5 presents DSC traces of a second heating of PHB/PES blends prepared at 170°C and different processing times, without and with catalyst (1 and 4 wt%). In all blend curves only the melt transition temperature (T_m) of PHB was detected. Results of DSC analysis are shown in Table 5 that provides information about the miscibility of PHB and PES. Blending the polymers with addition of a catalyst ($Sm(acac)_3$) aimed to bring some compatibility between the components. Although in theory this catalyst could promote exchange reactions between the polyesters, resulting in the formation of

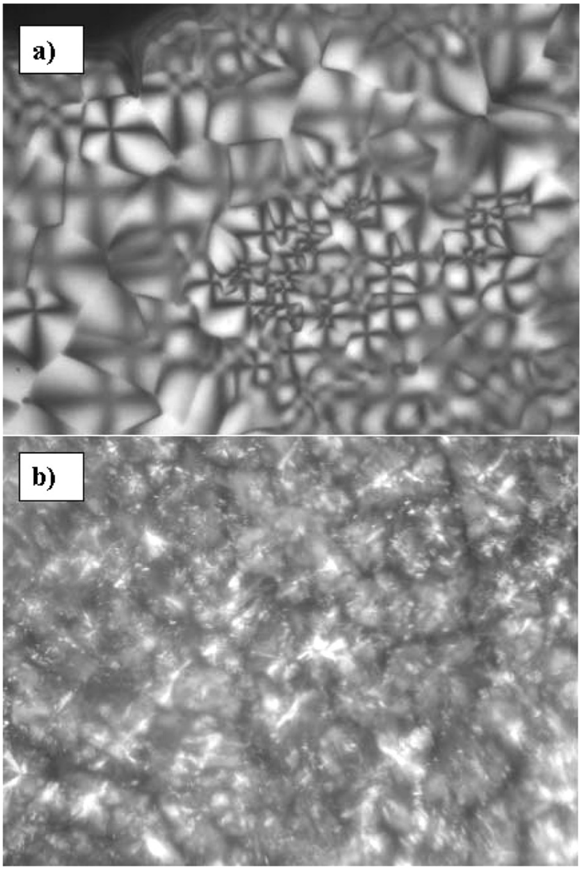

FIGURE 7 Optical images (40x) of a) PHB and b) PES.

copolymers that benefits interactions between the blends components [24], no evidence of miscibility was observed by the DSC analyses. However, the decrease in the PHB T_m was indicative of the influence of PES on the formation of PHB crystals. PES probably induced formation of less imperfect crystalline structures, decreasing of PHB Tm. The melting enthalpy (ΔH_m) and, as a consequence, the degree of crystallinity (X_c) of PHB in the blends decreased with the processing time (Figure 6). This behavior indicates that processing time interferes with the crystallization of PHB, reducing the formation of PHB crystals. The absence of PES melting peak indicated that this blend component constitutes the amorphous phase of the blend, being partially soluble in the amorphous phase of PHB.

For PHB/PES blends with and without catalyst only one crystallization temperature (T_c) was detected. The unique T_c was attributed to PHB crystallization, since in the DSC traces of PES no crystallization on cooling was observed. Comparing the blends with the homopolymers, a reduction in T_c, can be observed indicating the influence of PES in decreasing the rate of the crystallization of PHB. The T_c of PES was not detected probably due to the inadequate crystallization conditions for the reorganization of PES chains. Practically no change in the crystallization temperature was observed as the blends processing time was increased.

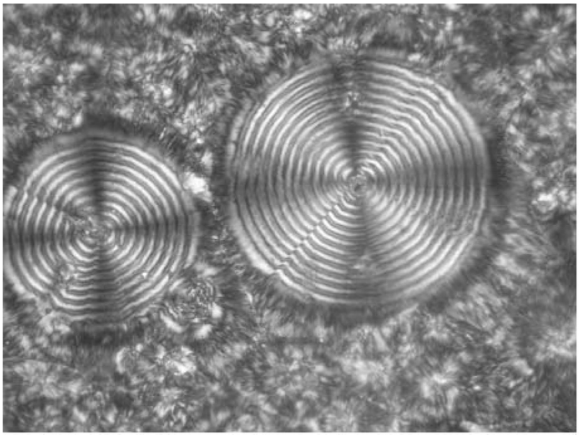

FIGURE 8 Optical image PHB/PES blends processed at 170°C for 20 min without catalyst (40x).

Morphology of the Blends

Figures 7–9 show the crystalline morphology of PHB, PES and their blends obtained by optical microscopy. PHB forms large perfect spherulites with the typical Maltese cross pattern while PES crystallites appear also as spherulites, however with sizes significantly smaller than that of PHB (Figure 7).

When the two polymers are blended without catalyst, drastic changes in the crystalline morphology are observed. The quantity of spherulites decreases and their sizes increase. In this case, the pattern of the crystals is completely different, showing concentric halos (Figure 8). The crystalline blend pattern became completely different

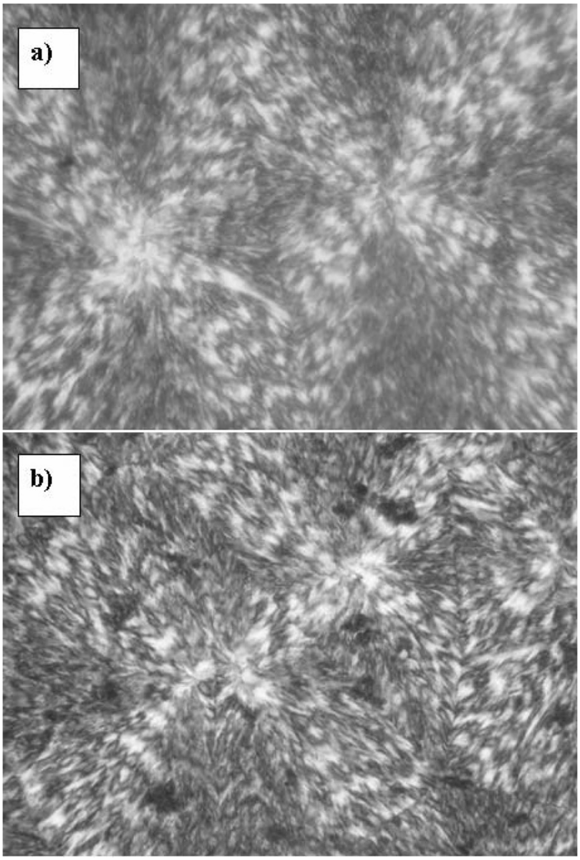

FIGURE 9 Optical images (40x) of PHB/PES blends processed at 170°C for 20 min with: a) 1 wt% catalyst and b) 4 wt%.

when a catalyst is used for the blend preparation. Spherulites became larger, probably as the result of the interference of the PES on PHB nucleation (Figure 9). Some small dark points in the images suggested some degree of phase segregation. The dark phase may be PES.

CONCLUSION

Low molecular weight poly(ethylene succinate) synthesized by bulk condensation polymerization was blended with PHB at 170°C in the presence of $Sm(acac)_3$, which was employed as transesterification catalyst. Even when using high content of catalyst (4 wt%) long reaction times and high temperatures (200°C), no evidence of the desired transreaction was observed. Nevertheless, under the drastic reaction condition employed, chain degradation is observed. This degradation is characterized by significant decrease of molecular weight (MW) of PHB which is the component with the higher MW. This decrease in the MW was associated with a catalytic effect of Sm. The impossibility of transreactions is attributed to the impossibility of processing the polymers at higher temperatures in which the transesterification have been reported for aromatic polyesters, such as PET, PBT and PC, because in the case of PHB and PES they suffer severe degradation at such high temperatures.

PHB/PES blends form immiscible systems in which the PHB continues showing the crystallization on cooling. However, its crystallization is significantly influenced by the presence of PES that does not crystallize at conditions in which PHB is crystallized. The presence of PES decreases the degree of crystallinity of PHB phase in the blend, but it makes the PHB crystallize as large spherulites.

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