Poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate)/Poly-L-Lactide Blends: Thermal and Mechanical Properties

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SYNOPSIS

Blends of poly(3-hydroxybutyrate)–poly(3-hydroxyvalerate) (PHBV) and poly(L-lactides) (PLLA) have been prepared by solvent casting. Compatibility, thermal behavior, morphology, and mechanical properties of systems with various compositions were studied using differential scanning calorimetry (DSC), dynamic mechanical measurement, tensile tests, scanning electron microscopy (SEM), and wide-angle X ray (WAXS). Glass transition temperature of solvent cast materials, detected by dynamic mechanical analysis (DMA), showed partial molecular interactions between PHBV and PLLA. Crystallinity of the PLLA phase slightly decreased with increasing amount of PHBV, confirming the partial dispersion of PLLA in the PHBV phase. Mechanical properties were analyzed with theoretical models able to predict the behavior of heterogeneous systems. Phase separation was confirmed by SEM observations. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Aliphatic polyesters have been considered to be the most attractive and promising family of biodegradable materials for biomedical applications. Among them poly(α-hydroxy acids) such as poly(glycolic acid) (PGA) and poly(lactic acid) (PLA) have been extensively studied and reviewed.[1] The microbial polyester family represents another source of biodegradable materials. Different poly(hydroxy-alkanoates) copolymers such as poly(hydroxybutyrate)-co-(hydroxyvalerate) (PHBV) are obtained through several microorganisms. Their properties can be modified by changing the composition of the copolymer through variation of the feed of the bacteria, and this has been reviewed by Doi.[2]

The increasing use of biodegradable polymers in medicine, as sutures, surgical implants, and components for controlled-release formulation of drugs, has stimulated a remarkable and growing interest in new materials. The control of the kinetics of property decay during degradation, together with specific properties required for specific applications, is the driving force of these studies.

Extensive effort has been devoted to the study of the effect of copolymerization of these poly(hydroxyacids) on the physical and chemical properties of the final products. Copolymers of poly-L lactide (PLLA) and PGA have been[1] produced to control the degradation rate through compositional modification. Hydrophilicity, which is another important factor for many applications, can be modified by inserting poly(ethylene glycol) in the PLA backbone. The rates of drug release from these systems and of polymer degradation have been modified by balancing the amounts of hydrophobic–hydrophilic segments in the copolymer chain.

Few such studies are devoted to polymer blends and alloys, an emerging class of multicomponent systems. They represent a more cost-effective way of modifying properties than is chemical modification. Macroscopic properties of materials like impact strength, rigidity, tensile strength, barrier properties, processability, and others can be modified through an opportune choice and composition of the second polymer, and this has been the object of many pat-

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ents and publications.[3–5] The variation of these properties can be developed by modification of physical characteristics such as glass transition temperature, crystallinity, density, and morphology depending on the compatibility of the two materials.

The principles controlling the properties of these systems have been explored in the field of biodegradable polymers to tailor-make materials with desired features.[6–8] Miscibility is not always required when a biodegradable polymer is mixed with another nonbiodegradable polymer or with a slowly degradable polymer. In fact, when the degradation phenomenon is controlled by the surface interaction between the material and the environment, the accessibility of the inner surfaces can be modified through the composition of the system, and it can be simulated using percolation theory.[7] The results show how this is dependent on the initial concentration, which controls the level of segregation or continuity of the second phase from the outer surface to the inner portion of the sample.

Blending of PHBV with other polymers has been the subject of an increasing number of studies to provide potential methods for improving the processing characteristics and for enlarging the range of applicability of these biopolymers. Most of the work has been mainly devoted to the study of miscibility of PHB and PHBV with other polymers.[9–12]

It has been reported that PHBV [16% hydroxyvalerate (HV)] forms an immiscible system with poly(D-lactide) (PDLA).[10] In this work the behavior of blends of PHBV and PLLA was investigated with attention to compatibility and its effect on the thermal and the mechanical behavior of these blends. Differential scanning calorimetry (DSC), tensile tests, dynamic mechanical properties, scanning electron microscopy (SEM), and wide-angle X ray (WAXS) were used for analysis.

MATERIALS AND METHODS

Preparation of Blends

PHBV copolymer with 20% HV, under the trade name Biopol (purchased from Malborough Biopolymers Ltd., United Kingdom), was used in this study. PLLA was supplied by NOVAMONT S.p.A. (Novara-Italy). Thin films of PHBV–PLLA blends with weight ratios of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100, were prepared by casting from a solution of chloroform at room temperature. The films were then kept under vacuum overnight at 50°C to allow the evaporation of the solvent. Films were finally thermally treated for 1 h at 100°C.

Calorimetric Analysis and Glass Transition Temperature

Calorimetric analyses were performed using a Mettler DSC model TA 30 at a heating rate of 10°C/min under nitrogen atmosphere. Samples were first heated from −40 to 200°C to study the thermal properties of the solvent cast materials. They were then cooled to 0°C over 20 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 from DSC endotherms and/or exotherms.

The glass transitions of the PHBV phase of the solvent cast systems were studied through dynamic mechanical analysis (DMA) using a DuPont DMA 983. The data were fitted by a theoretical model in order to evaluate the molecular parameters associated with the transitions.

Isothermal Crystallization

A Polyvar polarizing optical microscope equipped with a Mettler hot stage, connected to an image analyzer system, was used to crystallize isothermally thin cast films (20 μm) of PHBV–PLLA blends. They were first heated to 200°C for 2 min, then cooled at 35°C/min to the crystallization temperature T_c under a continuous stream of nitrogen to minimize thermal degradation. The samples were kept at T_c for 15 min to allow the crystallization of the samples, and the temperature was then slowly raised (5°C/min) to observe the melting of the crystals. The melting point T_m was measured detecting the optical disappearance of the birefringence pattern.

X-ray Measurements

Wide-angle X-ray diffractograms were obtained in transmission using a RIGAKU powder diffractometer. The radiation was used in the angular range 5°–50°. The raw spectra were analyzed by graphic software. The crystallinity of the films was determined by subtracting the amorphous halo from the original diffractogram and calculating the respective area values by digital integration.

Mechanical Properties and Morphology

Mechanical properties of the samples were studied by an Instron 4202 on dumbell shape samples ac-

Table I   Calorimetric Results of I and III Scan[a]

	I Scan		III Scan					
% PLLA	T_m	H_m	T_{g1}	T_{g2}	T_c	T_m	H_c	H_m
100	177.8	34.8		61.0	109.2	179.2	27.9	39.0
80	177.8	31.0	−1.02	59.8	108.8	178.8	21.1	34.5
60	177.1	23.5	−3.60	58.9	105.0	178.0	10.8	29.5
40	177.2	33.0	−2.59	57.7	105.7	177.2	10.0	31.2
20	175.4	28.5	−4.55	58.1		177.4		23.0
0			−3.97					

[a] Temperature in celsius and enthalpy in Joules per gram PLLA in blend.

RESULTS AND DISCUSSION

Calorimetric Analysis

cording to American Society for Testing and Materials standard ASTM D 638.

A Hitachi scanning electron microscope was used to observe their fracture surfaces, which were coated with a thin layer of gold. The samples were kept in liquid nitrogen before rupture in order to induce a brittle fracture of the materials.

The glass transition temperatures of the PHBV phase in the first scan were not easily detectable from calorimetric analysis due to their poor resolution. For this reason the discussion about the glass transitions of the solvent cast systems will be done via analysis of the dynamic mechanical properties.

The melting behavior of these solvent cast materials suggested the presence of crystalline phases related to the two parent polymers PLLA and PHBV. In Table I, the melting temperatures T_m (PLLA) and the heat of fusion of the PLLA phase for each composition are listed. From these results it appeared that while T_m remained constant with the variation of the microbial polyester content, the specific heat of fusion of the PLLA was decreasing.

The melting temperature of a crystallizable material in polymer blends is generally investigated because it gives a measure of the miscibility of the system. The constant values of T_m observed for the system PHBV–PLLA are an indication of the immiscibility of this system, but the decrease of the PLLA crystallinity suggested that not all the PLLA can crystallize due to the dispersion of part of the amorphous PLLA phase in the PHBV phase. As a matter of fact, ternary systems composed of a common solvent and two polymers are frequently used to form true solutions and to prepare pseudohom-

ogeneous systems after the removal of the solvent. This allows the formation of a large interfacial area between the two polymers, which stabilizes the dispersion.

During the cooling of the PLLA–PHBV samples from 200 to 0°C at 10°C/min, a partial crystallization can be observed (Fig. 1). The exothermal peaks can be attributed to the PLLA phase, since pure PHBV does not show any crystallization behavior at this cooling rate. During the third scan, as shown in Figure 2, all the samples showed crystallization and melting. The results are reported in Table I, where the pedices I and III are referred to the first and third calorimetric scan.

The blends were characterized by two distinct T_g values (Fig. 2), as listed in Table I: the first at about −4°C, of the PHBV phase, and the second, at about 60°C, of the PLLA phase. The two T_g values were essentially constant, and this suggests the presence of two separated phases after melting of the samples. For a better interpretation of the slight decrease of the T_g of the PLLA phase, the experimental results were analyzed comparing the data with the following
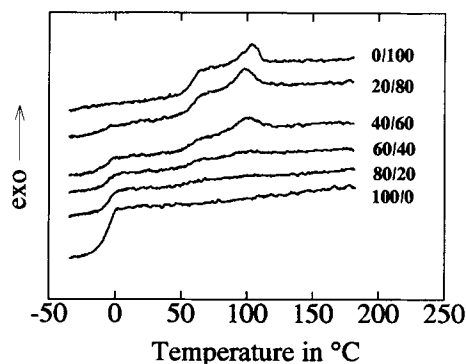
Figure 1   Calorimetric curves of blends during cooling (II scan). From top: PHBV–PLLA 0/100, 80/20, 60/40, 40/60, 20/80, 100/0.
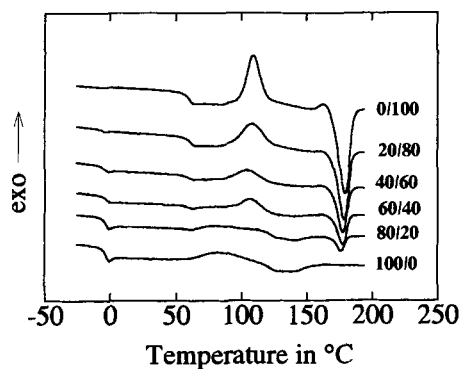
Figure 2 Calorimetric curves of blends during heating (III scan). From top: PHBV–PLLA 0/100, 80/20, 60/40, 40/60, 20/80, 100/0.

empirical relation derived from the Gordon–Taylor[13,14] equation:

$$w_1(T_{g_1} - T_g) + kw_2(T_{g_2} - T_g) = 0 \qquad (1)$$

The parameter k, equal to $\Delta C_{p2}/\Delta C_{p1}$ for miscible systems, was used as an empirical parameter to provide a measure of the miscibility. The best fit of the experimental T_g (PLLA) vs. w_2 was given by $k = 88.22$ (Fig. 3), which indicates very poor miscibility of the two systems after melting. The straight line for $k = 1$ is representative of the behavior of those blends that show experimental values of the T_g that are the weighted sum of the two T_g related to the parent polymers.

The crystallinity of the PLLA phase in the third scan was lower than that expected if the two materials were totally noninteracting (Table I). Also the observed crystallization and melting temperatures of the PLLA phase in the blends were slightly lower than those detected in the case of pure polymer. These results suggest that the crystallization process does not take place in entirely pure PLLA domains.

Crystallinity

In Figure 4, the X-ray spectra of the pure PLLA and PHBV and two blends of composition 20/80 and 80/20 (w/w PHBV/PLLA) are shown. The absence of peak shifts suggests that molecular distances in the crystalline structures are not affected and the two materials do not cocrystallize.

The crystallinity of the blends, X_c (blend), are listed in Table II together with the crystallinity of the PLLA phase in the blends calculated from DSC analysis by the following relation:

$$X_c(\text{PLLA}) = \frac{\Delta H^*}{\Delta H_{\text{PLLA}}} \qquad (2)$$

where ΔH^* is the apparent enthalpy of fusion per gram of PLLA in the blend. The enthalpy of fusion of the crystalline phase of PLLA, ΔH_{PLLA}, is calculated from DSC and X-ray data as follows

$$\Delta H_{\text{PLLA}} = 39/0.496 = 78.6 \text{ J/g} \qquad (3)$$

where 39 J/g is the enthalpy of fusion per gram of PLLA calculated from the DSC endotherm and 0.496 is the fraction of crystallinity calculated from the X-ray spectra. The value of ΔH_{PLLA} is in agreement with the value of 81 J/g reported by Fisher et al.[15]

Table II reports the crystallinity of the blends calculated from X-ray measurement, X_c (X ray), and the crystallinity of the PLLA phase, calculated from DSC measurements [X_c(DSC)]. These data were compared with the theoretical values obtained as the weighted sum of the crystallinity of the two pure polymers:

$$X_c(\text{X ray})_{\text{theor}} = W_{\text{PLLA}}X_c(\text{X ray})_{\text{PLLA}}$$
$$+ W_{\text{PHBV}}X_c(\text{X ray})_{\text{PHBV}} \qquad (4)$$

$$\Delta X_c(\text{X ray}) = 100 \frac{X_c(\text{X ray})_{\text{theor}} - X_c(\text{X ray})}{X_c(\text{X ray})} \qquad (5)$$

Analogous relations were used to calculate ΔX_c(DSC). Since ΔX_c(X ray) and ΔX_c(DSC), reported in Table II, are very similar, the lower crystallinity of the blends can be ascribed to the reduced crystallinity of the PLLA in the blends.
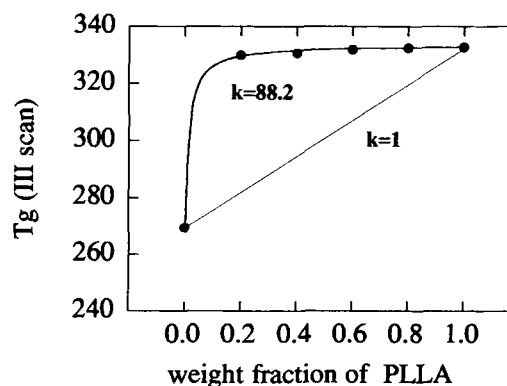
Figure 3 Experimental T_g (III scan) of PLLA phase (filled circles). Continuous lines represent theoretical values obtained by Eq. (1) for $k = 88.2$ and $k = 1$.
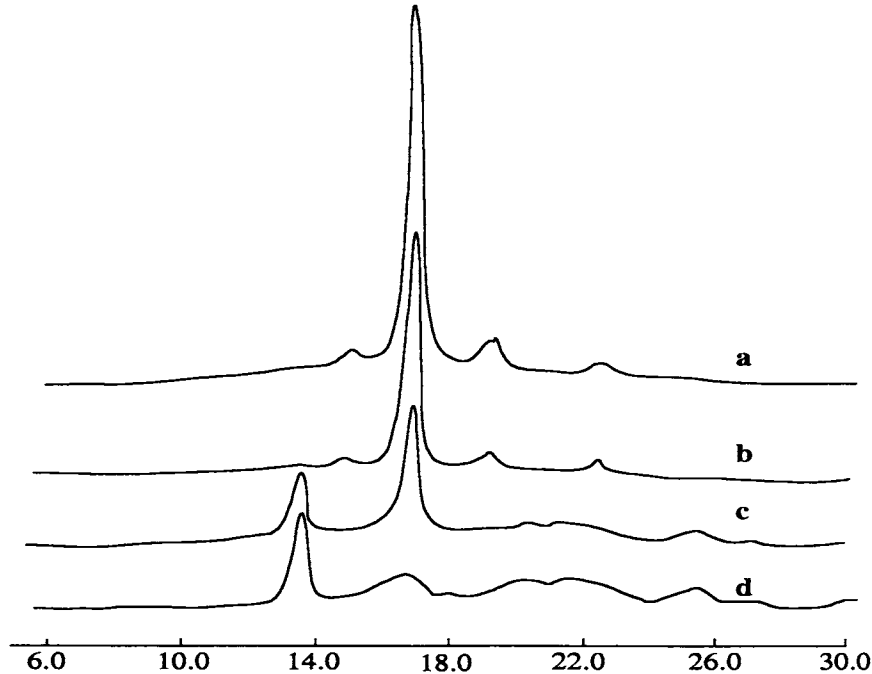
Figure 4 X-ray spectra of pure PLLA (curve a), PHBV–PLLA 80/20 (curve b), PHBV–PLLA 20/80 (curve c), pure PHBV (curve d).

Dynamic Mechanical Analysis

Dynamic mechanical measurements represent a powerful method to investigate relaxation phenomena in polymeric materials. The analysis of E'' as a function of temperature has been used to obtain information on the level of the miscibility of the blends. When the cooperative segmental motion of the polymer chains is altered by the contemporary presence of a second polymer, a variation in the glass transition temperature could occur. The use of T_g to determine the miscibility of a blend is based on the assumption that the domain size is below 15 nm.[16] Evidence of disagreement between results obtained with different methods (DSC, DMA, dielec-

Table II   Crystallinity of Blends Obtained by X-ray Analysis and DSC Analysis

% PLLA	X_c (X ray)	X_c (DSC)	ΔX_c (X ray)	ΔX_c (DSC)
100	0.496	0.496		
80	0.442	0.440	11.6	11.2
60	0.367	0.335	27.2	32.5
40	0.472	0.445	7.26	10.3
20	0.393	0.406	20.8	17.4
0	0.517			

tric)[3] has been observed by several authors, and this is related to the debate concerning the effect of the level of miscibility on the T_g of multicomponent systems.[17]

The dynamic mechanical results obtained from the PHBV–PLLA blends were analyzed by the following Fuoss–Kirkwood equation[18,19]:

$$E''(\omega, T) = 2E''_{max} \frac{(\omega\tau)^m}{1 + (\omega\tau)^{2m}} \qquad (6)$$

where τ is the characteristic relaxation time of the material at the temperature T which is assumed to follow an Arrhenius-type equation[19]:
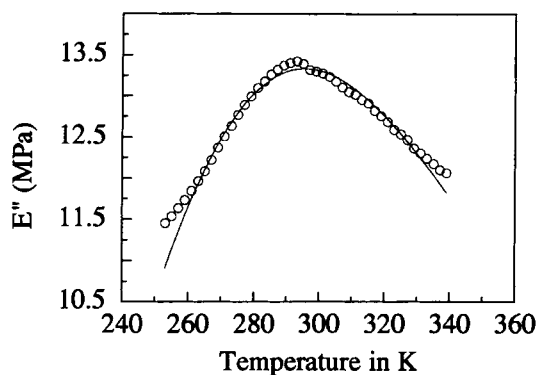
$$\tau(T) = \tau_0 \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \qquad (7)$$

where τ_0 is the relaxation time at temperature T_0, E_a the activation energy of the relaxation phenomenon, R the universal gas constant, and m is a parameter that takes into account the distribution of all the relaxation times and can assume values between 0 and 1.

The experimental E''-vs.-temperature dependence for the pure PHBV and the PHBV–PLLA 80/20 blend are shown in Figures 5 and 6, respectively. The temperature was chosen in a range encompass-
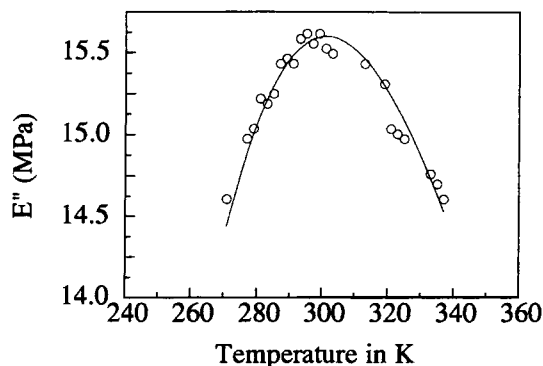
Figure 5 Experimental (open circles) loss modulus of pure PHBV compared with best fitting curve obtained by Eqs. (5) and (6).

Table III Best Fitting Parameters of Experimental Loss Modulus of Solvent Cast Blends

% PHBV	T_0 (°C)	E_a (kJ/mol)	m
100	288	239	0.040
80	290	130	0.0235
60	288	141	0.0254
40	287	110	0.0160
20	287	120	0.0185

ing the glass transition of the PHBV phase since the temperature of this second-order transition was sufficiently low and did not interfere with the melting transitions that occur at temperatures closer to the glass transition of the PLLA phase.

Experimental data were fitted by the equation derived from Eqs. (6) and (7) and the theoretical curves were compared with the experimental values in Figures 5 and 6 (continuous curves). The parameters of the best fitting curve (T_0, m, and E_a) are shown in Table III.

The glass transition temperature (T_0) of the PHBV phase was essentially constant with the composition; on the other hand, the blends showed a decrease of both the activation energy E_a and the parameter m, which is the consequence of a broadening of the transition. The enlargement of the transition observed for the blends indicated 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 was thought to be responsible for this broadening effect, which at the same time contributed to the formation of an interphase between domains composed by nearly pure PHBV and PLLA. This also explains the reduction of the PLLA crystallinity, since the fraction of PLLA molecules dispersed in the PHBV phase was not able to crystallize.

Isothermal Crystallization from Melt

Equilibrium melting points of the PLLA phase of the pure polymer and the blends were evaluated using the Hoffman–Weeks method.[20] The melting points T_m of the PLLA phase, measured by optical microscopy after the isothermal crystallization at T_c, were reported versus T_c, as suggested by Hoffman and Weeks. The experimental data of the pure PLLA and of the blend containing the 20% PLLA (Fig. 7) followed quite well a linear trend, in agreement with the theoretical treatment. The extrapolation of the linear fitting curve to the line $T_m = T_c$ allows the determination of the equilibrium melting point T_m°, which was 189.3°C for the pure PLLA. The slight T_m° depression observed for the blends (Fig. 8) cannot be interpreted easily with the Flory–

Figure 6 Experimental (open circles) loss modulus of pure PHBV–PLLA 80/20 compared with best fitting curve obtained by Eqs. (5) and (6).

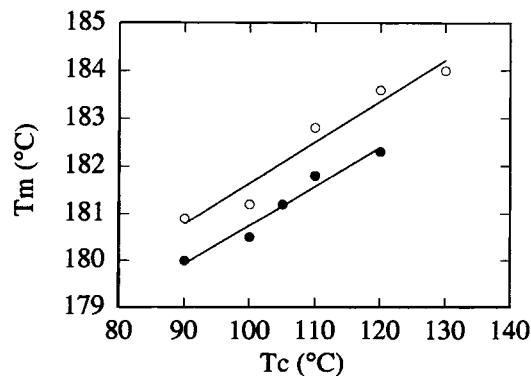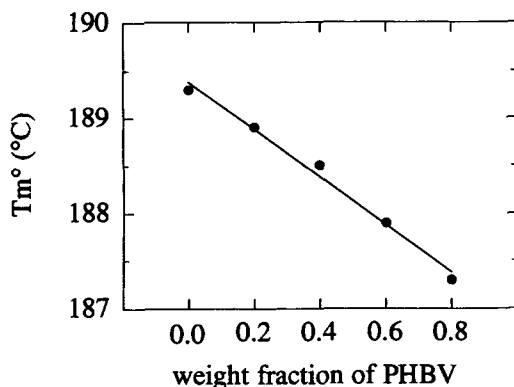**Figure 7** T_m vs. T_c obtained by isothermal crystallization of pure PLLA (open circles) and PHBV–PLLA 80/20 (filled circles).

Figure 8 Equilibrium melting temperatures of PLLA phase obtained by Hoffman–Weeks method. Note small effect of composition on T_m°.

Huggins theory,[21] which is valid for a crystallizable polymer in a compatible mixture with an amorphous polymer. The Nishi–Wang equation,[22] frequently used to evaluate miscibility in crystallizable blends, is based on the assumption that the crystals grow from a single-phase melt and that the presence of the second component does not induce changes in the lattice spacing or lamella thickness.[23] The small effect on T_m° could be related to either the limited dispersion of the PHBV component in the PLLA melt phase or morphological effects induced by the melt PHBV domains.

Tensile Properties

The stress–strain curves of the PLLA–PHBV systems are reported in Figure 9. The mechanical behavior of the pure PLLA (curve a) showed characteristics typical of glassy polymers with low deformation at break. On the contrary, pure PHBV (curve f) exhibited a mechanical behavior typical of sys-
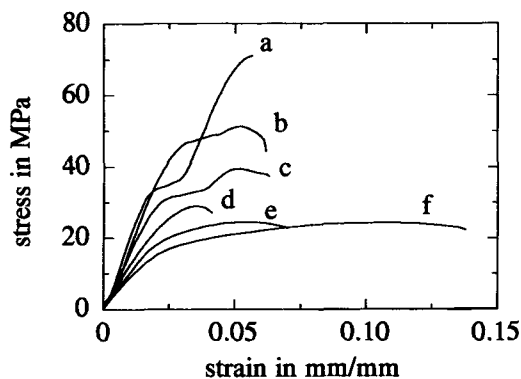
Figure 9 Stress–strain curves for PHBV–PLLA blends: a, 0/100; b, 20/80; c, 40/60; d, 60/40; e, 80/20; f, 100/0.

tems well above their glass transition temperature with uniform quasi-viscous flow.

Adding the 20% of the microbial copolyesters to the PLLA phase, the stress-induced crystallization appeared reduced and also the onset of plasticity was observed. The latter is typical for a two-phase polymer system where a rubber is added to a glassy material. The mechanism of strain energy dissipation during the deformation of these systems leads to tougher materials that show a yield behavior or a plastic deformation.[5] As reported in Table IV, the system containing 20% PHBV possesses a higher value of the energy at break than the pure PLLA. An increase of the PHBV content produced systems with lower elongation, which reached a minimum for a content of PHBV around 60% (w/w).

Figure 10 shows the maximum stress for the compositions studied. Since the breaking and the dewetting behavior depend upon the surface area of the second phase in the blend, the Nicolais–Narkis equation[24] was used to analyze the experimental values. The authors have shown that the stress at break of particulate composites decreases with increasing content of the filler. With poor adhesion between the polymer matrix and the filler, the latter does not carry any load and all the stress is carried only by the matrix. Based on geometrical considerations, the stress decreases with the following relationship:

$$\sigma_{\text{rel}} = 1 - 1.21\phi^{2/3} \tag{8}$$

where ϕ is the volume fraction of the filler and σ_{rel} the relative stress calculated as the ratio between the stress at break of the blend and the stress at break of the matrix.

The discrepancy between the theoretical and the experimental curves can be mainly ascribed to the particular blend morphology, which cannot simply be regarded as a composite system constituted by a matrix filled with an increasing content of spherical

Table IV Mechanical Properties of Solvent Cast Blends (Mean ± SD)

% PLLA	E (MPa)	σ_b (MPa)	ε_b (%)	Energy at Break
100	2415 ± 140	71 ± 3	5.6 ± 1.0	2.12 ± 0.24
80	2083 ± 45	54 ± 3	6.2 ± 0.5	3.15 ± 0.60
60	1552 ± 56	39 ± 2	6.7 ± 0.7	1.87 ± 0.26
40	1258 ± 17	29 ± 2	4.1 ± 0.4	0.78 ± 0.27
20	1076 ± 17	24 ± 1	6.9 ± 0.9	1.16 ± 0.30
0	882 ± 62	25 ± 3	13.8 ± 1.2	2.42 ± 0.50
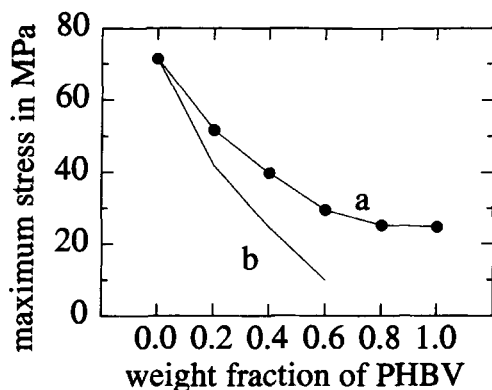
Figure 10 Yield stress vs. PHBV content in blend. Continuous curve was obtained by Nicolais–Narkis equation valid for composite systems with spherical particles.

particles.[24] As we will discuss later, a variation in the blend morphology was obtained, changing the composition, and co-continuous systems were observed when the amounts of the two components in the blend were similar.

The mechanical properties of blends at small deformation have been described by several authors,[5,25] and the interpretation of the experimental results can be done on the basis of hypotheses on the type of dispersion of the second phase, which can be (a) spherical inclusions of a polymer in a matrix, (b) dispersions of a phase containing a portion of polymeric matrix to form composite inclusions, and (c) interpenetrating co-continuous structures of more than one distinguishable phase.[26]

The modulus composition dependence shown in Figure 11 was analyzed using the Takayanagi model and the Halpin–Tsai equation. The first assumes that a multiphase polymer blend can be regarded as a composite system where the effect of the phases on the overall mechanical properties can be analyzed with a combination of series and parallel springs having the properties of the single-blend constituent. Using the convenient form with a single coupling parameter,[27] it is possible to obtain a useful expression that correlates the modulus of the blend with the composition of the system:

$$\frac{E_c}{E_1} = \frac{\phi_1 E_1 + (\alpha + \phi_2)E_2}{(1 + \alpha\phi_2)E_1 + \alpha\phi_1 E_2} \tag{9}$$

where E_c, E_1, and E_2 are, respectively, the modulus of the composite, the matrix, and the filler; ϕ_2 the volumetric fraction of the filler; and α a coupling parameter of the Takayanagi model.

Even though the model is not morphologically realistic, it is a useful tool for a phenomenological

description of the blend behavior. As a matter of fact, if the parameter $\alpha = 0$, then the two components behave as a parallel system, following the mixture rule:

$$E_c = E_1\phi_1 + E_2\phi_2 \tag{10}$$

In the case of $\alpha = \infty$, a simple series coupling can be considered:

$$\frac{1}{E_c} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2} \tag{11}$$

These two cases can be considered as the upper and lower bounds shown in Figure 11 as curves a and c, respectively.

The best fitting of the data gives $\alpha = 0.846$ for the systems where the glassy PLLA is the continuous phase. At low PHBV content the experimental point follows the upper bound curve, indicating that the systems behave more like parallel coupled springs.

With the hypothesis of a dispersion of rigid spheres of PLLA in a PHBV matrix, the semiempirical Halpin–Tsai equation can also be used[26]:

$$\frac{E_c}{E_1} = \frac{1 + AB\phi_2}{1 - B\phi_2} \tag{12}$$

where A is a parameter that can be used to adjust the effective properties between the limits of the parallel ($A = 0$) and series ($A = \infty$) bounds. The quantity B is defined as

$$B = \frac{E_2/E_1 - 1}{E_2/E_1 + A} \tag{13}$$
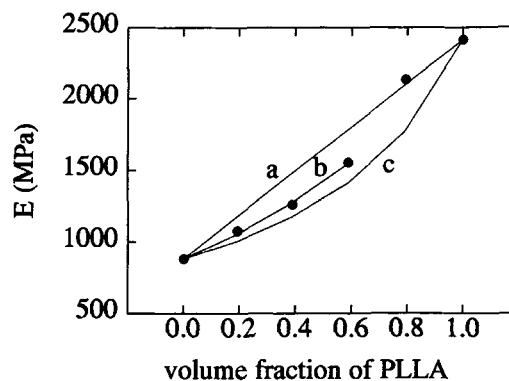
Figure 11 Experimental Young's modulus of blends (filled circles) are compared with the upper (curve a) and lower (curve c) bounds. Curve b was obtained by Halpin–Tsai equation with $A = 0.946$.
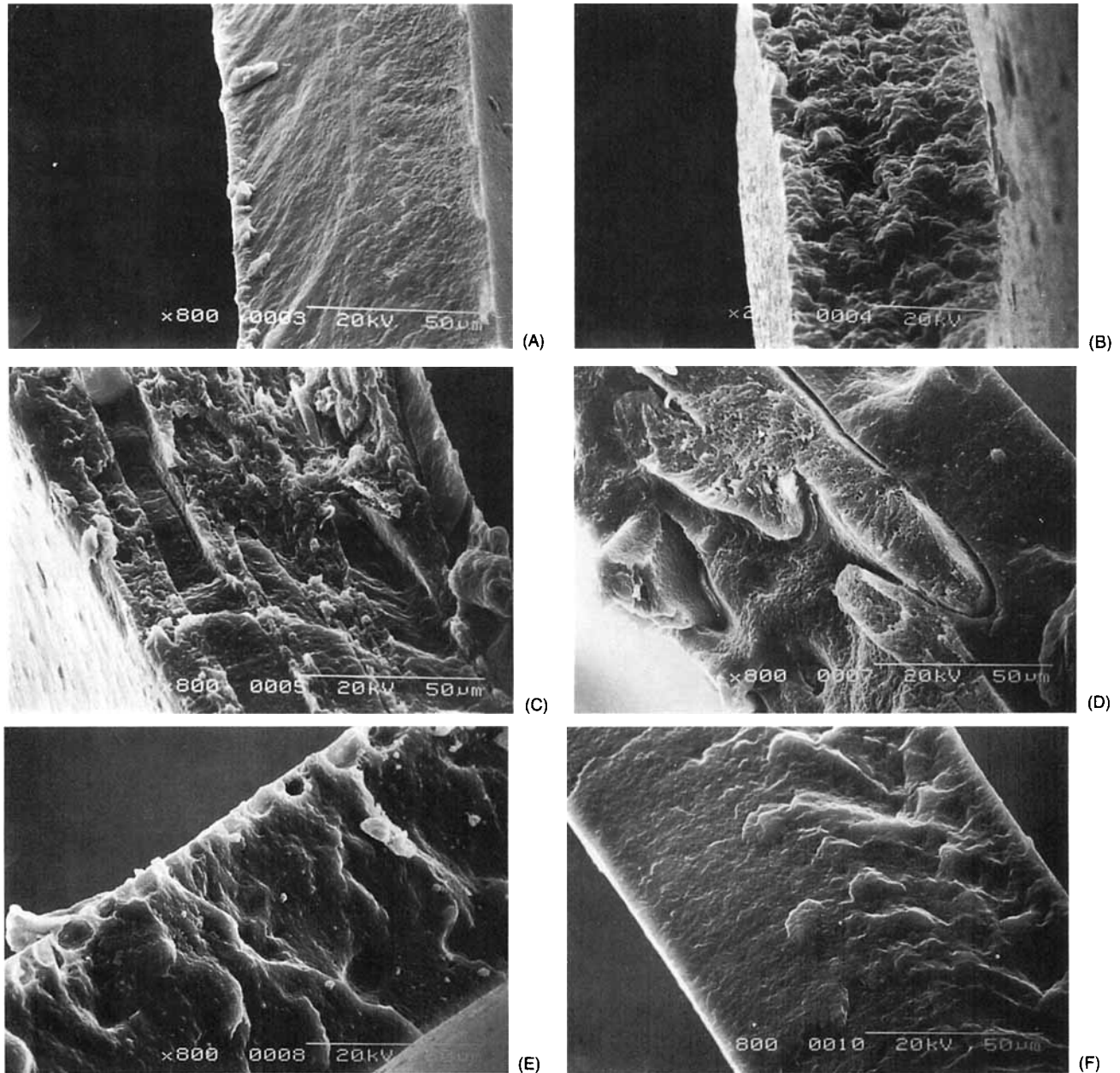
Figure 12 SEM micrographs of PHBV–PLLA blends fracture surface: (a) 0/100, (b) 20/80, (c) 40/60, (d) 60/40, (e) 80/20, (f) 100/0.

An analogous equation describes systems in which a phase inversion occurs and the more rigid phase becomes the continuous matrix phase.[28]

The best fitting curve is shown in Figure 11, where the value of the parameter $A = 0.946$.

Morphology

The morphological features detected in the electron micrographs confirmed the two-phase behavior of the system [Fig. 12(a)–(f)]. The fracture surface of the pure PLLA [Fig. 12(a)] was drastically modified when 20% PHBV was added as a dispersed component [Fig. 12(b)].

At compositions of 40% and 60% PLLA, two continuous phases were detected, according to the phase inversion that took place in a wide range of compositions. This was also revealed in the tensile properties. Comparing the SEM morphology of these phases with those relative to the parent polymers,

it seems that these two continuous phases are heterogeneous and they contain both components. As a matter of fact, the morphology of these separated phases showed more similarity to those observed for the 20/80 and 80/20 PHBV–PLLA systems rather than those of the pure components.

Theoretical Analysis of Miscibility

Miscibility between two polymers is a rare occurence if there is an absence of specific interactions that involve hydrogen bonds, which results in an exothermic enthalpy of mixing. If the exothermic interactions are absent, dispersive and polar forces can contribute to the miscibility of the system; the polymer–polymer interaction parameter χ has to be lower than the critical value χ_{crit}:[4]

$$\chi_{crit} = \frac{1}{2}\left(\sqrt{\frac{1}{N_A}} + \sqrt{\frac{1}{N_B}}\right)^2 \qquad (14)$$

where N_A and N_B are the degrees of polymerization. For our calculations we assumed $N_A = N_B = 1000$.

The Hildebrand interaction parameter χ can be written as

$$\chi \approx \tfrac{1}{6}(\delta_A - \delta_B)^2 \qquad (15)$$

where δ_A and δ_B are the solubility parameters of the two components. The Hoy group contribution method was used to estimate the solubility parameter of PHBV and PLLA.[29]

When dispersive, polar and hydrogen bonding force contributions are considered, the total solubility parameter of the polymer is given by

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (16)$$

Since blends containing copolymers interact through their blocks, David and Sincock[30] suggested a method to estimate the solubility parameter; they discussed the point that Eq. (16) can be used, with appropriate combinations of the individual contributions, to calculate the solubility parameter of the blend components and consequently a miscibility parameter, defined as

$$MP = (\delta_A - \delta_B)^2 \qquad (17)$$

In this approach, MP was used to evaluate the region of miscibility changing the weight fraction composition of one of the components in the copolymer.[30] This method, used to calculate the dif-

ferences of the solubility parameters, is different from that reported from Van Krevelen,[29] where

$$(\delta_A - \delta_B)^2 = (\delta_{dA} - \delta_{dB})^2 + (\delta_{pA} - \delta_{pB})^2 + (\delta_{hA} - \delta_{hB})^2 \qquad (18)$$

With the hypothesis that hydrogen bonding forces are not present in the PHBV–PLLA system, only the contributions of δ_d and δ_p were considered in our calculations. For PHBV, the solubility parameter was calculated by the following relation[30]:

$$\delta_{PHBV} = \delta_{PHB}\phi_{PHB} + \delta_{PHV}\phi_{PHV} \qquad (19)$$

where δ_{PHB} and δ_{PHV} are the contributions of the monomers HB and HV calculated with Eq. (16) without the contribution of the hydrogen bonding forces and the weight fractions ϕ_{PHB} and ϕ_{PHV} in the copolymer. With these assumptions the following values of solubility parameter were calculated: $\delta_{PHB} = 19.04$ and $\delta_{PLLA} = 19.38$. From these data and from Eq. (15) we obtained $\chi = 0.01953 > \chi_{crit} = 0.002$, which suggested immiscibility. On the other hand MP = 0.1156 [from Eq. (17)], and as the author pointed out,[30] this value is very close to that indicated to delineate the window of miscibility (MP ≈ 0.1).

This analysis can be used as a qualitative tool to confirm the experimental results described in this work due to the difficulties of calculating the solubility parameters of the polymers. Moreover, the assumptions regarding the degree of polymerization utilized for the theoretical calculations are not completely correct since the polymers are not monodisperse and generally $N_A \neq N_B$.

CONCLUSIONS

The detection of two glass transition temperatures for the PHBV–PLLA system suggested the presence of two distinct phases. The analysis of the T_g of the PHBV phase by means of dynamic mechanical measurements of the solvent cast materials showed that the molecular mobility of the copolyester chains were affected by the presence of PLLA, and this can be accounted for by a partial dispersion of low molecular weight PLLA or by the presence of an interphase containing both low molecular fractions of PLLA and PHBV which did not produce a remarkable shift in the glass transition temperatures but rather produced an enlargement of the T_g width. This led to a reduction of the crystallinity of the

PLLA phase and moreover contributed to the slight lowering of the PLLA melting temperature revealed by the isothermal crystallization.

Tensile properties of the solvent cast blends were interpreted on the basis of a heterogeneous structure, and the experimental results, analyzed by theoretical models, suggested that the two phases possessed good interfacial adhesion, at least for the systems containing a low amount of one component in the other. The SEM observations validated these results and moreover showed the different morphology obtained by changing the composition of the blend. These results were confirmed by the theoretical analysis of the miscibility of the blend.

Work on the degradation of these materials is in progress in order to investigate the effect of the degradation of a single constituent on the properties of the multicomponent system.

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