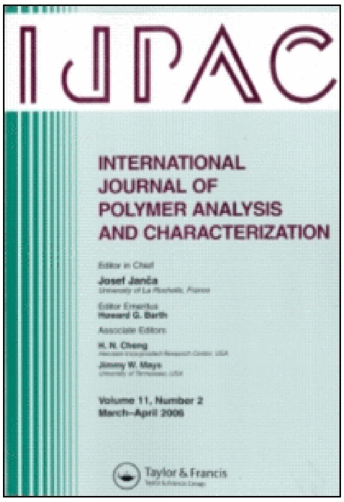

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Blends of Poly(Hydroxybutyrate) and Oligomeric Polyester

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Abstract: Blends of the commercial biodegradable polymer poly(hydroxybutyrate) (PHB) with an oligomeric polyester such as poly(ethylene isophythalate) (PEIP) were prepared in the molten state. PEIP was synthesized by bulk condensation polymerization using two types of catalysts. The occurrence of transesterification reaction during the blend processing using samarium acetilacetonate as catalyst was evaluated. The behavior of the blends was investigated by hydrogen nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The results show that PHB/PEIP blends are immiscible under the applied conditions, but a significant degradation of PHB occurs by the effects of time and temperature of processing.

Keywords: Blends; Degradation; PHB; Poly(ethylene isophthalate); Transesterification

INTRODUCTION

There has been great interest in blends of biodegradable polymers, such as poly(hydroxyalkanoates), owing to their potential application in fields such as biomedicine and packaging. The most representative

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member of the family, poly(hydroxybutyrate) (PHB), is a highly crystalline thermoplastic polyester that is completely biodegradable. It can be produced by bacteria growing in controlled fermentation conditions with a variety of resources like sugar, ethanol, and carbon dioxide and is applied like many conventional petrochemical-derived plastics currently in use.[1–7] PHB presents a melting point at about 180°C and degree of crystallinity around 70%,[8,9] but it has a narrow processing window, and, depending on the molecular weight, the material is quite brittle.[10–14]

Reactive blending is an interesting technology for preparing new polymer materials starting from different polymers, if they can undergo chemical reactions in the molten state[15] In the case of condensation polymers like polyesters, this requirement can be achieved since transreactions may occur during the melt processing at high temperatures, particularly if a catalyst is present.[16]

Several transition metal complexes have been described as good catalysts for these transreactions between polyesters.[17] As a polyester, PHB may form via transreaction in molten state, miscible blends with other main chain polyesters. Such a possibility is, however, greatly limited, since PHB is thermally unstable at high temperatures, and a drastic reduction of molecular weight occurs during processing at temperatures above 200°C.[18–20]

In the present work, blends of PHB with the synthetic semicrystalline polyester poly(ethylene isophthalate) (PEIP) were investigated, aiming to verify changes in the structure of the individual components during the preparation of blends. PEIP is an aromatic, thermoplastic with melting point around 240°C and glass transition at about 51°C.[21] As described for other blends, these polyesters could, in principle, react during the melt processing, resulting in copolymers containing unities of each homopolymer that constitutes the blend.[22–24]

EXPERIMENTAL SECTION

Materials

PHB (Biocycle) in the form of grains was supplied by PHB Industrial (Brazil) and used as received. PEIP was synthesized by a two-step bulk condensation polymerization of isophthalic acid and excess of ethylene glycol following a general technique described in the literature.[21] In the first step, transesterification was carried out using manganese acetylacetonate as catalyst with removal of water from the reaction medium. In the second step, phosphoric acid and antimony trioxide were added and ethylene glycol was removed by bubbling nitrogen at 200°C for 2 h. PEIP was obtained as a brittle white solid with molecular weight M_w of 5,600 g/mol determined by gel permeation chromatography (GPC).

Blend Preparation

Blends of commercial PHB with PEIP were prepared in a Haake Rhecord 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. 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 benzene polymer solution with ethanol.

Thermal Treatment

With the aim of submitting PHB/PEIP blends to more drastic reacting conditions, a blend processed in the Haake mixer in a 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 at 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 the chemical shifts. GPC was performed on a Waters system using $CHCl_3$ as solvent, a set of Phenomenex columns, and monodisperse polystyrene as calibration standard.

Spherulite sizes and their size distribution in the homopolymers and some of the blends were evaluated by optical microscopy in an Olympus BX 50 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 of 40°–200°C in the following sequence: first heating at 10°C/min, cooling at 10°C/min, and 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 as 146 J/g for PHB.[25]

The samples of PHB and PEIP were analyzed by thermogravimetric analysis using a TA Instruments Q500 Thermal Analyser under nitrogen flow from 25° to 700°C at the rate of 10°C/min.

RESULTS AND DISCUSSION

Structure of Polymers after Processing

Figure 1 shows the ^{1}H NMR spectra of PHB, PEIP, and a PHB/PEIP blend obtained without any catalyst. The spectrum of the blend showed that no transesterification reactions occurred when the blend is prepared in the absence of additional catalyst (PEIP contains residual $Mn(acac)_2$ and Sb_2O_3 catalyst), since characteristic peaks of only the homopolymers

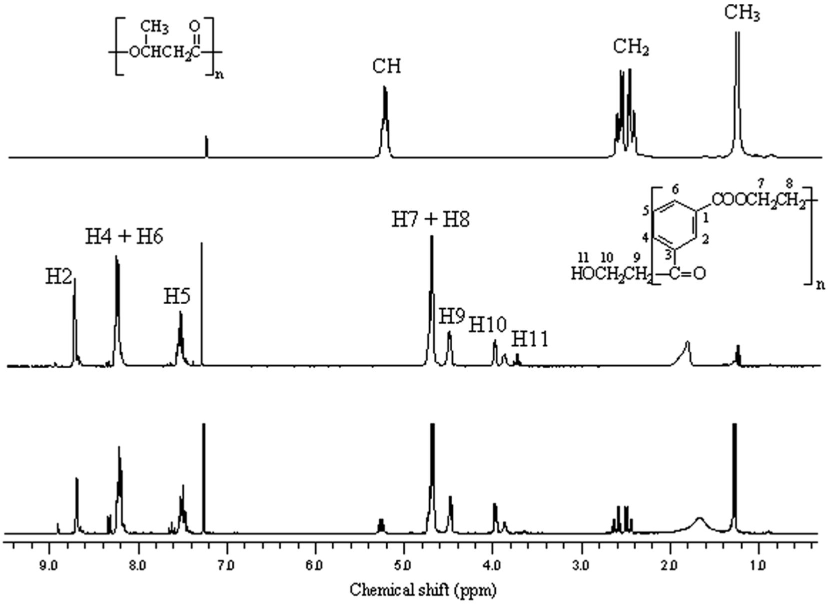

Figure 1. ^{1}H NMR spectra of (a) PHB, (b) PEIP, and (c) PHB/PEIP blend prepared without catalyst at 170°C for 20 min.

Table I. ^{1}H NMR chemical shifts for PHB and PEIP

		δ (ppm)		
Polymer	Hydrogen type	Experimental	Literature	Reference
PEIP	H2	8.66–8.69	8.73	27
	H4 + H6	8.18–8.24	8.15	
	H5	7.48–7.55	7.35	
	H7 + H8	4.68–4.70	4.60	
	H9	4.47–4.49	4.45	
	H10	3.96–3.99	3.74	
	H11	3.85–3.89	—	
PHB	CH	5.22–5.28	5.16–5.35	18,19
	CH_2	2.42–2.64	2.48–2.59	
	CH_3	1.26–1.28	1.24–1.30	

were detected. Chemical shifts of PHB and PEIP obtained from ^{1}H NMR analyses are presented in Table I.[18,19,26]

The peaks that appeared in the spectrum of PEIP at 1.22–1.26 and 3.72–3.74, 1.83, and 3.86–3.89 ppm are attributed to the presence of ethanol, water, and CH_2CH_2OH end groups in the sample, respectively.[27]

The spectrum of the blend processed with 4 wt% of $Sm(acac)_3$ for 20 min is presented in Figure 2. With the addition of the catalyst, no change is also seen, although one new peak at 3.67 ppm is evident. This peak was assigned to the presence of the residual ethanol.

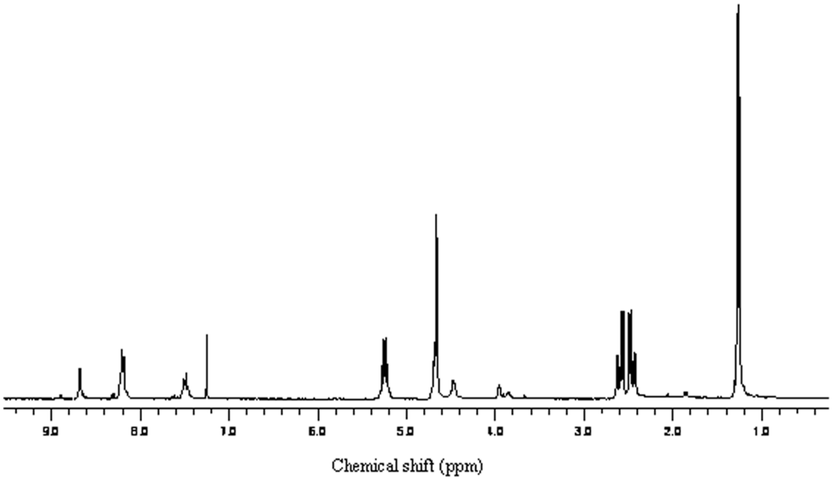

Figure 2. ^{1}H NMR spectrum of PHB/PEIP blend prepared in presence of 4 wt% of catalyst at 170°C for 20 min.

Table II. OCH_2CH_2O/CH ratio for PHB/PEIP blends prepared without and with $Sm(acac)_3$ catalyst

Processing time (min)	$Sm(acac)_3$ (wt%)	(OCH_2CH_2O/CH) ratio
20	0	14.4
20	1	14.5
5		14.3
10	4	10.7
20		1.42
40		1.56

Processing temperature: 170°C.

The ^1H NMR spectra were used to calculate the OCH_2CH_2O/CH ratio, which is obtained by integration of intensities of PEIP methylenes and PHB methyne. Table II contains the results obtained and shows that for the blend processed for 20 min without a catalyst or with 1 wt% of Sm $(acac)_3$ the OCH_2CH_2O/CH ratio was invariable and equal to 14.5.

The blend with 4 wt% of $Sm(acac)_3$ processed for 5 min presents a value of OCH_2CH_2O/CH ratio = 14.3, indicating that under these processing conditions, the content of PEIP in the blend is equal to those of blends processed for 20 min. When the same blend was processed at times between 5 and 40 min, a dramatic decrease in the OCH_2CH_2O/CH CH ratio was observed. The result suggests that with increase in processing time, a large fraction of PEIP was removed from the blend during the purification method (acetone extraction). The higher solubility of PEIP may have occurred due to 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, thermal treatment at 170°C for times of up to 16 h or at a higher temperature (200°C) was applied to blends previously prepared at 170°C for 5 min. To avoid the extraction of PEIP from the blend observed when the purification was carried out by extraction with acetone, the purification of these thermally treated samples was done by precipitating the blend chloroform solution with ethanol. The results are shown in Table III.

An increase in the OCH_2CH_2O/CH ratio is observed as the processing time or temperature was increased. ^1H NMR spectra also showed that no transestrification reaction took place, even under the drastic reaction condition used. Figure 3 shows the spectrum of the blend thermally treated at 170°C for 2 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, the signals are associated with the thermal degradation of

Table III. 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 time (h)	Processing temperature (°C)	(OCH_2CH_2O/CH) ratio
2	170	0.39
4		0.86
6		1.26
16		5.69
2	200	7.36

PHB.[19] Thus, the increase of OCH_2CH_2O/CH ratio with the increase of processing time can be related to the degradation of PHB. The peaks are broadened probably due to the presence of residual catalyst used.

Changes in Molecular Weight

From the GPC analyses, the information on the molecular weight (MW) of the individual homopolymers in the blends was obtained (Table IV).

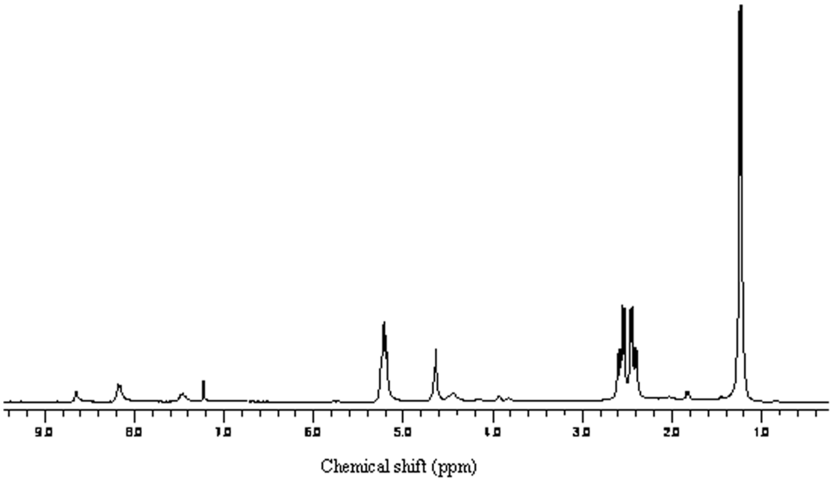

Figure 3. ^1H NMR spectra of PHB/PES blend prepared in a mixer (4 wt% of catalyst) at 170°C for 5 min and thermal treated at 170 for additional 2 h (signals at 1.8, 5.8, and 6.9 ppm are associated with PHB thermal degradation[19]).

Table IV. Molecular weights and polydispersity of PHB and PEIP in the blends

PHB/PEIP	% Sm(acac)$_3$	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}	24.9	3,400	5,600	5,000	1.6
60/40	—	170	20	19.2/25.2	187,200/2,400	393,000/4,300	309,700/4,300	2.1/1.8
	1		20	19.9/24.9	147,400/3,000	237,800/4,800	163,300/4.900	1.6/1.6
			5	20.2/25.0	111,000/3,000	191,600/4,700	130,300/4,400	1.7/1.6
			10	20.5/25.2	91,100/2,700	131,100/4,500	101,700/4,300	1.4/1.5
			20	20.9/25.4	72,000/2,000	86,900/3,400	74,500/4,700	1.2/1.7
			40	21.0/25.5	59,400/1,900	81,700/3,500	69,400/4,600	1.4/1.8
	4		120	23.6	5,300	10,900	8,200	2.0
			240	23.7	5,200	13,000	12,400	2.5
			360	23.9	3,700	8,800	9,100	2.4
			960	24.7	3,000	5,800	5,600	1.9
		200	120	24.8	2,700	4,200	4,000	1.5

[a] Processing temperature.
[b] Processing or thermal treatment time.
[c] Unprocessed sample.

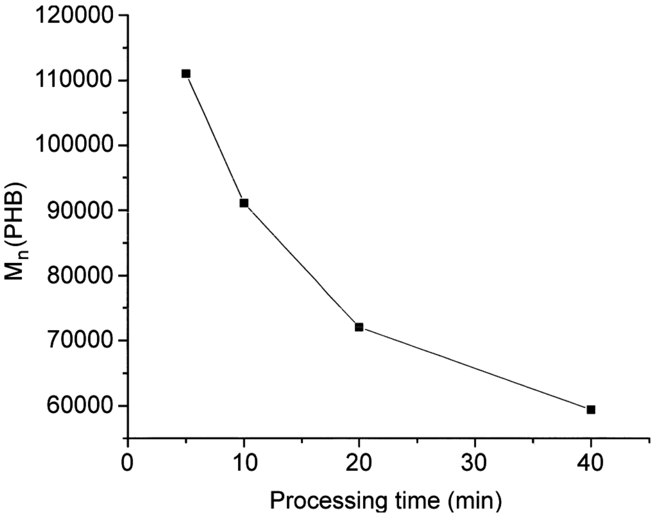

Figure 4. Number average molecular weight of PHB vs. processing time of PHB/PEIP blends processed at 170°C with 4 wt% catalyst.

Blend samples submitted to long heating times and/or high temperature presented only one peak shifted to lower elution volumes, indicating the decrease in the MW of PHB and probable overlap of the curves. The table also shows that PHB has higher MW than PEIP, which is an oligomer with $M_w = 5{,}600$ g/mol. As expected, the MW of both polymers decreases when they are processed. PHB M_w significantly decreases as the processing time and catalyst concentration were 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 in Figure 4.

Thermal Behavior

TGA analyses were carried out for PHB and PEIP (Figure 5) in order to gain insight on the degradation behavior of both polymer constituents of the blend. The results confirmed that PEIP is more thermally resistant than PHB, which is thermally unstable at temperatures above 200°C. For these PHB and PEIP samples, onset temperatures of 204° and 364°C and maximum degradation temperatures of 268° and 433°C were found, respectively.

Figure 6 presents DSC traces of a second heating of PHB/PEIP blends prepared at 170°C and different processing times, without and

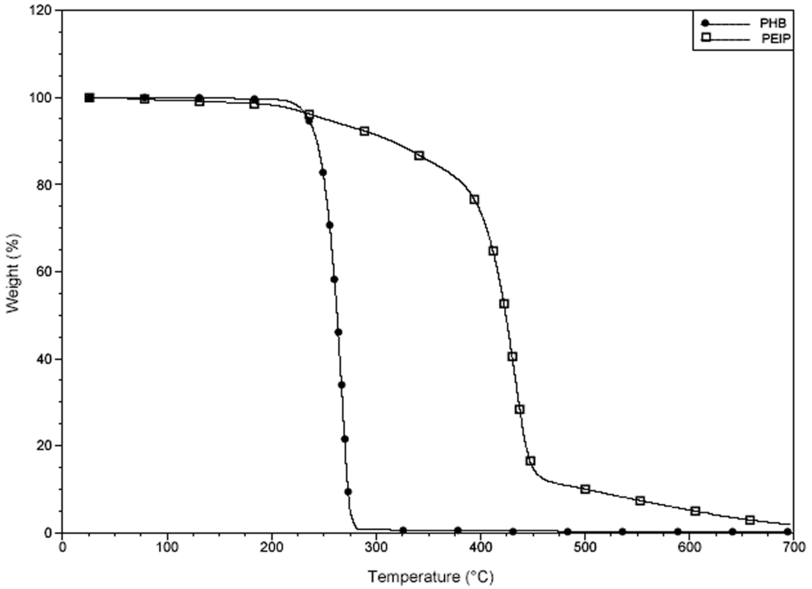

Figure 5. TGA of samples PHB and PEIP.

with the catalyst (1 and 4 wt%). Although PEIP presented a certain degree of crystallinity and a melt transition temperature (T_m) at 112°C, for all blend curves only the bimodal T_m of PHB was detected.

Results of DSC analyses are shown in Table V, which also provides information on the miscibility of the PHB/PEIP system. Blending the polymers with the addition of a catalyst ($Sm(acac)_3$) was intended to bring some compatibility between the components. Although in theory this catalyst could promote exchange reactions between the polyesters, resulting in the formation of copolymers that benefits interactions between the blend components,[28] no evidence of miscibility was observed from the DSC analyses. However, the decrease in the PHB T_m was indicative of the influence of PEIP on the formation of PHB crystals. PEIP probably induced the formation of less imperfect crystalline structures, decreasing PHB T_m. The melting enthalpy (ΔH_m) and, as consequence, the degree of crystallinity (X_c) of PHB in the blends decreased with processing time. This behavior indicates that processing time affects the crystallization of PHB, reducing the formation of PHB crystals. The absence of PEIP melting peak indicated that this blend component constitutes the amorphous phase of the blend, being partially soluble in the amorphous phase of PHB.

All PHB/PEIP blends presented cold crystallization (T_{ch}), which was attributed to PHB crystallization. Practically no change in this T_{ch} was

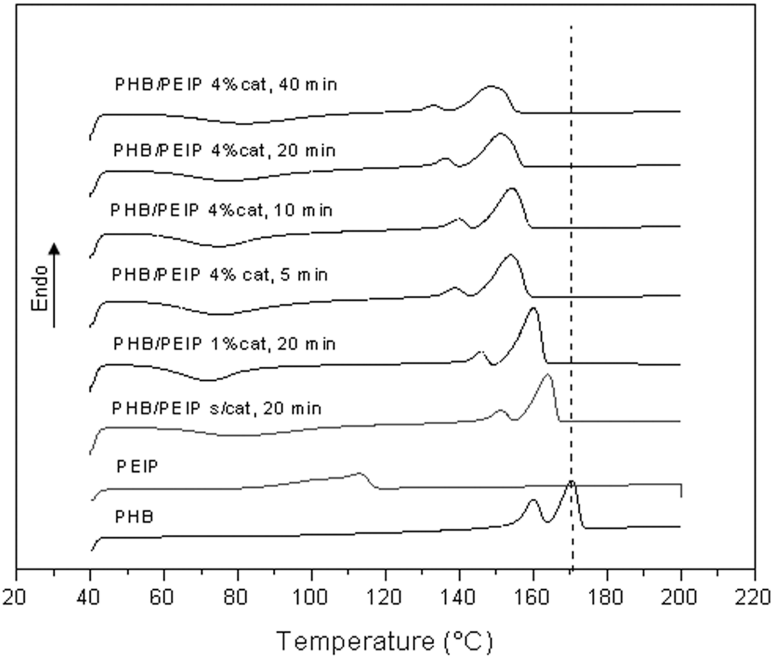

Figure 6. DSC thermal curve of second heating of PHB/PEIP blends processed at 170°C and different times without and with catalyst (1 and 4 wt%).

Table V. Thermal properties and crystallinity of PHB/PEIP blends

PHB/PEIP	$Sm(acac)_3$ (%)	t_p (min)	T_{cc} (°C)	T_{ch} (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
100/0[a]	—	—	82.6	—	170.4	86.8	59.5
0/100[a]	—	—	—	—	112.7	48.4	—
	—	20	—	79.5	164.0	51.4	35.3
	1	20	—	71.9	160.1	51.1	35.1
60/40		5	—	75.3	153.9	53.9	37.1
	4	10	—	75.3	154.1	57.6	39.6
		20	—	76.8	151.1	52.6	36.1
		40	—	81.6	148.4	46.4	31.9

Processing temperature: 170°C, t_p = processing time, T_{cc} = crystallization temperature on cooling, T_{ch} = crystallization temperature on heating (cold crystallization), T_m = mean melting temperature, ΔH_m = melting enthalpy, X_c = degree of crystallinity.

[a] Unprocessed samples.

observed as the processing time was increased. The blends did not show any crystallization on cooling at 10°C/min from 200°C to room temperature.

Morphology of the Blends

Figures 7–9 show the crystalline morphology of PHB, PEIP, and their blends obtained by optical microscopy. PHB forms large perfect

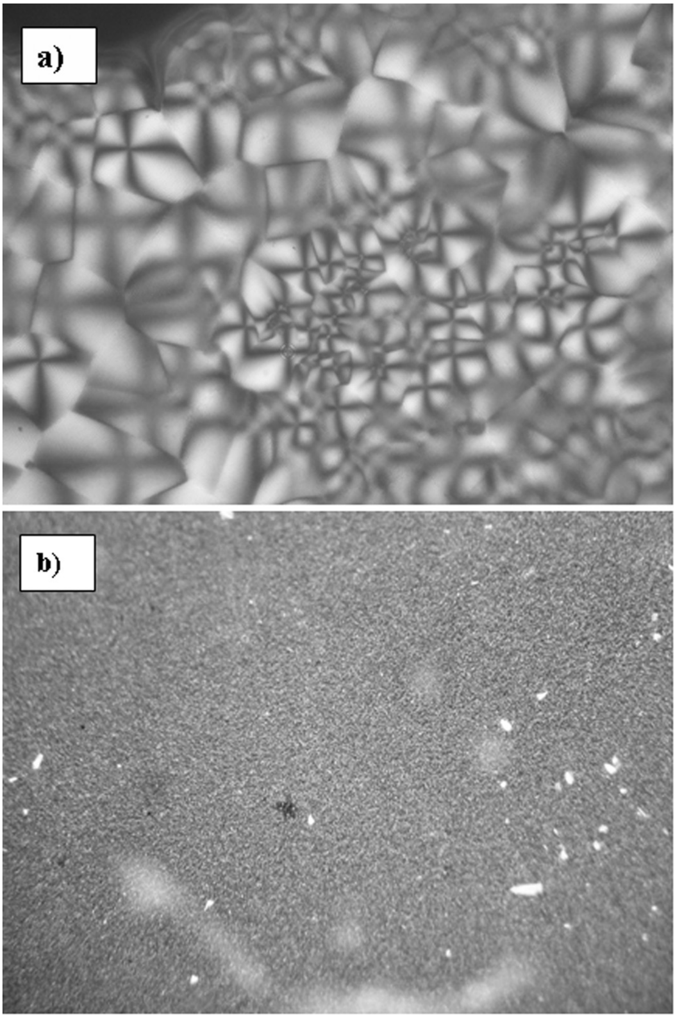

Figure 7. Optical images (10×) of (a) PHB and (b) PEIP.

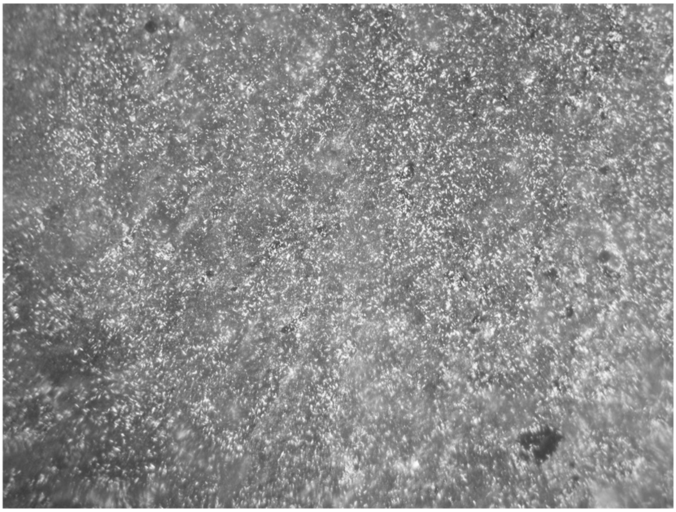

Figure 8. Optical image (10×) of PHB/PEIP blends processed at 170°C for 20 min without catalyst.

spherulites with the typical Maltese cross pattern, while PEIP crystallites appear also as small crystals with sizes significantly smaller than those of PHB (Figure 7).

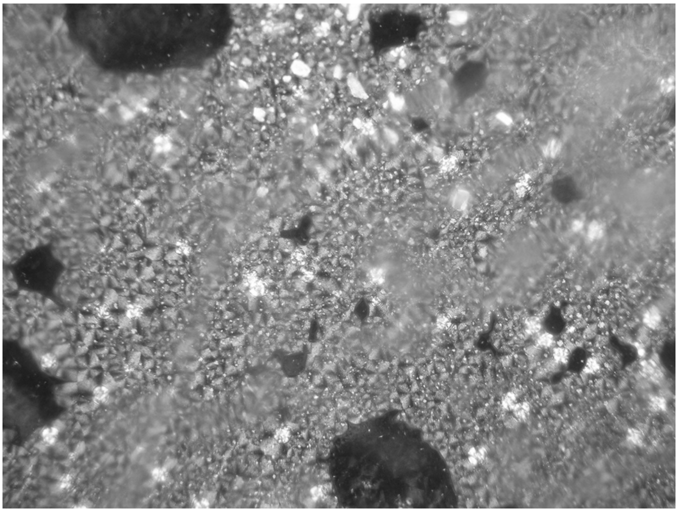

Figure 9. Optical image (10×) of PHB/PES blends processed at 170°C for 20 min with 4 wt% catalyst.

When the two polymers are blended without catalyst, drastic changes in the crystalline morphology were observed, as shown by the patterns in Figures 8 and 9. The blends are crystalline materials containing a large quantity of small crystals like PEIP (Figure 7). The blend prepared in the presence of 4 wt% catalyst indicated, however, the evidence of spherulite formation in addition to black spots indicative of phase separation.

CONCLUSION

Poly(ethylene isophthalate) (PEIP) was synthesized by melt bulk condensation polymerization using manganese and antimony catalysts. Due to the impossibility of using a stage of solid-state polymerization, a process normally employed to produce high MW aromatic polyesters, low MW was obtained. Blends of PHB with this low MW PEIP form immiscible systems. Attempts to generate transreactions between the blend components by either using $Sm(acac)_3$ as transesterification catalyst or carrying out thermal treatment for longer times or at a higher temperature below the known PHB onset degradation temperature (200°C) were unsuccessful. Instead of transesterification, only degradation was observed. This degradation is characterized by significant decrease of the MW of PHB, which is the component with the higher MW. The dramatic decrease in the MW is associated with the catalytic effect of Sm. The reason there were no transreactions is attributed to the impossibility of processing the polymers at higher temperatures at which transesterification has been reported for aromatic polyesters, such as PET, PBT, and PC. The addition of PEIP to PHB influences the blend crystallization, decreasing the degree of crystallinity of PHB phase.

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