

Films of PLLA/PHBV: Thermal, Morphological, and Mechanical Characterization

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ABSTRACT: Blends of poly(L-lactic acid)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PLLA/PHBV), both semicrystalline polymers, were prepared in different compositions (100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100) and characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), polarized light microscopy (PLM), and tensile tests. Although PLLA/PHBV blends do not present clear phase separation by SEM, the analyses by TGA, DSC, and DMA showed that

the PLLA/PHBV blends are immiscible. The cross sections observed by SEM showed that the morphology of the blends changes from porous to dense, due to the composition. DSC and DMA data showed two distinct glass transition and melting temperatures. However, the DMA analysis related to frequency variation showed partial molecular interactions between PHBV and PLLA. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2898–2906, 2002

Key words: blends; films; polyesters; biomaterials

INTRODUCTION

Aliphatic polyesters derived from glycolic acid, D- and L-lactic acid, β -hydroxybutyrate, and ϵ -caprolactone are the most important biodegradable polymers. The growing study of biodegradable polymers, as well as that of new materials, generated an increase of polymer use in medicine, such as for sutures, surgical implants, and components for the controlled liberation of drugs.^{1–8}

Poly(L-lactic acid) (PLLA) has some potential advantages such as its high strength, thermoplastic behavior, biocompatibility, and availability from renewable sources and has been classified as water-sensitive since it degrades slowly compared to water-soluble or water-swollen polymers.⁵ PLLA degrades by hydrolysis, in the presence of water, to lactic acid and is thereby suitable as a resorbable, nontoxic material for surgical use.³

The microbial polyester family represents another source of biodegradable materials. Different polyhydroxyalkanoate copolymers such as polyhydroxybutyrate-co-hydroxyvalerate (PHBV) are obtained through several microorganisms. Their properties can be modified by changing the composition of the copolymer by

variation of the feed of the bacteria.^{1,9,10} Polyhydroxyalkanoates (PHAs), produced by the fermentation of a large variety of bacteria, are environmentally degradable thermoplastics that can be processed with conventional equipment. Among the PHAs, poly(3-hydroxybutyrate) (PHB) is the most studied and the easiest to produce. It has thermal and mechanical properties similar to those of polypropylene (PP).

Molded PHB shows ductile behavior, but progressive crystallization at ambient temperature causes embrittlement due to the constraining of the amorphous chains between the crystals.¹¹ A method to improve the mechanical properties is the incorporation of 3-hydroxyvalerate (3HV) units into the PHB backbone during the fermentation process. This produces poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB-co-3HV), or simply PHBV, copolymers, which have improved flexibility and lower melting points than those of PHB.¹¹

The blending of polymers is an effective alternative way of acquiring new materials with desired properties. Generally, blends exhibit advantageous physical and mechanical properties that each individual polymer does not have. Depending on the thermodynamic compatibility of the two chosen polymers, phase-separated polymers can be obtained, imposing different morphologies and matrix characteristics.^{6–10}

Blends in which both components are semicrystalline polymers are more complex and thus open up new ways of studying the relations between phase behavior and structure development in polymeric mixtures. The formation and morphology of the semi-

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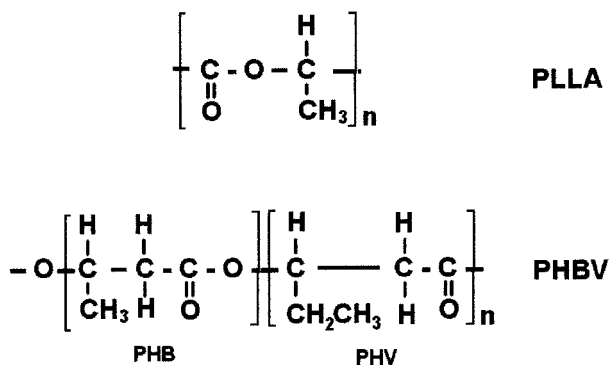


Figure 1 Chemical formulas of PLLA and PHBV.

crystalline/semicrystalline state is particularly interesting, since it involves the crystallization of two different polymers, each within its specific temperature regime.¹²

PLLA, submitted *in vitro* or *in vivo* studies, loses its mechanical strength very quickly,⁴ while PHBV maintains its mechanical properties for a long time at 37°C and pH 7.4.^{13,14} The aim of this work was to investigate the thermal, morphological, and mechanical properties of PLLA/PHBV blends for use in the medical area.

EXPERIMENTAL

In this work PLLA, molar weight, $M_w = 100,000$ (Medisorb, Cincinnati, OH; DuPont), and PHBV, with 12% of hydroxyvalerate (HV; Aldrich, Milwaukee, WI), were used. The solvent was methylene chloride (Synth, Diadema, Sao Paulo, Brazil).

The chemical formulas of the polymers are shown in Figure 1.

Blend preparation

Polymers were dissolved separately in methylene chloride, at a concentration of 5% (w/v) and stirred for complete dissolution. The final compositions of the PLLA/PHBV blends were 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 (w/w), which were stirred to complete homogenization, and the mixture of PLLA/PHBV was poured onto a glass plate. The glass plate containing the blend in a solution was placed in a glass box to dry, saturated with vapor from the solvent. After the evaporation of the solvent, membranes with a thickness of approximately 0.14 mm were obtained. After drying, the membranes were maintained under a vacuum. Samples were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), polarized light microscopy (PLM), and tensile tests.

TGA

For the TGA analysis, the equipment used was an STA 409C thermal analyzer of NETZSCH-Gerätebau GmbH. The samples were heated from 25 to 400°C with a heating ramp of 10°C/min in an atmosphere of helium.

DSC

Thermal transitions of the blends were measured by DSC, using an STA 409C thermal analyzer of NETZSCH-Gerätebau GmbH at a heating rate of 10°C/min in an atmosphere of helium. Samples were first heated from 25 to 200°C to study the thermal properties of the solvent-cast materials. The samples were maintained at this temperature for 5 min, until completely melted, thus eliminating the thermal history. They were then cooled to -20°C for more than 5 min and heated again to 200°C to study the behavior in the absence of the previous thermal histories. The melting temperatures of the two phases and the heat associated with the melting and/or crystallization were determined by DSC.

DMA

The glass transitions of the PLLA and PHBV phases of the solvent-cast systems were studied by DMA using a NETZSCH dynamic mechanical analyzer 242. The samples were cooled to -25°C and soon after heated to 200°C, with a heating ramp of 5°C/min, under air, with a maximal dynamic force of 1 N, a frequency of 1 Hz, and width of 15 μm by the tension system.

For the DMA analysis with frequency variation, samples were submitted to cooling until -20°C and soon after heated to 200°C, in 20 steps of 11°C, with a heating ramp of 5°C/min, at frequencies of 0.1, 0.25, 0.5, 1, and 2 Hz and a width of 15 μm. The analyses were carried out in the tension system.

SEM analysis

A JEOL electronic microscope JXA 840A (tension of 10–20 kV) was used to observe the fracture surfaces of the blends in different compositions, which were coated with a thin layer of gold, using a BAL-TEC SCD 050 sputter coater.

PLM analysis

Films of about 40-μm thick pressed between two cover glasses were obtained by melt pressing at 200°C for 1 min at 34 kg/cm². Before crystallization, the samples were first heated to 200°C for 1 min, after which they were cooled to $T_{c1} = 100^\circ\text{C}$ and $T_{c2} = 75^\circ\text{C}$. A Zeiss Axiophot polarizing microscope equipped with a hot

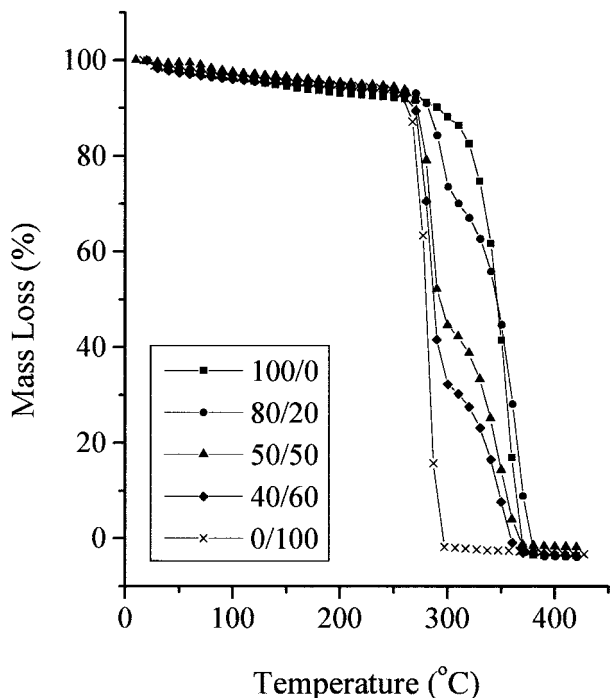


Figure 2 TGA thermograms of PLLA/PHBV blends in different compositions: 100/0, 80/20, 50/50, 40/60, and 0/100. stage (Mettler FP82) was used to visualize the morphology.

Tensile tests

For tension testing, 0.15-mm-thick samples cut in a rectangular format of 5×2.5 mm (each sample was measured seven times) were used. A tension system-type analysis was carried out, at a rate of 10 mm/min, using an equipment for mechanical tests: Instron Corp. Seriate IX Automated Materials Testing System 1.09.

RESULTS AND DISCUSSION

TGA

Figure 2 shows the curves obtained by TGA for different blend compositions. It can be observed that the degradation of each polymer occurred separately.

According to Table I, PHBV began to degrade around 270°C (T_{onset}), reaching a peak temperature (T_{peak}) around 283°C followed by its complete degradation. PLLA began to degrade approximately at 330°C, and its peak temperature was around 352°C. Above 250°C, the thermal stability of the blends was relatively improved by the addition of PLLA to the blend.

DSC

Curves obtained from the first heating (Fig. 3) showed only glass transition temperatures (T_g) of PLLA and

TABLE I
Degradation Temperatures of PLLA/PHBV Blends in Different Compositions Obtained by TGA

	T_{onset} (°C)		T_{peak} (°C)	
	PHBV	PLLA	PHBV	PLLA
100/0		330		356
80/20	284	344	295	366
50/50	275	330	283	352
40/60	273	331	281	352
0/100	271		286	

T_{onset} = temperature of the beginning mass loss; T_{peak} = temperature of the maximum mass loss.

melting temperatures (T_m) of PHBV and PLLA. On the other hand, from the second heating (Fig. 3), it is possible to observe glass transition temperatures (T_g) of PHBV and crystallization (T_c) and melting (T_m) temperatures for two polymers separately. These data are summarized in Table II.

It can be observed that the glass transition temperature (T_g) of PLLA was around 50°C and that of PHBV was around -1 °C, and they did not suffer significant variation with the blend composition. Nevertheless, when the first heating began at a temperature below the T_g of PHBV, this was only obtained in the second heating. The T_g did not appear because PHBV is a polymer that crystallizes very fast and the amorphous areas do not present enough mobility to characterize

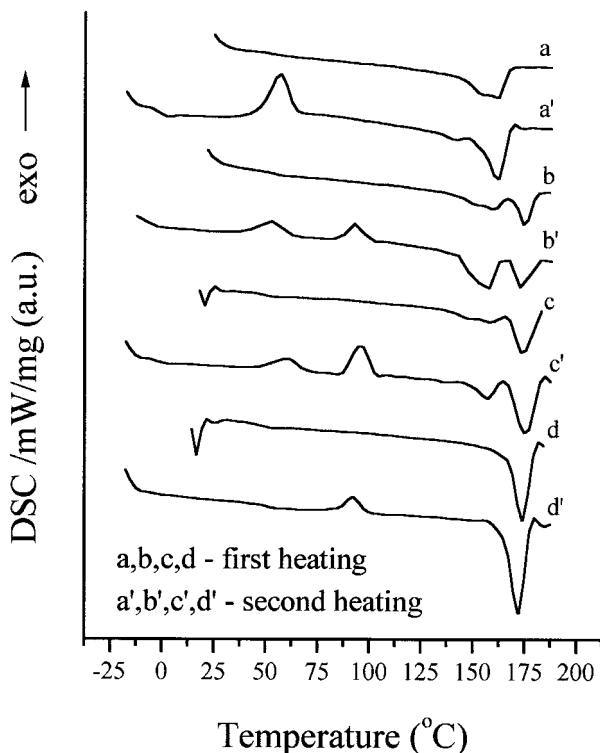


Figure 3 DSC thermograms of PLLA/PHBV blends in different compositions: (a) 0/100, (b) 40/60, (c) 60/40, and (d) 100/0, first and second heatings.

TABLE II
Glass Transition (T_g), Crystallization (T_c), and Melting (T_m) Temperatures, Crystallization (ΔH_c) and Melting (ΔH_f) Enthalpies, and Crystallinity Degree (χ) Obtained by DSC for PLLA/PHBV Blends in Different Compositions

DSC	Heat	T_g (°C)		T_c (°C)		ΔH_c (J/g)		T_m (°C)		ΔH_f (J/g)		χ (%)
		PHBV	PLLA	PHBV	PLLA	PHBV	PLLA	PHBV	PLLA	PHBV	PLLA	
100/0	1°		47								39	42
	2°		49		93		8		175		42	
80/20	1°		49								30	40
	2°		52		87		17	154	175	4	41	
60/40	1°		48					158	175	6	19	34
	2°	-1		60	95	9	15	138-158	175	13	27	
50/50	1°		53					160	175	7	14	30
	2°	0		58	98	11	11	139-159	176	16	19	
40/60	1°		52					160	175	11	10	27
	2°			53	93	9	8	157	175	25	14	
20/80	1°		54					153-161	176	22	5	27
	2°	0		63	103	27	3	143-162	177	31	5	
0/100	1°							156-161		30		
	2°	-2		57		25		141-161		38		

the T_g .² The T_g of PLLA, when mixed with PHBV, was observed only in the first heating, because, in the second heating, the T_g was overlaid by the PHBV crystallization peak.

It can be observed in Table II that the T_c for PHBV and for pure PLLA was around 58 and 95°C, respectively. Those values show a minimal variation due to the blend composition. According to Iannace et al.¹ and Penning and Manley,¹² this is an indication that cocrystallization did not occur; thus, the crystallization of each of the two blend components represents a phase-separation process in which the polymers partially segregate from the mixture to form a pure phase. The fact that T_c was only observed in the second heating means that the process used to obtain the membranes was slow enough to crystallize all the crystals, while the thermal treatment from DSC analysis did not avoid complete crystallization.

Melt temperatures were 145 and 160°C for PHBV and 175°C for PLLA. It was observed that the melting transitions of PHBV generally occur in two stages: According to Verhoogt et al.,¹¹ the presence of two or more peaks can be due to the thickness of the crystals and/or recrystallization that occurs during the heating in the DSC. Usually, the lower-temperature peak is considered to be the "true" melting point, since it most closely represents the behavior of the original, unannealed crystals.

It can be noticed that there was no variation in the melt temperature of PLLA with the blend composition. The fact that the melting temperature (T_m) peak of both polymers remained constant and the system shows two glass transitions temperatures in relation to the composition is an indication of the immiscibility of the blends.^{15,16} These results agree with Zhang et al.'s results for PHB/PLLA blends.²

Table II shows crystallization and melting enthalpy variations for different blend compositions. As ex-

pected, with decrease of the polymer composition in the blend, its crystallization and melting enthalpies decreased.

It was possible to obtain the crystallinity degree (χ %) of the PLLA in the blend from the data of the experimental melting enthalpy, the experimental crystallization enthalpy, and the calculated melting enthalpy of the PLLA, considering the polymer to be 100% crystalline, 93.7 J/g,¹⁷ as shown in the following equation:

$$\chi = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100$$

where ΔH_m is the experimental melting enthalpy (J/g), ΔH_c is the experimental crystallization enthalpy (J/g), and $\Delta H_m^0 = 93.7$ J/g.¹⁷ The values of ΔH_m obtained from the analysis of DSC were recalculated considering the composition of the polymer in the blend. The values obtained for the crystallinity degree are in Table II. With increase of PHBV in the blend, the degree of crystallinity of PLLA, due to the mixture, decreased. The increase of PHBV in the blend may have interfered with the nucleation density of PLLA. Penning and collaborators¹² observed the same behavior in PVF₂/PBA blends, two semicrystalline polymers.

DMA

Figure 4 shows the data obtained by DMA for blends in different compositions. In analyzing the curve of the storage modulus (E') (Fig. 4), a vitreous behavior of the membrane was observed up to -5°C (except for the pure PLLA), where the viscoelastic behavior of PHBV with its vitreous transition (10°C) begins. At a temperature of approximately 50°C, the viscoelastic behavior of PLLA begins with the vitreous transition

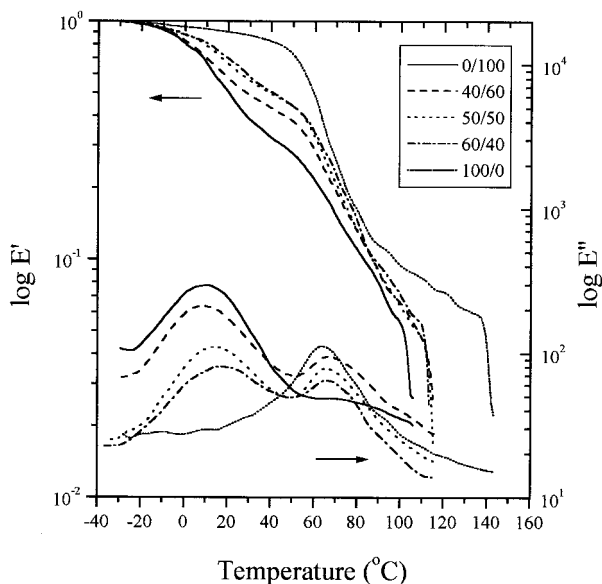


Figure 4 Dynamic storage modulus (E') and loss modulus (E'') of various PLLA/PHBV blends.

(65°C) (except for the pure PHBV, which began before, as mentioned previously). After that, the blends presented elastic behavior to 110°C, for the pure PHBV, where the melting of PHBV occurred, and the blend presented viscous behavior. With increasing of the amount of PLLA in the blend, the elastic behavior extended to 140°C, where the melting of PLLA occurred.

The T_g was obtained from the maximum peaks of the $E'' \times T$ and $\tan \delta \times T$ curves. The T_g values for PHBV and PLLA were around 14 and 67°C in the $E'' \times T$ curve and 21 and 80°C in the $\tan \delta \times T$ curve, respectively (Table III). As verified in the DSC analysis, the presence of two distinct values of T_g is also an indication of the immiscibility of the systems. In the $\tan \delta \times T$ curves, it was not possible to observe any transition of second order of type β or γ for the blends.

It is interesting to observe that both polymers were influenced in their T_g by the presence of another poly-

TABLE III
Glass Transition Temperatures (T_g) Obtained by DMA from Loss of Modulus (E'') and Damping ($\tan \delta$) for Different PLLA/PHBV Blend Compositions

PLLA/PHBV	T_g (°C) E''		T_g (°C) $\tan \delta$	
	PHBV	PLLA	PHBV	PLLA
100/0		64		75
80/20	19	72	29	83
60/40	18	66	26	81
50/50	14	65	21	81
40/60	9	67	16	^a
20/80	12	70	18	^a
0/100	10		17	

^a Not possible to observe.

TABLE IV
Activation Energy (E_a) from PHBV in Different PLLA/PHBV Blend Compositions Obtained from $\tan \delta \times T$ Curves from DMA Frequency Assay

PLLA/PHBV	$E_{a\text{PHBV}}$ (kJ/mol)
0/100	327
20/80	271
40/60	312
50/50	288
60/40	214
80/20	249

mer in the blend, that is, as the amount of PLLA in the blend increased, so did the T_g of PHBV increase, from 10 to 19°C in the E'' and from 17 to 29°C in the $\tan \delta$ curves (Table III). The same occurred for PLLA: With increase of PHBV in the blend, its T_g increased from 64 to 70°C in the E'' and from 75 to 81°C in the $\tan \delta$ curves. This is an indication that both polymers influence each other, and the result is a decrease in the mobility of the amorphous chains.

DMA: frequency variation

By using the DMA frequency assay, it is possible to obtain the activation energy for the different blend compositions. Study of the activation energy (E_a) can provide some information about the thermal behavior of the blend and thus give information on probable miscibility at the molecular level of the blends.

The activation energy (E_a) was obtained using the Arrhenius method¹⁸:

$$\frac{d \ln k}{dT} = \frac{E_a}{(RT)^2}$$

or

$$k = A e^{-E_a/(RT)}$$

where E_a is the Arrhenius activation energy; k , the specific rate constant; A , the preexponential factor; R , the general constant of gases; and T , the temperature. In other words, by plotting the logarithm of the rate constant with regards to $1/T$, a straight line, where the angular coefficient is E_a/R , is obtained. The Arrhenius method gives one E_a for each substance.

Table IV shows the E_a for PHBV in each PLLA/PHBV blend obtained by the DMA frequency assay in the $\tan \delta \times T$ curves. It is possible to observe that E_a is in the range of 327–214 kJ/mol for the blends. This indicates the presence of interactions at the molecular level between the two polymers. The dispersion and/or the miscibility of low molecular weight fragments of PLLA can be responsible for that enlargement effect, at the same time contributing to the for-

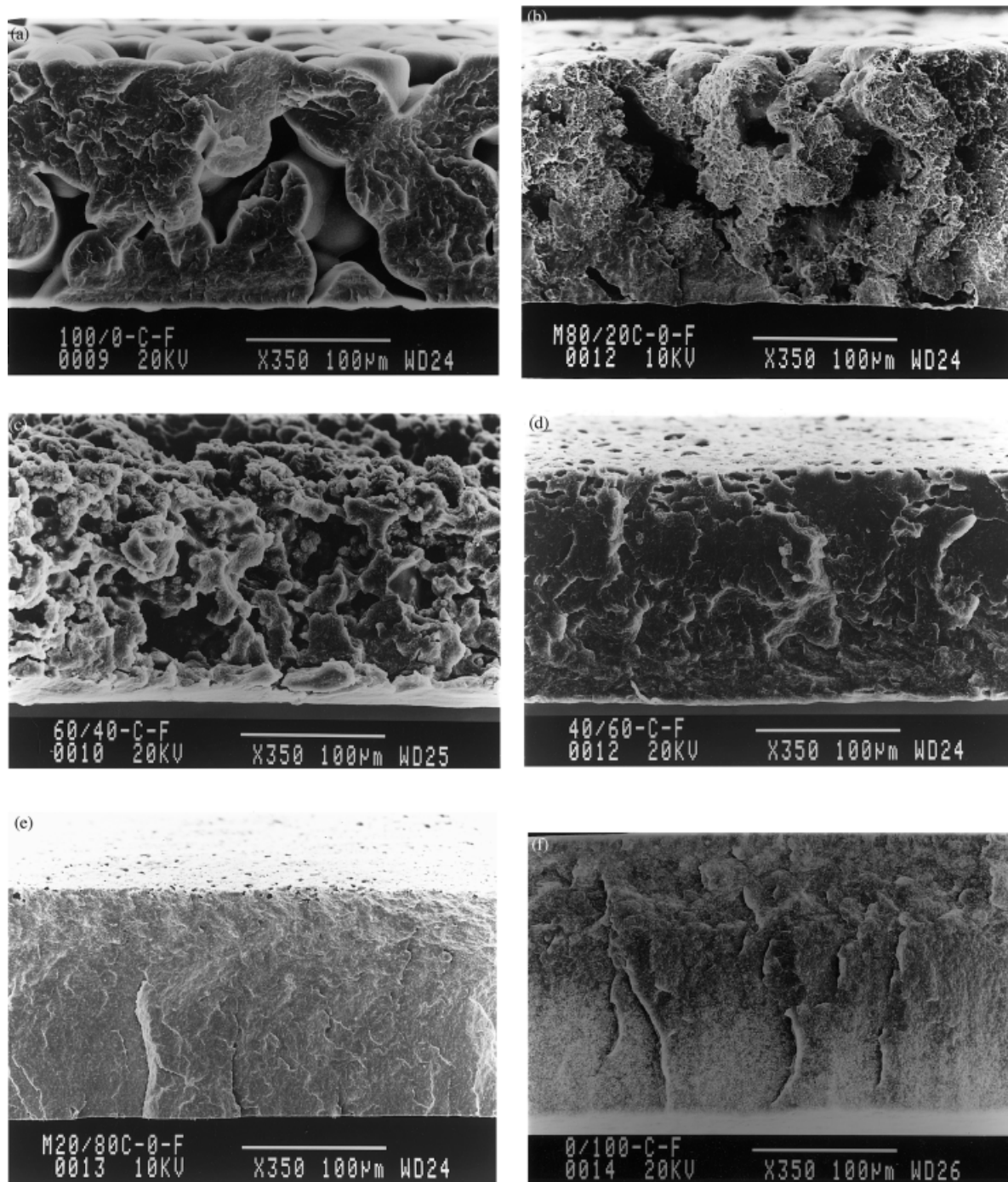


Figure 5 Electron micrographs of the fracture surfaces of PLLA/PHBV blends in different compositions: (a) 0/100; (b) 80/20; (c) 60/40; (d) 40/60; (e) 20/80; (f) 0/100.

mation of an interface between the domains composed of pure PHBV and PLLA. The same results were observed by Iannace et al.¹ The authors discussed that the decrease of crystallinity of PLLA in the blend can be due to the dispersivity of part of the polymer in the PHBV phase. This can be observed in Table II, where the crystallinity degree of PLLA decreases from 42 to 27%.

SEM

The morphological features detected in the electron micrographs show a one-phase behavior of the system [Fig. 5(a–f)]. The cross section of the 100/0 blend [Fig. 5(a)] shows that the membrane is porous, with a globular aspect on the surface. This morphology was dras-

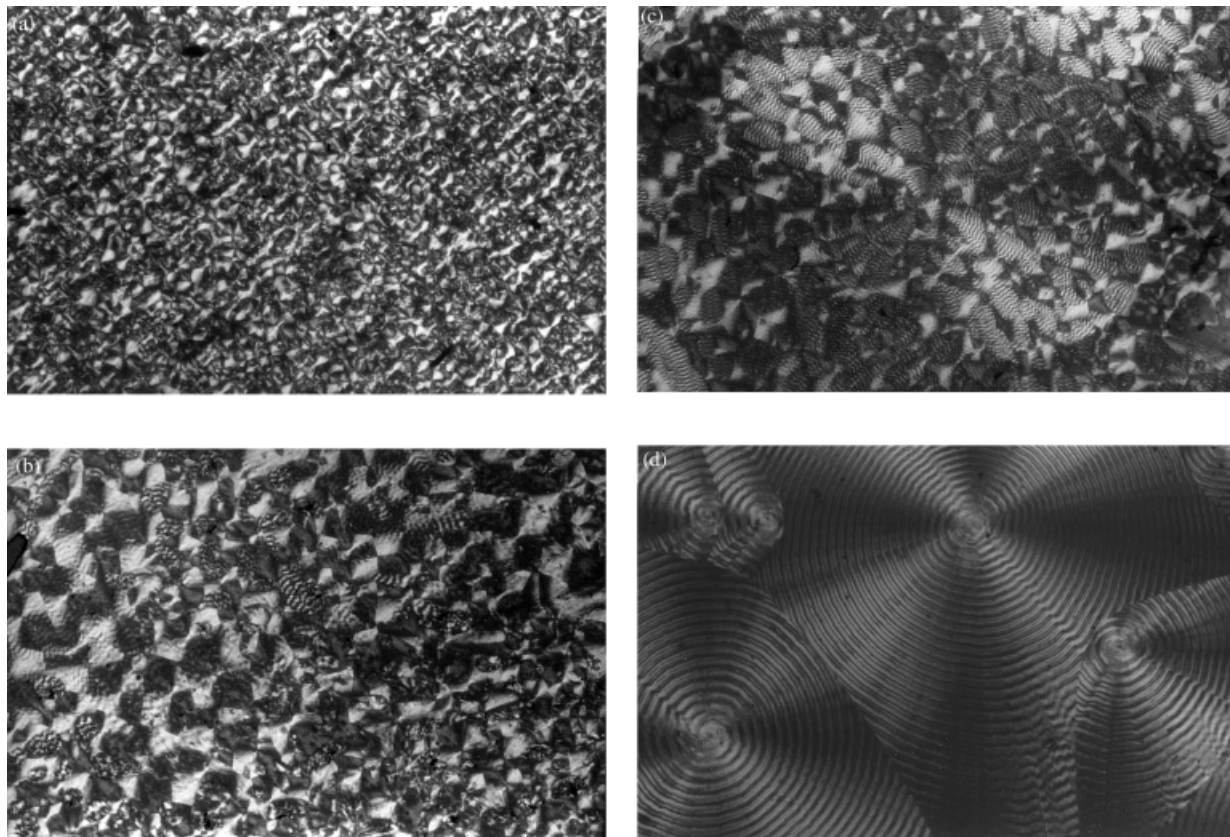


Figure 6 Light polarized micrographs of PLLA/PHBV blends in different compositions: (a) 100/0; (b) 60/40; (c) 40/60; (d) 0/100.

tically modified when 20% PHBV was added as a dispersed component [Fig. 5(b)]. It was still porous, but the morphology showed a rugous aspect.

At compositions of 40% PHBV, the morphology shows an increase of porosity and loss of the globular aspect [Fig. 5(c)]. With increase of PHBV [Fig. 5(d)], it is possible to observe a porous surface and the cross section shows a tendency to a dense morphology. This was confirmed for the 20/80 blend [Fig. 5(e)]. Pure PHBV shows a completely dense morphology [Fig. 5(f)]. In this kind of analysis, it was not possible to observe any phase separation, even though the blend presented characteristics of no miscibility in the previous analysis (TGA, DSC, and DMA).

PLM

Figure 6 exhibits the micrographs obtained by PLM of the PLLA/PHBV blends in different compositions. In Figure 6(a) (pure PLLA), it is observed that the crystals are small when compared to the crystals in Figure 6(d) (pure PHBV). In the blend [Fig. 6(b,c)], it can be observed that the crystals are separate, in spite of the alteration of the size of the PHBV crystals. That alteration in the formation of the crystals is related to the mixture of the components, due to the presence of

PHBV. In the mixture, the density of PLLA nucleation decreased.¹² PHBV then grew inside the remaining spaces. When PHBV was alone, it formed big crystals, due to its high-speed crystal growth, as can be seen in Figure 6(d).

Blümm and Owen observed that the spherulites of pure PLLA are generally dendrites and they grow much more slowly than do the spherulites of PHB.³ The spherulites of PLLA show a maximum growth rate of $9 \mu\text{m}/\text{min}$ for $T_c = 105^\circ\text{C}$, while the crystals of PHB grow to a maximum rate of $230 \mu\text{m}/\text{min}$ for $T_c = 90^\circ\text{C}$.³ This leads us to believe that the same happens with the PLLA/PHBV blend, but at a slightly lower rate and crystallization temperature for PHBV.

Due to the wide difference in the crystallization temperature, the two polymers crystallize in different temperature regimes. In the light microscopy, the temperatures of crystallization used were 100°C for PLLA and 75°C for PHBV. PLLA will always be partially solidified before the crystallization of PHBV begins. Due to this separation in the crystallization regimes, cocrystallization does not occur between the two polymers. The crystallization of each one of the two blend components represents a separation process in which

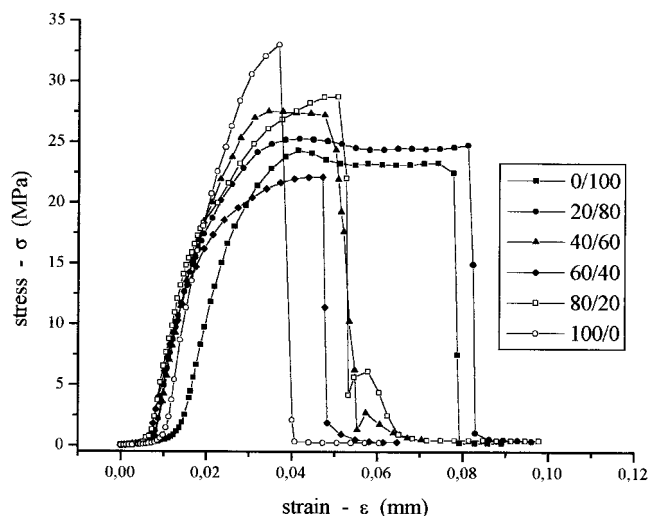


Figure 7 Stress–strain curves for PLLA/PHBV blends in different compositions: 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0.

one polymer segregates partially from the mixture to form a pure phase.¹²

Tensile testing

Figure 7 shows stress–strain curves of PLLA/PHBV blends in different compositions obtained by tensile testing. It can be noticed that PLLA has characteristics of a typical glassy polymer with a low deformation at the point of rupture, unlike PHBV, which presented characteristics of a polymer with a larger viscoelastic flow.¹⁹ PLLA has a greater modulus than has PHBV, but the stress at maximum load was almost the same (Table V and Fig. 7). When comparing these results with those obtained by Iannace et al. for PLLA/PHBV blends containing 20% HV, it was verified that the modulus (E) values were similar, but stress at maximum load (σ) values for PLLA/PHBV blends, 100/0 and 80/20, were smaller than those of Iannace et al. (71 ± 3 MPa for 100/0 and 54 ± 3 MPa for 80/20 blends).¹ This can be because the PLLA film obtained in our study was porous and the PHBV film was dense, contrary to those of Iannace et al., who obtained only dense films, and it was because of this that

Iannace et al. found the stress at maximum load greater for PLLA.

In the case of the blends, adding PHBV to PLLA, the films gain plasticity. The mechanism of strain energy dissipation during the deformation of these systems leads to tougher materials that show yield behavior or plastic deformation.¹

CONCLUSIONS

PLLA/PHBV blends showed two different glass transition and melting temperature values by DSC. Besides this, the values of the melting temperature did not vary in relation to the blend composition. These data are an indication of the immiscibility of the blends.

DMA analysis showed two distinct values of T_g for all the blends. This is an indication of the immiscibility of the blends, according to the DSC data. The DMA assay in relation to the frequency showed a decrease in the activation energy (E_a) value with an increase of PLLA in the blends. This showed that, in spite of its immiscibility, the blend had some molecular interaction.

The micrographs obtained by SEM showed that the blends present a porous morphology with increase of PLLA in the blend; however, a clear phase separation was not observed. Through PLM, it was possible to observe the crystalline formation both for pure polymers and for the blends. PLLA seemed to be composed of a great number of crystals, while PHBV presented a smaller number of crystalline nuclei, but larger crystals.

The tensile testing showed that the stress at maximum load and the modulus values for the blends are between the values of the pure polymers. A great variation in the strain for the samples was noticed. Pure PLLA has vitreous characteristics but it presents elasticity with the addition of PHBV in the blend.

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TABLE V
Stress at Maximum Load and Modulus from PLLA/PHBV Blends in Different Compositions Obtained by Tensile Tests

	Stress at maximum load σ (MPa)	Standard deviation (MPa)	Modulus E (MPa)	Standard deviation (MPa)
100/0	29.7	3.8	2.031	238
80/20	27.8	1.0	1.761	209
60/40	22.2	0.4	1.580	32
40/60	25.1	3.3	1.301	320
20/80	24.9	1.0	1.631	151
0/100	22.8	1.7	1.302	328

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