

Miscibility and Hydrolytic Degradation of Bioreabsorbable Blends of Poly(*p*-Dioxanone) and Poly(L-Lactic Acid) Prepared by Fusion

A. P. T. Pezzin,¹ E. A. R. Duek²

¹Departamento de Engenharia de Materiais, Faculdade de Engenharia Mecânica, Universidade Estadual de Campinas (UNICAMP), Cx. P. 6122 - CEP 13083-970 Campinas-SP, Brazil

²Centro de Ciências Médicas e Biológicas, Pontifícia Universidade Católica de São Paulo, Praça Dr. José Ermírio de Moraes, 290, 18030-230, Sorocaba, SP, Brazil

Received 13 June 2005; accepted 15 September 2005

DOI 10.1002/app.23646

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Blends of two semicrystalline polymers, poly(L-lactic acid) (PLLA) and poly(*p*-dioxanone) (PPD), were prepared by melting the polymers in different proportions. The miscibility, thermal behavior, dynamic-mechanical properties, and morphology of these blends were studied using differential scanning calorimetry (DSC), dynamic-mechanical analysis (DMA), and scanning electron microscopy (SEM). The melting temperature of PPD, determined by DSC, did not change with increasing PLLA content, suggesting that this system was immiscible. The presence of two glass transition temperatures detected by DMA also indicated the total immiscibility of the two polymers and this

phase separation was confirmed by SEM. The stability of blends immersed in tubes containing phosphate buffer (pH = 7.4) in a thermally controlled bath at (37 ± 1)°C was assessed using DSC, thermogravimetric analysis (TGA), and SEM. PLLA degraded more slowly than PPD, whereas the blends had a degradation rate that was intermediate to these two polymers. This finding indicated that it was possible to control the degradation rate of the blend by changing its composition. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1899–1912, 2006

Key words: polyesters; biodegradable; blends; miscibility

INTRODUCTION

The miscibility and phase behavior of binary polymer blends has been a subject of continuous interest in polymer research. Among the great variety of polymeric mixtures, those involving bioreabsorbable polymers are particularly interesting, especially poly(L-lactic acid) (PLLA), poly(glycolic acid) (PGA), poly(ϵ -caprolactane), and poly(*p*-dioxanone) (PPD). These materials have been intensively studied because of new potential medical applications, such as drug delivery systems and bioreabsorbable sutures.^{1–4} Bioreabsorbable polymers are also indicated for various devices, including plates, pins, and screws for the fixation of internal bone fractures,^{5–8} as well as for membranes used in cell cultures and guided regeneration in soft tissue.^{9,10} Among bioreabsorbable polymers, PLLA has the longest degradation time and can be found in the organism up to five years after the original implantation.¹¹

Since PLLA has poor processing properties, it crazes easily because of its high crystallinity and requires a long time for degradation. Consequently, the applica-

bility of this polymer has been limited.^{12–15} There are several approaches for producing PLLA-based materials with a wide range of properties and improved processability. These approaches include copolymerization, stereocomplexation, and polymer blending.^{16–25} On the other hand, PPD, a bioreabsorbable, biocompatible polymer with good flexibility and tensile strength^{4,26} has been used to make monofilament sutures with good tenacity and knotting, and can substitute for PGA and PLLA in multifilament sutures.^{25,26} Blends of PLLA with PPD would be expected to enhance the degradation rate of PLLA and dynamic-mechanical properties in functions of compositions of polymers. In this article, we described the mechanical properties, thermal behavior, morphology, and hydrolytic degradation of blends of PLLA and PPD prepared by melting these semicrystalline polymers.

EXPERIMENTAL

Blend preparation

The poly(L-lactic acid) (PLLA) (M_w = 100,000 Da) used was supplied by Medisorb. Poly(*p*-dioxanone) (PPD) was obtained from Johnson and Johnson in the form of violet polydioxanone sutures (PDS®). The dye

Correspondence to: E. A. R. Duek (eliduek@fem.unicamp.br).

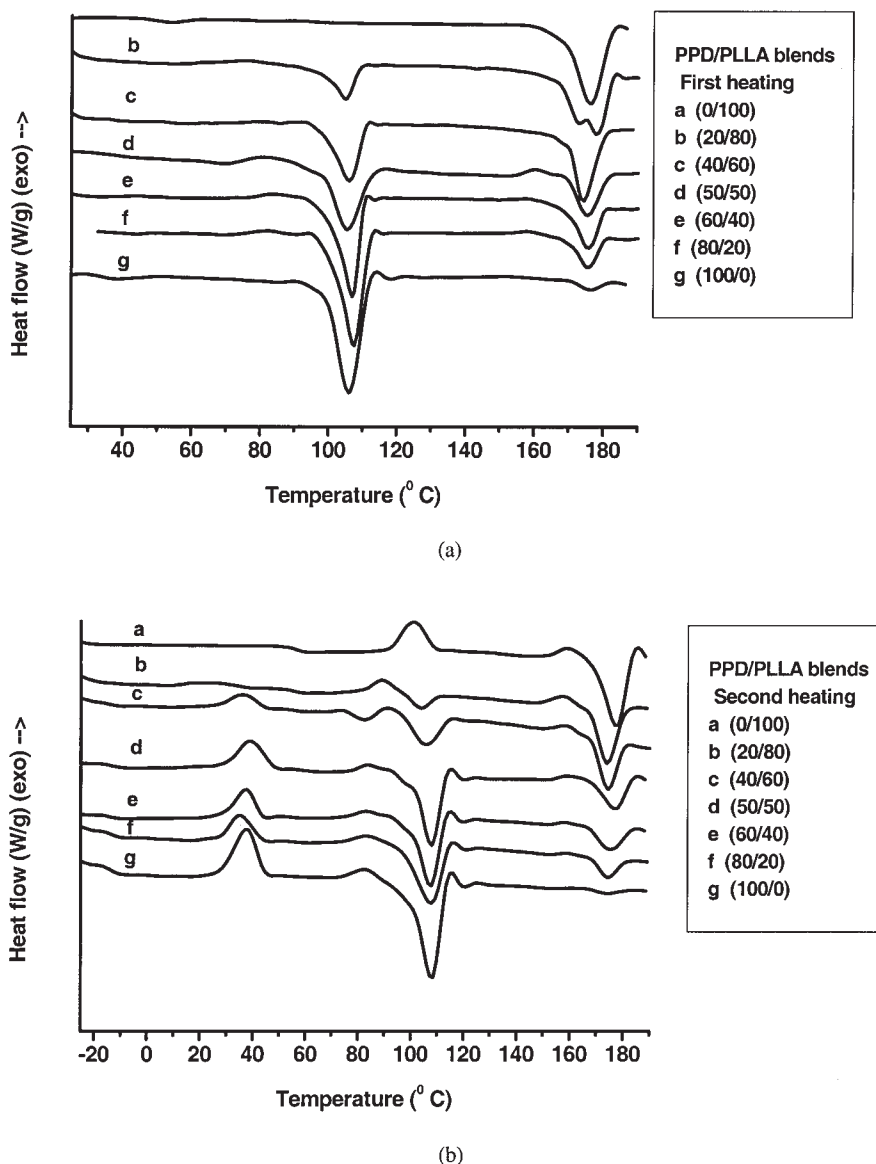


Figure 1 DSC curves for the PPD/PLLA blends. (a) first heating and (b) second heating.

was completely extracted in methylene chloride (Synth) by stirring for 24 h at room temperature prior to use. The PPD/PLLA blends were prepared by fusion using weight ratios of 0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0% (w/w) to produce pins (31 mm in diameter and 90 mm long). The blends were processed in a mini-injector (mini-Max LMM-2017) at 210°C. The samples were kept at the injection temperature for 1 min and then subjected to a constant rate of shearing (120 rpm) for 1.5 min. The temperature of the heating system was 120°C. After molding, the pins were cooled at room temperature for 30 min. The miscibility of the blends was evaluated by dynamic-mechanical analysis (DMA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

TABLE I
DSC Data for the PPD/PLLA Blends, Showing the Melting Peak Temperature (T_m) and Melting Enthalpy (ΔH_m) Obtained from the First Heating

Composition (PPD/PLLA)	PPD		PLLA	
	T_m (°C)	ΔH_m (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)
0/100	—	—	178	42
20/80	106	88	173/179	44
40/60	107	64	175	55
50/50	108	77	177	43
60/40	107	65	176	42
80/20	108	58	176	48
100/0	109	58	—	—

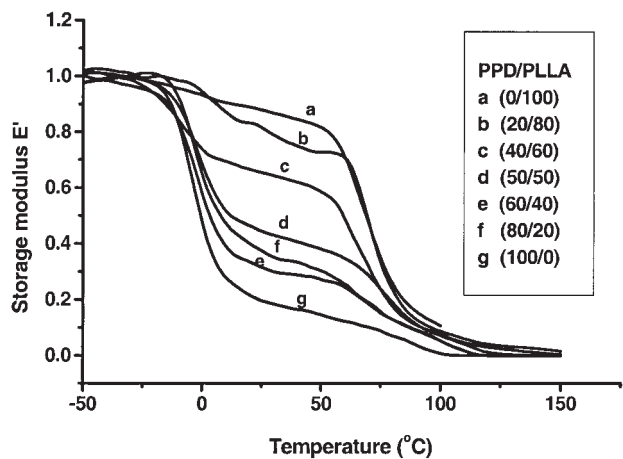
TABLE II
DSC Data for the PPD/PLLA Blends, Showing the Melting Peak Temperature (T_m), Melting Enthalpy (ΔH_m), Crystallization Peak Temperature (T_c), and Crystallization Enthalpy (ΔH_c) Obtained from the Second Heating

Composition (PPD/PLLA)	PPD				PLLA			
	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_c (J g ⁻¹)
0/100	—	—	—	—	177	51	101	28
20/80	106	86	—	—	176	57	90	16
40/60	81/108	69	36	45	176	59	92	12
50/50	109	85	39	60	177	43	—	—
60/40	108	71	37	35	176	44	—	—
80/20	106	63	36	26	176	58	—	—
100/0	108	71	37	39	—	—	—	—

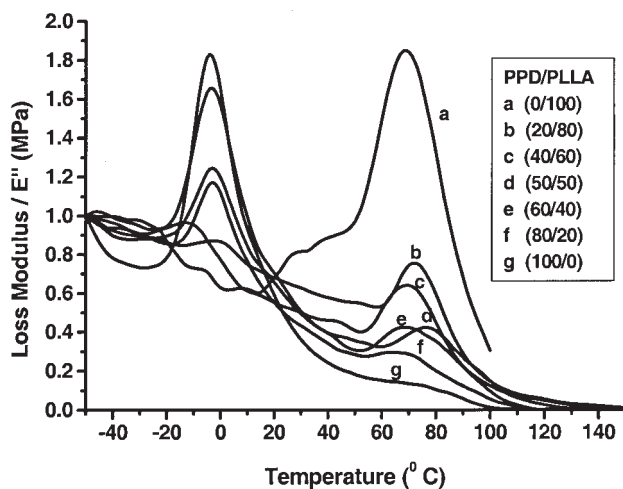
Degradation *in vitro*

Samples pins (31 mm in diameter and 90 mm long) were immersed in tubes containing phosphate buffer

(pH 7.4) in a thermally controlled bath at (37 ± 1)°C. After 2, 4, 8, 10, 12, 15, and 32 weeks, the samples were removed, washed with distilled water, vacuum dried, and studied by DSC, thermogravimetric analysis (TGA), and SEM.



(a)



(b)

Figure 2 DMA curves for PPD/PLLA blends. (a) $E' \times T$ and (b) $E'' \times T$.

Characterization

Differential scanning calorimetry

DSC measurements were done using a Netzsch STA 409C thermal analyser under helium. Samples (6–11 mg) sealed in aluminum pans were heated from 25 to 200°C at a heating rate of 5°C min⁻¹ (first heating), with the maximum temperature being maintained for 2 min. The samples were subsequently cooled to at a heating rate of 10°C min⁻¹, and then held at -30°C for 2 min. The crystallized blends were heated to 200°C at a heating rate of 5°C min⁻¹ (second heating). The melting peak temperature (T_m) and melting enthalpy (ΔH_m) were determined in the first heating and the crystallization peak temperature (T_c) and crystallization enthalpy (ΔH_c) were determined in the second heating.

Dynamic mechanical analysis

DMA measurements were done using a Netzsch-Dynamic Mechanical Analyser-242 and a tension system, according to the norm DIN 53457. The pins were

TABLE III
Glass Transition Temperatures (T_g) for PPD/PLLA Blends Obtained by DMA from Loss Modulus (E'') Curves

PPD/PLLA	T_g of PPD (°C)	T_g of PLLA (°C)
0/100	—	69
20/80	-3	72
40/60	-13	69
50/50	-3	76
60/40	-3	68
80/20	-3	64
100/0	-4	—

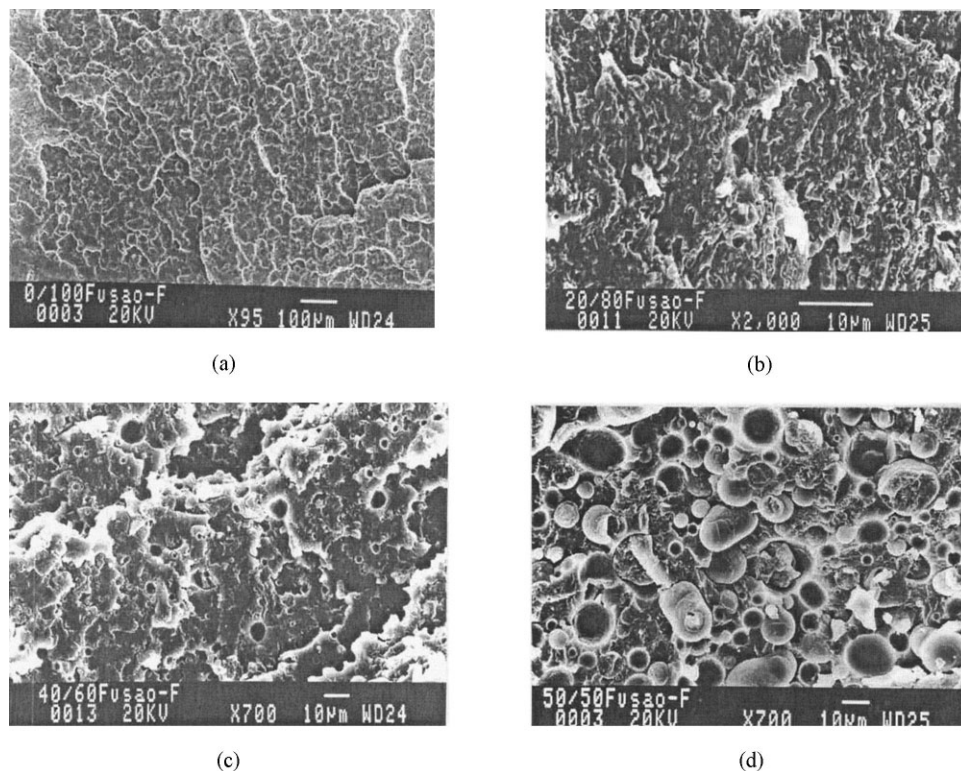


Figure 3 Scanning electron micrographs of the fracture surface of PPD/PPLA blends. (a) 0/100, (b) 20/80, (c) 40/60, (d) 50/50, (e) 60/40, (f) 80/20, and (g) 100/0.

cooled to -50°C and then immediately heated to 200°C at a heating rate of $5^{\circ}\text{C min}^{-1}$, under air, at an amplitude of $240\ \mu\text{m}$ and a frequency of $10,000\ \text{Hz}$. The miscibility of the blends was assessed based on using the glass transition temperature.

Thermogravimetric analysis

Netzsch STA 409 thermal analyser was used to evaluate the degradation of the blends. The samples were heated from 25 to 450°C at a heating rate of $10^{\circ}\text{C min}^{-1}$ under helium.

Scanning electron microscopy

SEM was done to examine the phase morphology and degradation of the blends. A scanning electron microscopy (JEOL- JXA 840A) operated at 10 – $20\ \text{kV}$ was used to observe the samples fractured in liquid nitrogen, and coated with a thin layer of gold by vacuum deposition using a Sputter Coater BAL-TEC SCD 050.

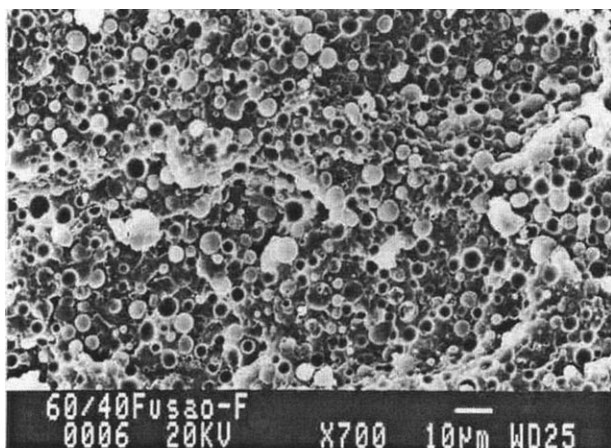
RESULTS AND DISCUSSION

Calorimetric analysis

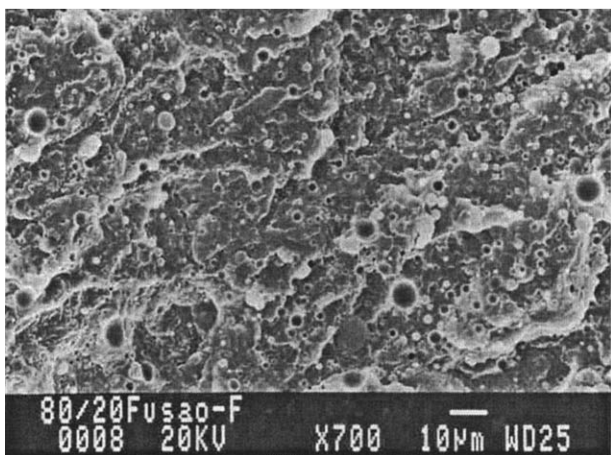
The DSC curves for the different PPD/PLLA blends and homopolymers in the first and second heatings

are shown in Figure 1(a, b), respectively. The crystallization peak temperature (T_c), crystallization enthalpy (ΔH_c), melting peak temperature (T_m), and melting enthalpy (ΔH_m) of the PPD/PLLA blends were determined from DSC thermograms and the results are summarized in Tables I and II.

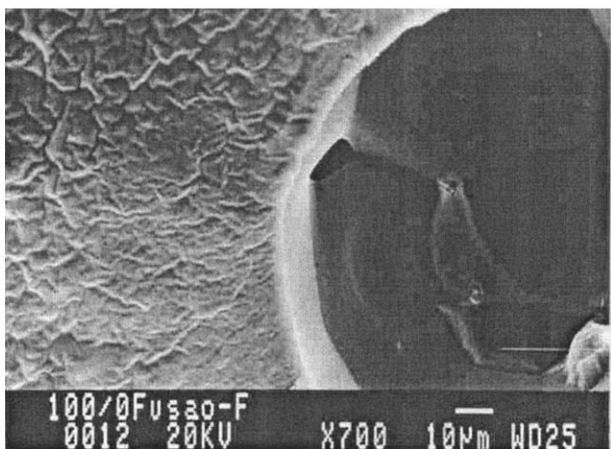
The glass transition temperatures of both polymers were not easily detectable by calorimetric analysis because of the high crystallinity of the blends. For this reason, the discussion of the glass transitions of the blends will be based on the dynamic-mechanical analysis. The ΔH_m values for PPD and PLLA were normalized relative to their respective concentration. In the first heating, two endothermic peaks attributed to the fusion of PPD crystals at 109°C and to the fusion of PLLA crystals at 178°C were observed. Table I shows that although the T_m remained constant as the PLLA content varied, the melting enthalpy of PPD increased when the PLLA content of blend was 40% . The melting enthalpy of PLLA was also increased by the presence of 40 and 80% of PPD, indicating an enhanced crystallinity of the polymers in the blends. This variation may be related to the selection applied to the process conditions, since, in the first heating, the samples are analyzed with their thermal history. The crystallization of PLLA was slightly affected by the presence of PPD, as shown by the appearance of two endothermic peaks for PLLA in the blend 20/80.



(e)



(f)



(g)

Figure 3 (Continued from the previous page)

In the second heating, it was possible to compare the samples because the thermal history had not been totally eliminated. The T_m of PPD and PLLA remained constant and equal to the T_m seen in the first heating. The values of ΔH_m for PPD and PLLA were higher

than those obtained in the first heating. These values varied little over a small range and were considered to be constant. The T_c of the PLLA and PPD homopolymers appeared at 101°C and 37°C, respectively. The T_c of PPD remained constant, a decrease from 9 to 11°C was seen for PLLA in the blends. This decrease reflected the fact that the crystallization peak of PLLA was overlain by the melting temperature of PPD. For this reason, it was very difficult to detect the T_c of PLLA in the other blends. This situation was aggravated by the lower concentration of PLLA in these blends. Therefore, it was not possible to determine the degree of crystallinity for PLLA and PPD.

The ΔH_m of PLLA and PPD and, consequently, the degree of crystallinity were higher for all blends in the second heating than in the first, and may be related to the controlled cooling before the second heating. DSC showed that the T_m of both polymers remained constant, indicating that the blends were immiscible.

Dynamic mechanical analysis

Dynamic-mechanical analysis is a powerful method for investigating several transitions in polymeric materials. Analysis of the loss modulus as a function of temperature ($E'' \times T$) is used to obtain information about blend miscibility.²⁷ The use of T_g to determine the miscibility of blends is based on the fact that the size of a domain is generally lower than 15 nm.²⁸ The maxima of the $E'' \times T$ curves obtained by DMA for the different pairs of blends and for the homopolymers are shown in Figure 2(a). Two distinct and nearly constant T_g equal to the values of the homopolymers are shown in Table III for all of the blends and suggest immiscibility of the system. The T_g values of both polymers in the blends were constant within the range of experimental error. The T_g was obtained from the maxima of the $E'' \times T$ curves and not from the curves of $\tan \delta \times T$ because $\tan \delta$ is not a pure value. $\tan \delta$ expresses the ratio between the loss energy and the storage energy, and has no direct molecular significance.²⁸ The influence of polymer concentration on the dynamic-mechanical behavior of the blends [Fig. 2(b)] shows that, in the plastic region, the storage modulus (E') of PPD was lower than that of PLLA, whereas the blends showed intermediate behavior between the homopolymers.

Morphology

Figure 3 shows SEM micrographs of the fracture surfaces of the homopolymers and of the blends obtained by fusion. The surface of PLLA was dense and smooth [Fig. 3(a)], while that of PPD was dense and wrinkled [Fig. 3(g)].

The 20/80 and 80/20 blends showed greater homogeneity than the others, probably because of low con-

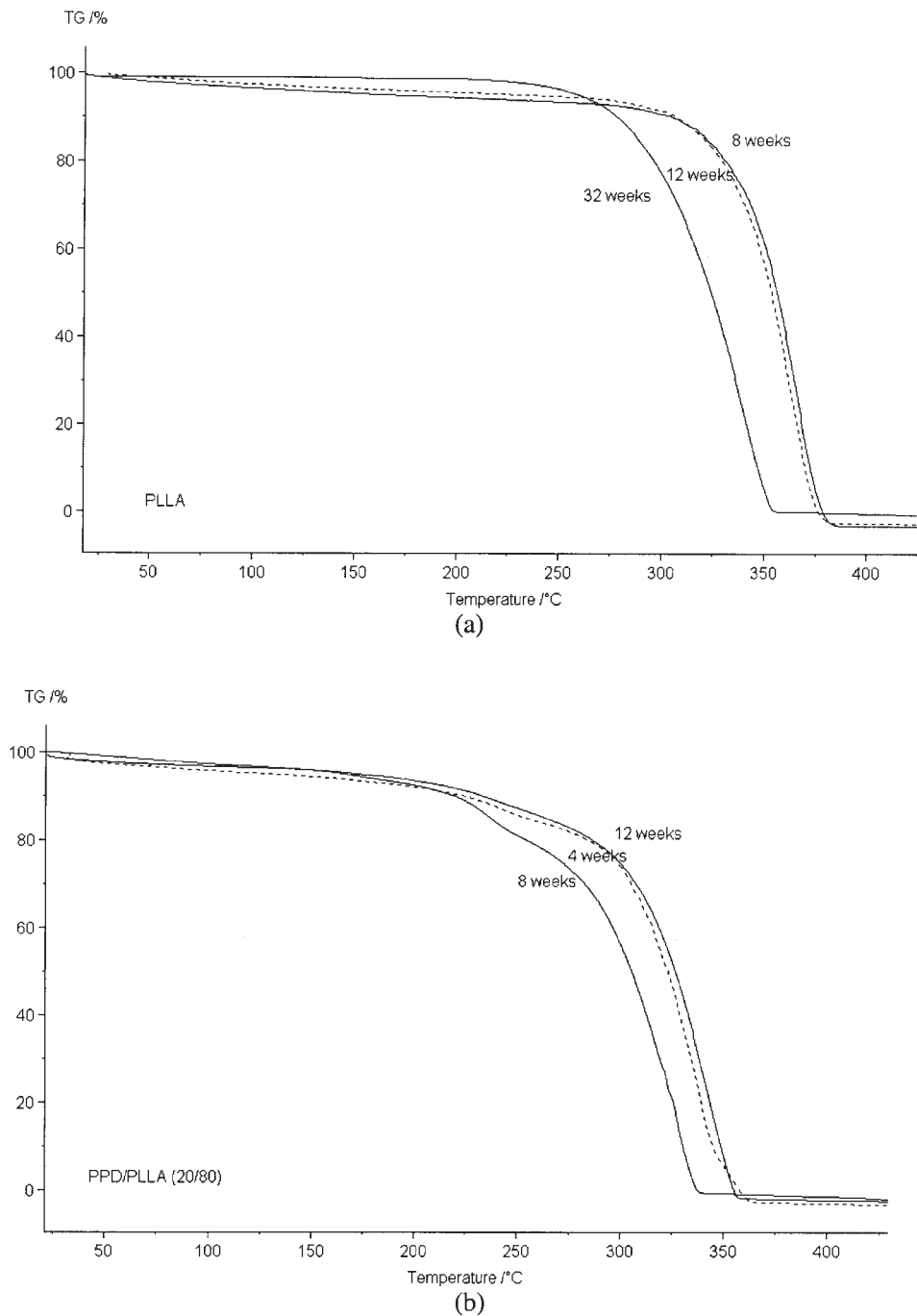


Figure 4 TGA curves of PPD/PLLA blends. (a) 0/100, (b) 20/80, (c) 50/50, and (d) 100/0 degraded *in vitro*.

centration of the second component [Fig. 3(b,f)]. SEM was unable to identify the two phases in the 20/80 blend. On the other hand, 40/60, 50/50, 60/40, and 80/20 blends [Figs. 3(c–f)] showed a clear phase separation in their morphology, thus DMA

and DSC data regarding the immiscibility of these blends. The holes seen in these blends, especially in the 50/50 blend, were produced during cryofracture of the samples and indicated low adhesion between the polymers.

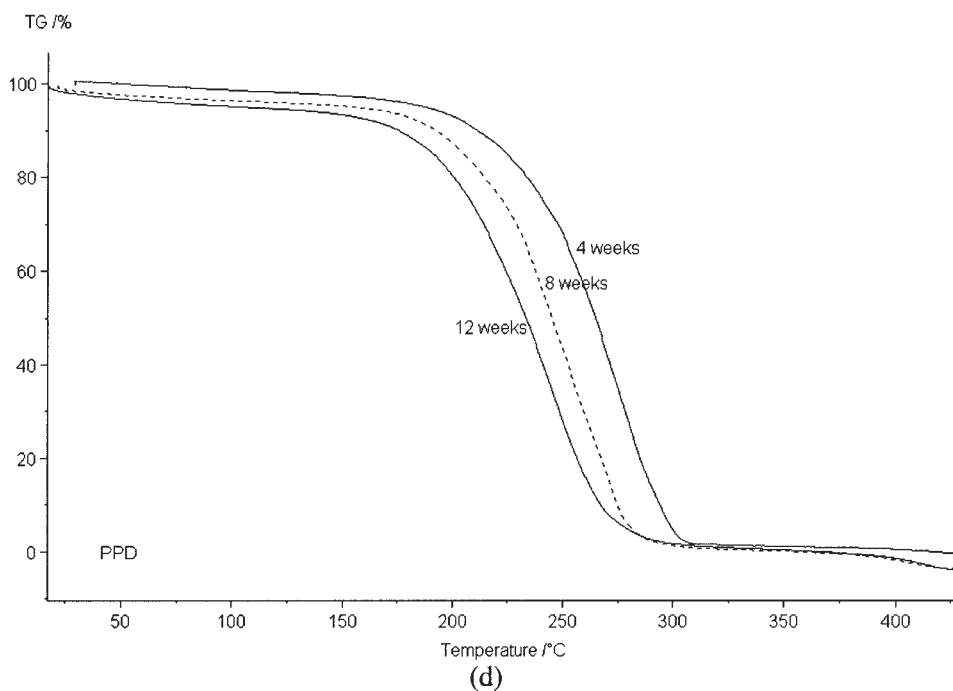
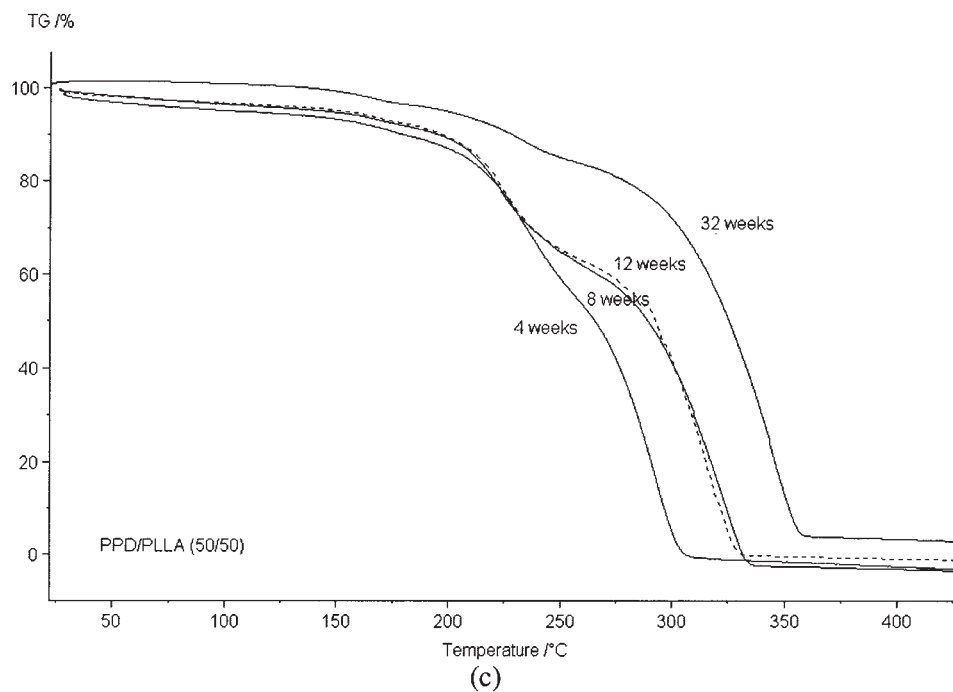


Figure 4 (Continued from the previous page)

The DMA and DSC data showed that the blends were immiscible. The SEM micrographs confirmed the presence of two distinct phases in the blends, and showed better homogeneity for the blends when one of the polymers was present in a low amount. These results agree with those obtained for films of PPD/PLLA prepared by casting.²⁹

Thermogravimetric analysis

Figure 4 shows some TGA curves for the PPD/PLLA blends after hydrolytic degradation. The degradation temperatures for the blends obtained from the TGA curves are shown in Table IV. Only one stage of mass loss and a decrease in the initial temperature of mass loss (T_{onset}) and temperature of maximum mass loss

TABLE IV
Crystallization (T_c) and Melting (T_m) Temperatures and Crystallization (ΔH_c) and Melting (ΔH_m) Enthalpies Obtained by DSC for the PPD/PLLA 0/100 Blend As a Function of Degradation Time

Time (weeks)	Heating cycle	T_c (°C)		ΔH_c (J g ⁻¹)		T_m (°C)		ΔH_m (J g ⁻¹)	
		PPD	PLLA	PPD	PLLA	PPD	PLLA	PPD	PLLA
0	1°	—	—	—	—	—	178	—	42
	2°	—	101,159	—	25,6	—	177	—	44
4	1°	—	—	—	—	—	175	—	44
	2°	—	94,160	—	11,2	—	175	—	48
8	1°	—	—	—	—	—	176	—	46
	2°	—	—	—	—	—	163,173	—	43
10	1°	—	—	—	—	—	172	—	53
	2°	—	—	—	—	—	163,172	—	52
12	1°	—	—	—	—	—	174	—	50
	2°	—	93	—	7	—	163,173	—	SO
15	1°	—	—	—	—	—	171,179	—	56
	2°	—	87	—	4	—	162,172	—	45
32	1°	—	—	—	—	—	167	—	61
	2°	—	86	—	19	—	154,163	—	44

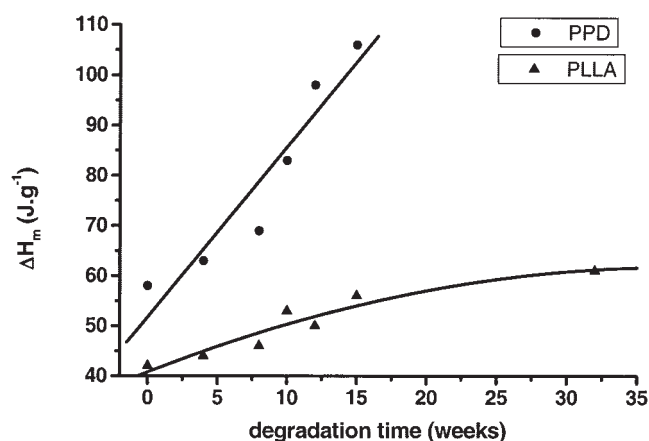


Figure 5 Initial temperature of mass loss (T_{onset}) for PLLA in PLLA/PPD blends. The data were obtained by TGA after different periods of degradation in weeks.

(T_{peak}) values as a function of degradation time were observed for the pure polymers. From 4 to 8 weeks, the T_i of PPD decreased by 29.8%, while from 8 to 12 weeks, this value decreased only 2.9%. PPD degraded faster in the first weeks as also observed for films prepared by casting.²⁹

In contrast, PLLA did not degrade during the first weeks. From 8 to 12 weeks, the decrease in T_{onset} was 1.2%, while from 12 to 32 weeks, this decrease was 11.6%.

Two stages of mass loss were observed in the 20/80 and 50/50 blends, with the first being attributable to PPD and the second to PLLA.

A decrease in the T_{onset} and T_{peak} values as a function of the degradation time was observed for the pure polymers and reflected their degradation into smaller chains that allowed degradation to start at lower tem-

TABLE V
Crystallization (T_c) and Melting (T_m) Temperatures, Crystallization (ΔH_c) and Melting (ΔH_m) Enthalpies Obtained by DSC for the PPD/PLLA 100/0 Blend As a Function of Degradation Time

Time (weeks)	Heating cycle	T_c (°C)		ΔH_c (J g ⁻¹)		T_m (°C)		ΔH_m (J g ⁻¹)	
		PPD	PLLA	PPD	PLLA	PPD	PLLA	PPD	PLLA
0	1°	—	—	—	—	109	—	58	—
	2°	37,82	—	39,7	—	108	—	61	—
2	1°	—	—	—	—	109	—	63	—
	2°	22,65	—	11,5	—	102	—	53	—
4	1°	—	—	—	—	103	—	69	—
	2°	44	—	3	—	84	—	46	—
8	1°	—	—	—	—	89,103	—	83	—
	2°	43	—	3	—	88	—	44	—
10	1°	—	—	—	—	76,99	—	98	—
	2°	33	—	1	—	53,76	—	36	—
12	1°	—	—	—	—	97	—	95	—
	2°	—	—	—	—	84,103	—	15,7	—
15	1°	—	—	—	—	96	—	106	—
	2°	37	—	3	—	80	—	34	—

TABLE VI
Crystallization (T_c) and Melting (T_m) Temperatures, Crystallization (ΔH_c) and Melting (ΔH_m) Enthalpies Obtained by DSC for the PPD/PLLA (20/80) Blends As a Function of Degradation Period

Time (weeks)	Heating cycle	T_c (°C)		ΔH_c (J g ⁻¹)		T_m (°C)		ΔH_m (J g ⁻¹)	
		PPD	PLLA	PPD	PLLA	PPD	PLLA	PPD	PLLA
0	1°	—	—	—	—	105	173,178	77	43
	2°	—	90,156	—	14,6	106	176	44	48
2	1°	—	—	—	—	104	173	68	44
	2°	—	82,151	—	4,3	100	172	22	44
4	1°	—	—	—	—	95	173	44	44
	2°	—	75,143	—	2,1	92	171	9	50
8	1°	—	—	—	—	95	171	64	45
	2°	—	140	—	3	74	170	15	50
10	1°	—	—	—	—	95	174	48	57
	2°	—	154	—	3	—	173	—	56
12	1°	—	—	—	—	94	174	41	49
	2°	—	150	—	2	—	172	—	50
15	1°	—	—	—	—	92	171	38	44
	2°	—	—	—	—	—	170	—	46
32	1°	—	—	—	—	99	170	30	64
	2°	—	—	—	—	—	157,169	—	52

TABLE VII
Crystallization (T_c) and Melting (T_m) Temperatures, Crystallization (ΔH_c) and Melting (ΔH_m) Enthalpies Obtained by DSC for the PPD/PLLA 50/50 Blend As a Function of Degradation Time

Time (weeks)	Heating cycle	T_c (°C)		ΔH_c (J g ⁻¹)		T_m (°C)		ΔH_m (J g ⁻¹)	
		PPD	PLLA	PPD	PLLA	PPD	PLLA	PPD	PLLA
0	1°	—	—	—	—	108	177	64	45
	2°	39	83,162	60	9,8	108	177	72	43
2	1°	—	—	—	—	106	173	72	55
	2°	28	83,151	30	8,5	103	172	47	60
4	1°	—	—	—	—	102	170	63	47
	2°	32	77	16	21	97	170	16	54
8	1°	—	—	—	—	82,96	165	68	61
	2°	—	—	—	—	80	153	5	58
10	1°	—	—	—	—	84,99	166,171	78	50
	2°	34	—	8	—	94	171	13	49
15	1°	—	—	—	—	95	163,168	70	58
	2°	42	—	3	—	80	151	3	54
32	1°	—	—	—	—	97	170	29	84
	2°	—	63	—	4	—	160	—	65

TABLE VIII
Values of Initial Temperature of Mass Loss (T_{onset}) and the Temperature of Maximum Mass Loss (T_{peak}) for the PPD/PLLA Blends

Blend PPD/PLLA (0/100)	T_{onset} PPD (°C)	T_{onset} PLLA (°C)	T_{peak} PPD (°C)	T_{peak} PLLA (°C)
8 weeks	—	340	—	366
12 weeks	—	336	—	363
32 weeks	—	97	—	341
PPD/PLLA (20/80)				
4 weeks	224	310	241	339
8 weeks	211	300	236	328
12 weeks	—	314	—	344
PPD/PLLA (50/50)				
4 weeks	210	276	228	322
8 weeks	204	295	224	325
12 weeks	206	293	226	322
32 weeks	199	312	233	346
PPD/PLLA (100/0)				
4 weeks	295	—	333	—
8 weeks	207	—	258	—
12 weeks	201	—	247	—

These data were obtained by TGA after different periods of degradation time.

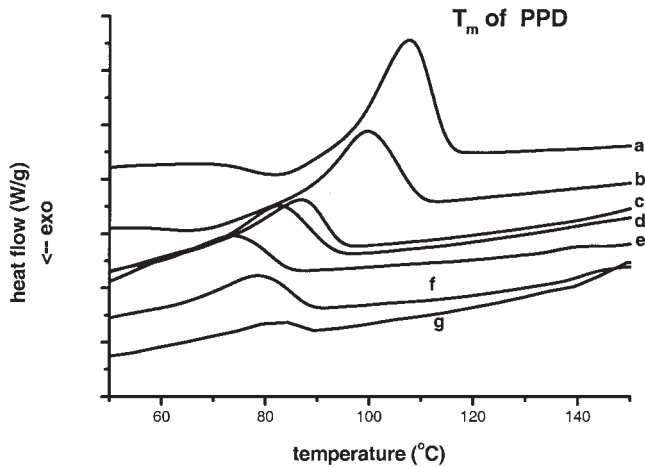


Figure 6 Melting enthalpy for PLLA and PPD (ΔH_m) obtained by DSC (first heating) as a function of the degradation time.

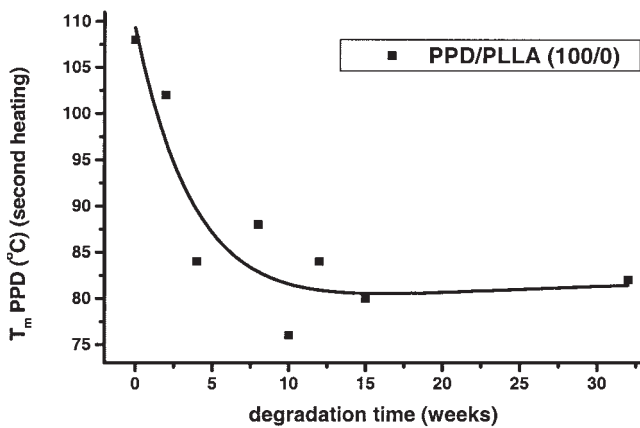


Figure 7 DSC curves (second heating) for PPD degraded *in vitro*. (a) 0, (b) 2, (c) 4, (d) 8, (e) 10, (f) 15, and (g) 32 weeks.

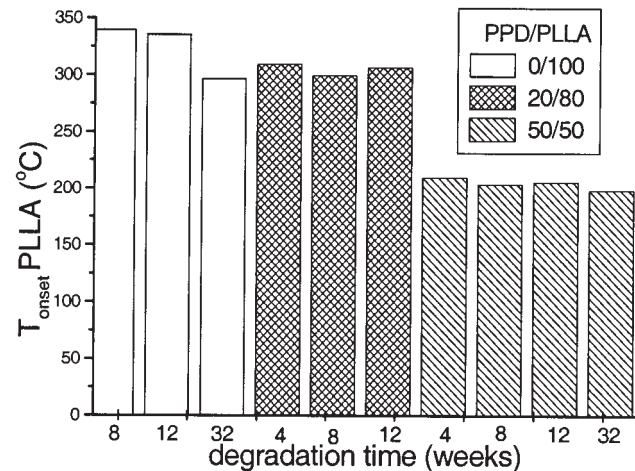
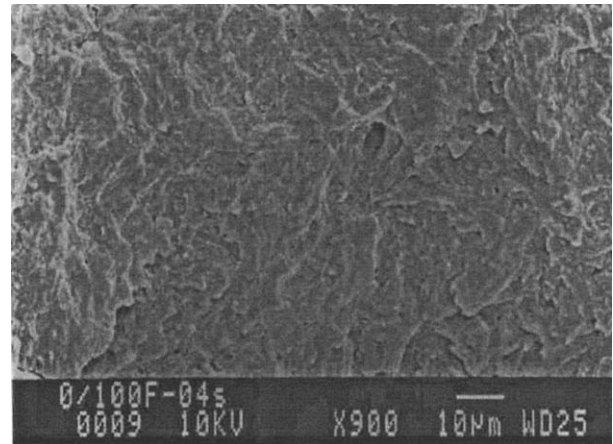
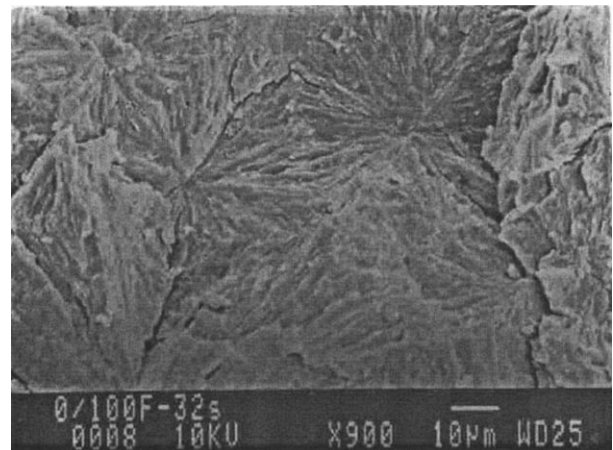


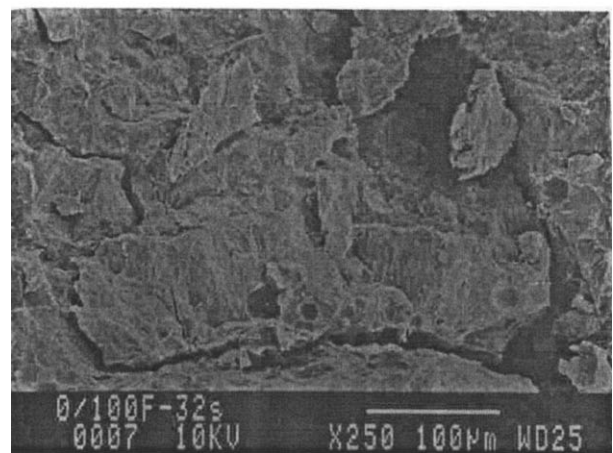
Figure 8 T_m for PPD as a function of the degradation time (weeks). The data were obtained from the DSC curves of the second heating.



(a)



(b)



(c)

Figure 9 Scanning electron micrographs of the fracture surface of the PPD/PPLA 0/100 blend after (a) 4, (b) and (c) 32 weeks of degradation.

peratures. In contrast the blends behaved differently. For the 50/50 and 20/80 blends, the values of T_{onset} and T_{peak} were increased with increasing degradation time. This behavior reflected the degradation of PPD

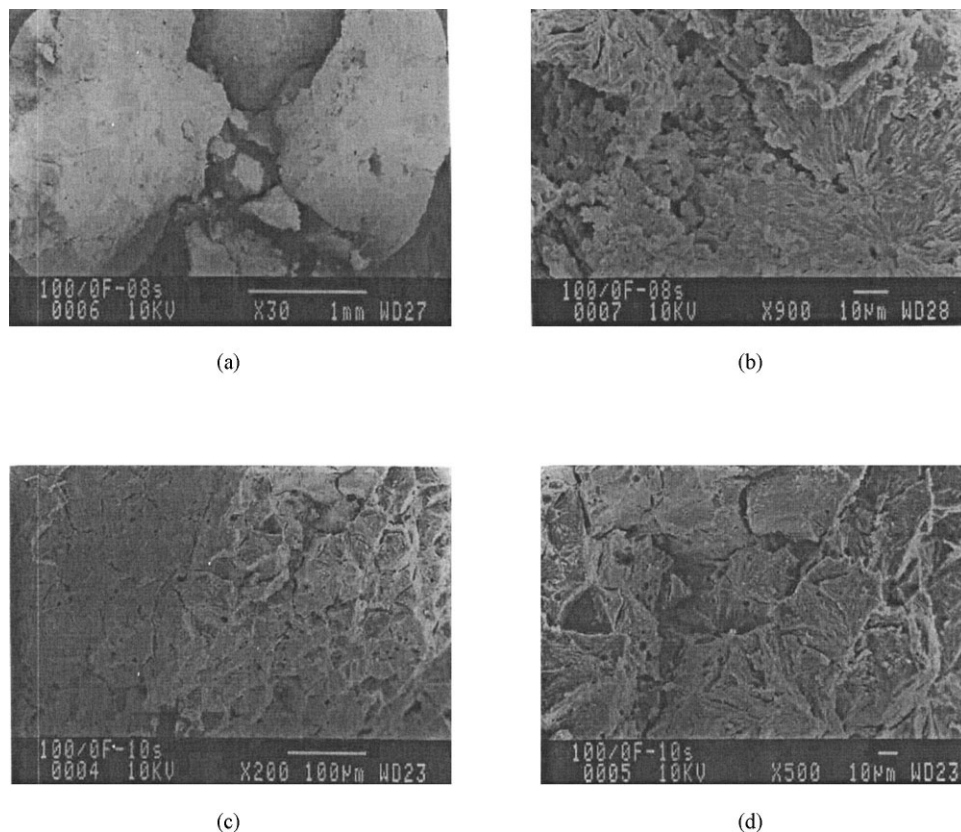


Figure 10 Scanning electron micrographs of the fracture surface of the PPD/PPLA 100/0 blend after (a) 0, (b) 8, (c) 8, and (d) 10 weeks of degradation.

to leave only PLLA, which has a higher T_{onset} than PPD. This behavior was more intense for the 50/50 blend.

Figure 5 shows that the T_{onset} for PLLA decreased as the content of PPD increased. Hence, increasing the PPD content of the blend significantly enhanced the degradation of PLLA.

Hydrolytic degradation

Tables V–VIII show the results obtained from the DSC curves for PPD/PLLA blends after hydrolytic degradation for 4, 8, 10, 12, 15, and 32 weeks. The homopolymers and the blends characteristically showed a melting peak (T_m), glass transition temperature (T_g), and a crystallization peak, all of which were typical of semicrystalline polymers.

Table V shows the data obtained for pure PLLA. After 10 weeks, there was a 26% increase in the melting enthalpy (ΔH_m) of PLLA (first heating) and more than 15% increase in this value from 10 to 32 weeks. These findings indicated that degradation the PLLA was faster at the beginning of the process. After 10 weeks, the ΔH_m tended to stabilize.

For PPD (Table VI), there was a 69% increase in the ΔH_m (first heating) after 10 weeks in buffer solution,³⁰

indicating that PPD degraded faster than PLLA. The increase in the melting enthalpy meant an increase in the degree of crystallinity of the material,^{3,7} which is characteristic of these polyesters. The ΔH_m curves for PLLA and PPD clearly illustrate the relationship between degrees of crystallinity of these polymers during the degradation process (Fig. 6). These results were comparable to those of other authors who have studied the crystallinity of PLLA^{31,32} and PPD.^{3,33}

Lin et al.³ and Sabino et al.³³ reported that the crystallinity of PPD increased after hydrolysis in buffer solution. Chu and Browning³⁴ also observed an increase in the crystallinity of PGA after hydrolytic degradation.

The increase in the PLLA crystallinity as a function of the degradation time is attributed to the chain scission of hydrolytically unstable ester bonds and, consequently, to a decrease in the molar mass of the polymer. This chain scission reduces the entanglements of these chains and increases the crystallinity in the remaining segments.³³

Sabino et al.³³ measured the pH of the buffer solutions after each week of degradation and found that the pH values ranged from 7.14 to 5.64, indicating that polymer hydrolysis released acidic, low molar mass degradation products.

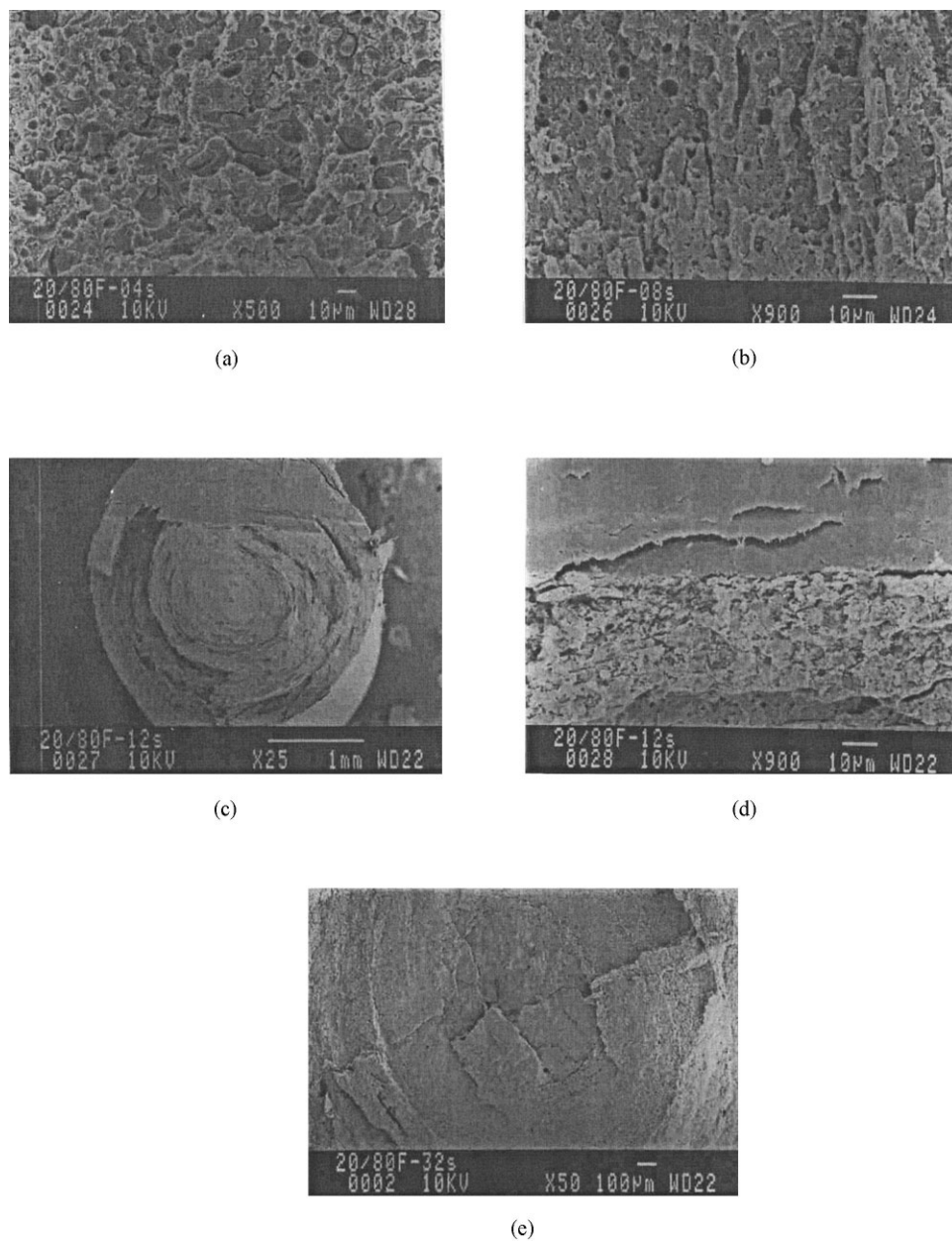


Figure 11 Scanning electron micrographs of the fracture surface of the PPD/PPLA 20/80 blend after (a) 4, (b) 8, (c) e, (d) 12, and (e) 32 weeks of degradation.

Figure 7 shows a decrease in the T_m of PPD as a function of time degradation. The values for the T_m of PPD in Figure 8 indicate that degradation was enhanced in the first 10 weeks, but remained almost constant after this period. These data agree with those reported in the literature.^{31,32,35,36}

Table V provides evidence of a second melting peak for PLLA from the eighth week of degradation. This peak became more distinguishable from the first peak as the degradation time increased. This result finding can be explained by the recrystallization of PLLA crystals during heating in DSC. This interesting result agrees with a previous report for PLLA.³²

Scanning electron microscopy

Pins of PPD/PLLA blends prepared by fusion were degraded *in vitro*, fractured in liquid nitrogen, and observed by SEM.

There were no cracks or erosion on the surface of fractured PLLA pins after 15 weeks, although after 10 weeks, an alteration in the morphology and appearance of the samples was observed. The specimens generally acquired a whitish color, with the clear formation of radial structures similar to spherulites. These structures were more intense after 32 weeks [Fig. 9(a, b)]. Nijenjuis et al.³⁷ attributed this whitening

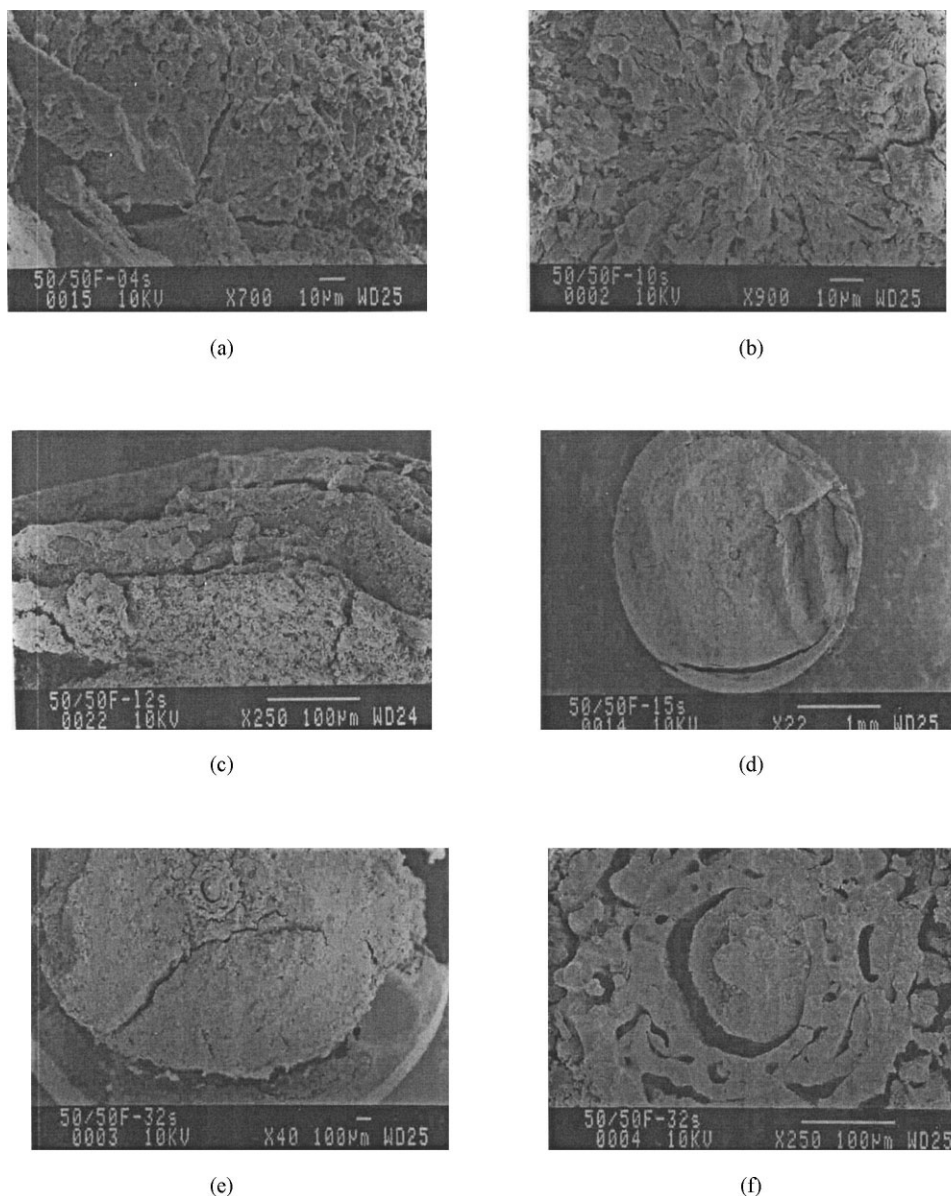


Figure 12 Scanning electron micrographs of the fracture surface of the PPD/PPLA 50/50 blend after (a) 4, (b) 10, (c) 12, (d) 15, (e) and (f) 32 weeks of degradation.

to the recrystallization of the polymers. After 32 weeks, several regions showed erosion and there was fragmentation of the samples [Fig. 9(c)].

In contrast, pins of PPD were completely degraded after 8 and 10 weeks (Fig. 10), indicating that PPD degraded faster than PLLA. On Figure 10(b, d), it was also observed structures similar to spherulites. After 10 weeks, it was impossible to prepare PPD samples for microscopy analysis, because of their fragility.

After 4 weeks, there was a discrete phase separation in the 20/80 blend. This blend consisted of a matrix of PLLA with anchored spheres of PPD, which started to detach from the matrix [Fig. 11(a)]. After 8 and 10 weeks, the blend had a porous morphology, which suggested that the PPD spheres had been completely removed,

while the PLLA matrix remained intact [Fig. 11(b)]. This same behavior in degradation was observed for films of PPD/PLLA prepared by casting.³¹ The addition of only 20% PPD accelerated the degradation of the blend. After 12 weeks, the presence of several layers was observed and degradation started from the extremity to the central region, with the formation of loose external layers [Fig. 11(c, d)]. After 32 weeks, the central region of the pins was also degraded [Fig. 11(e)].

The addition of 50% PPD accelerated the degradation of the blend. After 4 weeks, there was erosion on the surface of the fracture [Fig. 12(a)] and, after 10 weeks, the formation of spherulites [Fig. 12(b)] was observed. This formation was attributed to the increase in PLLA crystallinity caused by sample degra-

dition, as also observed for PLLA. After 12 weeks, the layers in the pins became clear [Fig. 12(c)] and, after 15 weeks, there was detachment of the external layer [Fig. 12(d)]. After 32 weeks, the samples were very fragile [Fig. 12(e)], and unusual structures with irregular empty spaces were seen; these structures probably corresponded to degraded PPD [Fig. 12(f)].

CONCLUSIONS

Two glass transition temperatures that remained nearly constant and were equal to those of the homopolymers, as well as constant values of T_m , were observed in all of the blends studied, thus indicating that the two polymers were immiscible. Phase separation was confirmed by SEM. DMA showed that the properties of blends were intermediate to those of the pure polymers. This suggested that it was possible to control the properties of the material changing by the blend composition.

The degradation of PPD were faster in the first weeks and was greater than that of PLLA. Increasing the PPD concentration accelerated the blend degradation, which indicated that it was also possible to control the rate degradation of by changing the blend composition. Pins with a higher PPD content were more flexible and degraded faster, whereas pins with a higher content of PLLA were more rigid and degraded more slowly.

References

- Heller, J. *Biomaterials* 1980, 1, 51.
- Jackanic, T. M.; Nash, H. A.; Wise, D. L.; Gregory, J. B. *Contraception* 1973, 8, 227.
- Lin, H. L.; Chu, C. C.; Grubb, D. J. *Biomed Mater Res* 1993, 27, 153.
- Ray, J. A.; Doddi, N.; Regula, D.; Williams, J. A.; Melveger, A. *Surg Gynecol Obstet* 1981, 153, 497.
- Leenslag, J. W.; Pennings, A. J.; Bos, R. M.; Rozema, F. R.; Boering, G. *Biomaterials* 1987, 8, 311.
- Bos, R. R. M.; Rozema, F. R.; Boering, G.; Nijenhuis, A. J.; Pennings, A. J.; Jansen, H. W. B. *Br J Oral Maxillofac Surg* 1989, 27, 467.
- Duek, E. A. R.; Zavaglia, C. A. C.; Belangero, W. D. *Polymer* 1999, 40, 6465.
- Bostman, O. M.; Makela, E. A.; Tormala, P.; Rokkanen, P. *J Bone Joint Surg* 1989, 71, 706.
- Wald, H. L.; Sarakinos, G.; Lyman, M. D.; Mikos, A. G.; Vacanti, J. P.; Langer, R. *Biomaterials* 1993, 14, 270.
- Robert, P.; Mauduit, J.; Frank, R. M.; Vert, M. *Biomaterials* 1993, 14, 353.
- Mainil-Varlet, P.; Rahm, B.; Gogolewski, S. *Biomaterials* 1997, 18, 257.
- Miller, R. A.; Brady, J. M.; Cutright, D. E. *J Biomed Mater Res* 1977, 11, 711.
- Vert, M.; Chabot, F.; Leray, J.; Christel, P. *Makromol Chem Suppl* 1981, 5, 30.
- Chu, C. C. *J Appl Polym Sci* 1981, 26, 1727.
- Fukuzaki, H.; Yoshida, M.; Asano, M.; Kumakura, M. *Eur Polym J* 1989, 25, 1019.
- Kricheldorf, H. R.; Kreiser-Saunders, I. K. *Macromol Symp* 1996, 103, 85.
- Vert, M.; Schwach, G.; Coudane, J. *J Macromol Sci Pure* 1995, A32, 787.
- Spinu, M.; Jackson, C.; Keating, M. Y.; Gardner, K. H. *J Macromol Sci Pure* 1996, A33, 1497.
- Stevens, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Makromol Symp* 1996, 102, 107.
- Stevens, W. M.; Bernard, A.; Van de Witte, P.; Dijkstra, P. J.; Feijen, J. *J Appl Polym Sci* 1996, 62, 1295.
- Reeve, M. S.; McCarthy, S. P.; Gross, R. A. *Macromolecules* 1993, 26, 888.
- Zhang, L.; Xiong, C.; Deng, X. *Polymer* 1996, 37, 235.
- Koyama, N.; Doi, Y. *Macromolecules* 1996, 29, 5843.
- Li, S. M.; Rashkov, I.; Espartero, J. L.; Manolova, N.; Vert, M. *Macromolecules* 1996, 29, 57.
- Guyuron, B.; Vaughan, P. A. C. *Plast Reconstr Surg* 1995, 98, 817.
- El-Mahrouky, A.; McElhaney, J.; Bartone, F. F.; King, L. *J Urol* 1987, 138, 913.
- Iannace, S.; Ambrosio, L.; Huang, S. J.; Nicolais, L. *J Appl Polym Sci* 1994, 54, 1525.
- Utracki, L. A. *Polymer Alloys and Blends, Thermodynamics and Rheology*; Hanser Publishers: New York, 1990.
- Pezzin, A. P. T.; Duek, E. A. R. *Polym Sci Technol* 2002, XII, 285.
- Assis, P. R. V.; Pezzin, A. P. T.; Zavaglia, C. A. C.; Duek, E. A. R. *Synthesis and characterization of polydioxanone synthesized by casting and phase separation in Anais do VI Simposio Latino Americano de Polimeros (SLAP VI), IV Congresso Ibero Americano de Polimeros (CIP IV) and IV Simposio Chileno de Química Y Físico Química de Polimeros (CHIPOL IV), Viña del Mar, Chile 1998, 1, 10.*
- Tsuji, H.; Ikada, Y. *Polym Degrad Stab* 2000, 67, 179.
- Tsuji, H.; Ikada, Y. *J Appl Polym Sci* 1997, 63, 855.
- Sabino, M. A.; González, S.; Márquez, L.; Feijoo, J. L. *Polym Degrad Stab* 2000, 69, 209.
- Chu, C. C.; Browning, A. *J Biomed Mater Res* 1988, 22, 699.
- Vert, M.; Li, S.; Garreau, H. *J Controlled Release* 1991, 16, 15.
- Migliaresi, C.; Fambri, L.; Cohn, D. *J Biomater Sci Polym Ed* 1994, 5, 591.
- Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Polym Bull* 1991, 26, 71.