

Biodegradable Polymer Blends of Poly(lactic acid) and Poly(ethylene glycol)

MIHIR SHETH,¹ R. ANANDA KUMAR,¹ VIPUL DAVÉ,¹ RICHARD A. GROSS,² STEPHEN P. MCCARTHY¹

¹ Department of Plastics Engineering, NSF Center for Biodegradable Polymer Research, University of Massachusetts Lowell, Lowell, Massachusetts 01854

² Department of Chemistry, NSF Center for Biodegradable Polymer Research, University of Massachusetts Lowell, Lowell, Massachusetts 01854

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ABSTRACT: Poly(lactic acid) (PLA) and poly(ethylene glycol) (PEG) were melt-blended and extruded into films in the PLA/PEG ratios of 100/0, 90/10, 70/30, 50/50, and 30/70. It was concluded from the differential scanning calorimetry and dynamic mechanical analysis results that PLA/PEG blends range from miscible to partially miscible, depending on the concentration. Below 50% PEG content the PEG plasticized the PLA, yielding higher elongations and lower modulus values. Above 50% PEG content the blend morphology was driven by the increasing crystallinity of PEG, resulting in an increase in modulus and a corresponding decrease in elongation at break. The tensile strength was found to decrease in a linear fashion with increasing PEG content. Results obtained from enzymatic degradation show that the weight loss for all of the blends was significantly greater than that for the pure PLA. When the PEG content was 30% or lower, weight loss was found to be primarily due to enzymatic degradation of the PLA. Above 30% PEG content, the weight loss was found to be mainly due to the dissolution of PEG. During hydrolytic degradation, for PLA/PEG blends up to 30% PEG, weight loss occurs as a combination of degradation of PLA and dissolution of PEG. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1495–1505, 1997

Key words: poly(lactic acid); poly(ethylene glycol); blends; biodegradability

INTRODUCTION

The use of polymers in the biomedical field has been widely accepted since 1960.¹ There has been an increasing number of studies on the use of high molecular weight poly(lactic acid) (PLA) polymers in drug delivery systems, including fertility and cancer control,² and in surgical repair materials such as sutures and fracture pins.³ Lactic acid can be produced from carbohydrate resources such as corn, whey, barley, sweet sorghum, and

sugar cane, and also from coal, petroleum, or natural gas. PLA can be prepared either by condensation polymerization of the free acid or by catalytic ring opening polymerization of the lactide, which is the dilactone of lactic acid.⁴ Lactic acid exists as two isomers, the D(–) compound and the naturally occurring L(+) lactic acid. PLA has good physical properties such as high strength, thermoplasticity, and fabricability,⁵ and in a suitable disposal site will degrade to natural, harmless products, rendering it biodegradable and bioenvironmentally compatible.

Kulkarni³ first proposed the use of poly(D,L-lactic acid) in a resorbable prosthetic device, recognizing the possibilities of this material for repair and reconstruction of traumatic wounds. Cutright⁶ demonstrated the use of PLA for bone

Correspondence to: S. P. McCarthy.

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implants having cross sections such as films and slabs. Yolles and associates⁷ proposed the use of polymers of lactic acid and glycolic acid degradable matrices for the sustained release of bioactive substances. Poly(D,L-lactic acid) has been suggested as a disposable plastic which incinerates well and poses no threat to the environment. PLA is used as a diverting agent in the petroleum industry.⁸

Polymers of ethylene oxide, in the form of relatively low molecular weight liquids and waxes, are commonly referred to as "polyethylene glycols" (PEG). The commercial manufacture of ethylene oxide employs oxidation of ethylene by air or oxygen to ethylene oxide. The ethylene oxide is then polymerized by oxyalkylation to obtain poly(ethylene oxide), which is a crystalline, thermoplastic, water-soluble polymer. The end groups are known to be hydroxyl only in the case of the lower-molecular-weight species. PEGs are available in molecular weights ranging from 1,000 to 20,000 and are all water soluble. The solubility decreases with increased molecular weight. PEG is also soluble in many polar solvents, such as chloroform, acetone, and alcohol, and is insoluble in hydrocarbons.⁹ PEG melts are Newtonian fluids above their melting temperatures. The glass transition temperature (T_g) of PEG varies from -60°C to -75°C , depending upon the molecular weight. PEGs are used as lubricants, intermediates, binders, solvents, carriers, and coatings in the cosmetic, pharmaceutical, paper, food, textile, and chemical specialty fields.¹⁰

Younes and Daniel¹¹ have carried out miscibility studies on poly(L-lactic acid) and PEG blends made by solution casting. Yasin and colleagues¹² have studied the hydrolytic degradation study of poly(hydroxybutyrate-co-valerate)/poly(ϵ -caprolactone) blends and have observed that polymers with low molecular weight and/or low crystallinity degrade faster than polymers with high molecular weight and/or high crystallinity.

In the present work, PLA and PEG are blended in various ratios through melt-blending techniques to develop a biodegradable blend with variable properties depending upon the requirements of a particular application. The main objective of this work was to study the blend miscibility and its effect on the mechanical properties, enzymatic degradation, and hydrolytic degradation.

EXPERIMENTAL

Materials

PLA used in this research was supplied by Cargill Inc., with 8% meso content (96% L) and molecular

weight of approximately 140,000 g/mole. PEG was obtained from Union Carbide with weight average molecular weight of 20,000 g/mole.

Methods

Processing

PLA and PEG were melt-blended using a counter-rotating twin-screw extruder in the ratios of 100/0, 90/10, 70/30, 50/50 and 30/70, where the first and second numbers represent PLA and PEG by weight percentage, respectively. The temperatures during processing were approximately 120°C (zone 1) and 180°C (zones 2 and 3). For formulations where the PEG content was more than 15%, the PEG was divided into two to three parts and blended with the PLA in different stages. All of the blends were then extruded into films using a 100-mm-wide push-pull sheet die. The thickness of the films was maintained in the range of 0.15 (\pm .02) mm by adjusting the speed of the take-up unit.

Thermal Analysis

A TA Instruments 912 differential scanning calorimeter was used to determine the thermal transitions of the polymer blends with weight of the samples ranging from 6 to 12 mg. Scans were carried out from 0 to 180°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Dynamic mechanical analysis was carried out on a TA Instruments DMA 983 system under flexural mode using a heating rate of $5^\circ\text{C}/\text{min}$ between 0 and 100°C .

Polarized Optical Microscopy

Crystallization behavior was observed under a Leitz polarized light microscope with a Mettler hot stage. Samples were heated to 175°C on a glass slide for 3 min and cooled to 130°C , followed by a controlled cooling rate of $0.2^\circ\text{C}/\text{min}$ to 20°C . The micrographs were recorded and the samples were heated to 80°C (above the melting point of PEG) and again the micrographs were recorded.

Mechanical Properties

Tensile testing of the films was carried out according to ASTM D882 using an Instron 1137 tensile tester. All the films were conditioned for 48 h. The test was carried out at a crosshead speed of 12.5 mm/min with a gauge length of 100 mm using film specimens 25 mm wide. Tensile strength, modulus, and percentage elongation

were calculated from the load-elongation curves obtained for five to seven specimens from each sample. The standard deviation values for yield strength and modulus were found to be within 5% and for elongation at break, 8%.

Enzymatic Degradation Study

PLA/PEG films with 20 mm × 10 mm size and average thickness of 0.15 mm were placed in disposable vials containing 5 mL of Tris/HCl buffer (pH 8.6), 1 mg of Proteinase K, and 1 mg of sodium azide. The degradation study was carried out at 37°C in a shaker bath at 200 rpm. Degradation studies for PLA/PEG 100/0, 90/10, and 70/30 films were carried out for 48 h; and for 50/50 and 30/70 films, studies were done for 16 h. Samples were taken out periodically, washed with distilled water, and dried in the vacuum oven at room temperature for 24 h. The dried samples were weighed to measure the weight loss.

Hydrolytic Degradation Study

Films of 100/0, 90/10, and 70/30 PLA/PEG blends with 20 mm × 10 mm size and average thickness of 6 mils were placed in disposable vials containing buffer solution of pH 10.6. Samples were degraded at 37°C in a shaker bath at 200 rpm. The degradation study was performed for 45 days. Samples were taken out every 5 days and were washed with distilled water and dried in the vacuum oven at room temperature for 24 h. The dried samples were weighed to measure the weight loss.

Proton NMR Spectroscopy

Proton (^1H) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WP-270 SY Spectrometer at 270 MHz for all the blends, using tetramethylsilane as an internal reference. Thirty to 40 mg of the sample was dissolved in 2 mL of CDCl_3 . ^1H -NMR peak areas were determined by spectrometer integration and are reported as relative intensities representing a given number of hydrogens. After 48 h of enzymatic degradation, compositions of 90/10 and 70/30 blends were determined. Compositions were determined after 8 h of enzymatic degradation for the 50/50 and 30/70 blends. For hydrolytic degradation, compositions of PLA/PEG-90/10 and -70/30 were determined after 45 days.

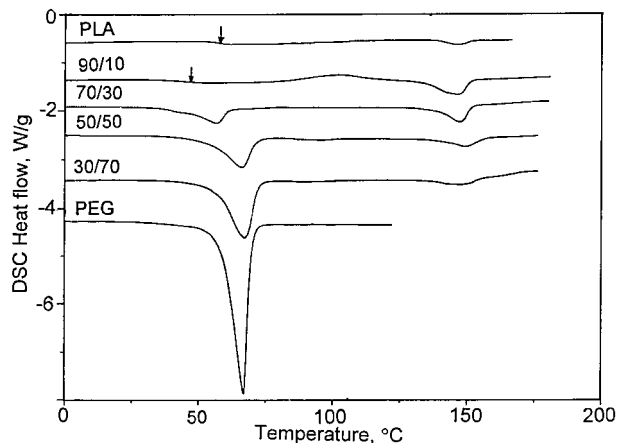


Figure 1 DSC scans of the PLA/PEG blends.

RESULTS AND DISCUSSION

Thermal Analysis

Differential scanning calorimetry (DSC) scans of all the melt-extruded films were carried out in order to characterize the thermal properties of the blends. Figure 1 shows the DSC traces of the PLA/PEG blends and the data are given in Table I. The T_g was taken as the midpoint of the inflection and the melting points are the peak temperatures of the melting endotherms. For pure PLA, the T_g was observed at approximately 57°C. At 10% PEG concentration, the T_g decreased to approximately 45°C. The 70/30 blend showed a glass transition at 37°C but for blend compositions having higher concentrations of PEG, the T_g could not be observed by DSC.

For pure PLA, no crystallization exotherm was observed but a small melting endotherm was seen. When 10% PEG was present, PLA crystallized significantly with an exothermic value of 20 J/g. This may be attributed to the plasticizing action of PEG. For higher concentrations of PEG the crystallization exotherm did not exist for PLA. It is possible that PEG increases the crystallization rate of PLA and these blends reach the maximum crystallization during the initial cooling. Even with 70% PEG the blend showed a melting endotherm, indicating that the crystallinity of PLA was enhanced rather than suppressed by the presence of PEG, as reflected by the higher values of the melting endotherms. The melting temperature (peak) of PLA was not affected by the presence of PEG. For PEG concentrations 30% and above, the melting endotherm of PEG was also observed. The normalized heat-of-fusion values for PEG were found to decrease with increasing

Table I Results from DSC for the PLA/PEG Blends

PLA/PEG	T_g (°C)	T_m (PEG) (°C)	T_m (PLA) (°C)	ΔH_f (PEG) (J/g)	ΔH_c (PLA) (J/g)	ΔH_f (PLA) (J/g)	$\Delta H_f - \Delta H_c$ (PLA) (J/g)
100/0	57.4	—	146	—	—	4.6	4.6
90/10	42.5	—	146	—	20.2	22.3	2.1 (2.33)
70/30	—	55.9	146	21.2 (70.6)	—	20.7	20.7 (29.6)
50/50	—	66.2	149	45.3 (90.6)	—	13.0	13.0 (26.0)
30/70	—	67.8	147	77.3 (110.4)	—	11.4	11.4 (38)
0/100	—	66.2	—	147.7	—	—	—

Values in parentheses indicate the endotherm values normalized for the concentration of the corresponding component. T_m values are the peak temperatures.

PLA concentration. Crystallization of PEG can occur at room temperature and it is possible that as the polymer cools from the melt, PEG remains soluble in PLA and hence does not achieve its maximum crystallinity.

Plots of storage and loss modulus as a function

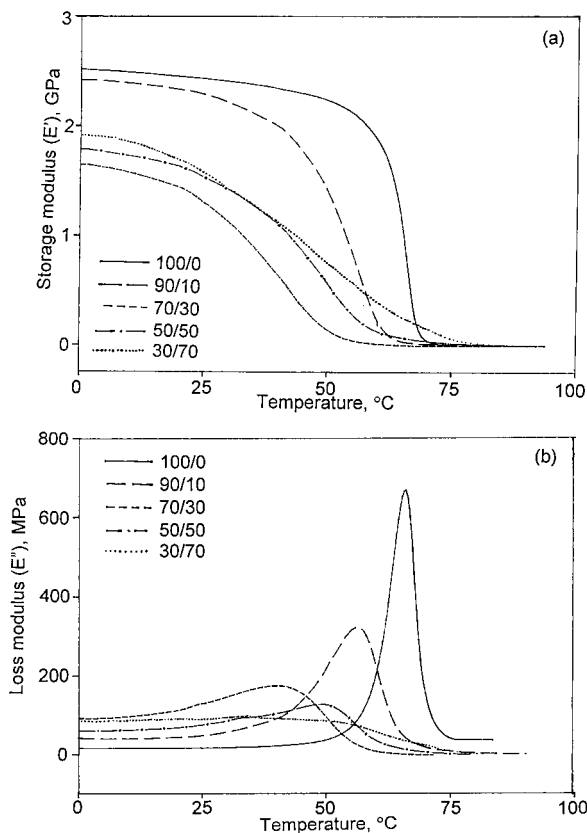


Figure 2 Plots of (a) storage modulus, E' , and (b) loss modulus, E'' versus temperature.

of temperature obtained from dynamic mechanical analysis are shown in Figure 2(a,b) and the data in Table II. For the neat PLA, the storage modulus fell abruptly at approximately 60°C, at the onset of the glass transition of PLA. For 10% PEG content, the decrease occurred at approximately 45°C, whereas at 30% PEG this decrease occurred at approximately 30°C. For higher concentrations of PEG, the transition seems to be occurring over a broader range of temperature and at higher temperatures than the 30% PEG, due to either crystallization effects or phase separation of the amorphous phase. At 0°C, neat PLA showed a modulus value of approximately 2.5 GPa. The addition of 10% PEG resulted in a decrease of this value to only 2.4 GPa, however the 30% PEG blend showed a more significant reduction in the modulus value to 1.65 GPa. Increasing concentrations of PEG above the 30% showed an increase in the modulus values which can be attributed to increasing crystallinity of PEG. For pure PLA, the glass transition occurred within a narrow temperature range whereas for the blends it occurred over a much broader range of temperature. This was particularly noticeable for the blends with 30, 50, and 70% PEG, where a significant reduction in the storage modulus occurred over the temperature range of 25–50°C and the melting of the PEG did not begin until 50°C (Fig. 1). The early softening of these blends before the melting of the crystalline portion of PEG was an indication of partially miscibility in the amorphous region.

Polarized Optical Microscopy

Polarized optical micrographs of neat PLA, PEG, and the blends obtained at a cooling rate of 0.2°C

Table II Results from DMA for the PLA/PEG Blends

PLA/PEG	E' (GPa)	E'' (MPa)	Transition Range (°C)	E'' Peak Temp. (°C)
100/0	2.51	15.6	60.9–68.5 (7.6)	65.5
90/10	2.42	43.7	44.6–61.4 (16.8)	56.1
70/30	1.65	95.7	27.2–52.1 (24.9)	40.9
50/50	1.80	62.3	33.6–60.1 (26.5)	49.5
30/70	1.96	86.3	23.4–69.6 (46.2)	55.1

Values in parentheses indicate the difference between the onset and end temperatures of transition.

are shown in Figure 3. It can be seen that for neat PLA, the final structure consists of a large number of small spherulites. In the case of blends of all compositions, the spherulitic structure of PLA dominated and the spherulite size increased with increasing concentrations of PEG. In the blends with 30, 50, and 70% PEG, the patterns appeared to be different from that of neat PLA where circular dark and bright rings are seen instead of the characteristic Maltese crosses. These samples were further heated to 80°C to melt the PEG component (Fig. 4). Upon melting of the PEG, it was observed that the dark rings became darker, however the original pattern remained unaltered. It is apparent that the presence of PEG facilitates the spherulitic growth of PLA. It has been found that the presence of some common plasticizers also enhance the spherulitic growth of PLA and do not affect the pattern.¹³ In general, it can be observed that PEG enhances the crystallization of PLA and even at high concentrations of PEG, PLA crystallizes from the melt followed by the crystallization of PEG at lower temperatures.

Mechanical Properties

Figure 5 shows the stress–strain curves for the PLA/PEG blends as calculated from the load–elongation curves. Tensile strength at yield was approximately 40 MPa for PLA and 28 MPa for the 90/10 blend. This drop was considerable where the addition of only 10% PEG content yielded a reduction in the tensile strength by approximately 30%. Tensile strength at yield was found to be reduced to 24.5 MPa and 18.9 MPa for the 70/30 and 30/70 blends, respectively. It is expected that the low T_g and higher mobility of

the PEG used, as compared with those of PLA, impart flexibility to the blend system, resulting in the tensile strength decreasing with increasing PEG content.

It was also found that the tensile modulus decreases with increasing PEG content up to 50% PEG. However, at 70% PEG content an increase in modulus as well as a decrease in elongation at break to 3% were found, both presumably due to the increase in crystallinity of the PEG.

Enzymatic Degradation Study

Melt-extruded films of PLA/PEG blends and pure PLA were subjected to degradation by the Proteinase K enzyme. Figure 6 shows the net weight loss (%) due to enzymatic degradation for PLA/PEG 100/0, 90/10, 70/30, 50/50, and 30/70 blends as a function of time. The net weight loss was calculated by subtracting the weight loss obtained without the enzyme from the total weight loss obtained with the enzyme. In this way the effect of dissolution of the PEG and the abiotic hydrolytic degradation of the PLA which would occur in the absence of the enzyme would not be included. Therefore the net weight loss is the additional degradation, which is attributed to the enzyme. As indicated in Figure 6, this additional weight loss due to the enzyme was seen to increase as the amount of PEG increased. A possible explanation is that following dissolution of some of the PEG there will be an increase in the porosity of the blends, leading to a greater surface area for enzyme to access the PLA. Other possible explanations include an increase in hydrophilicity of the surface, which accelerates the degradation, or an increase in the mobility of the PLA molecules, which could also facilitate the enzymatic

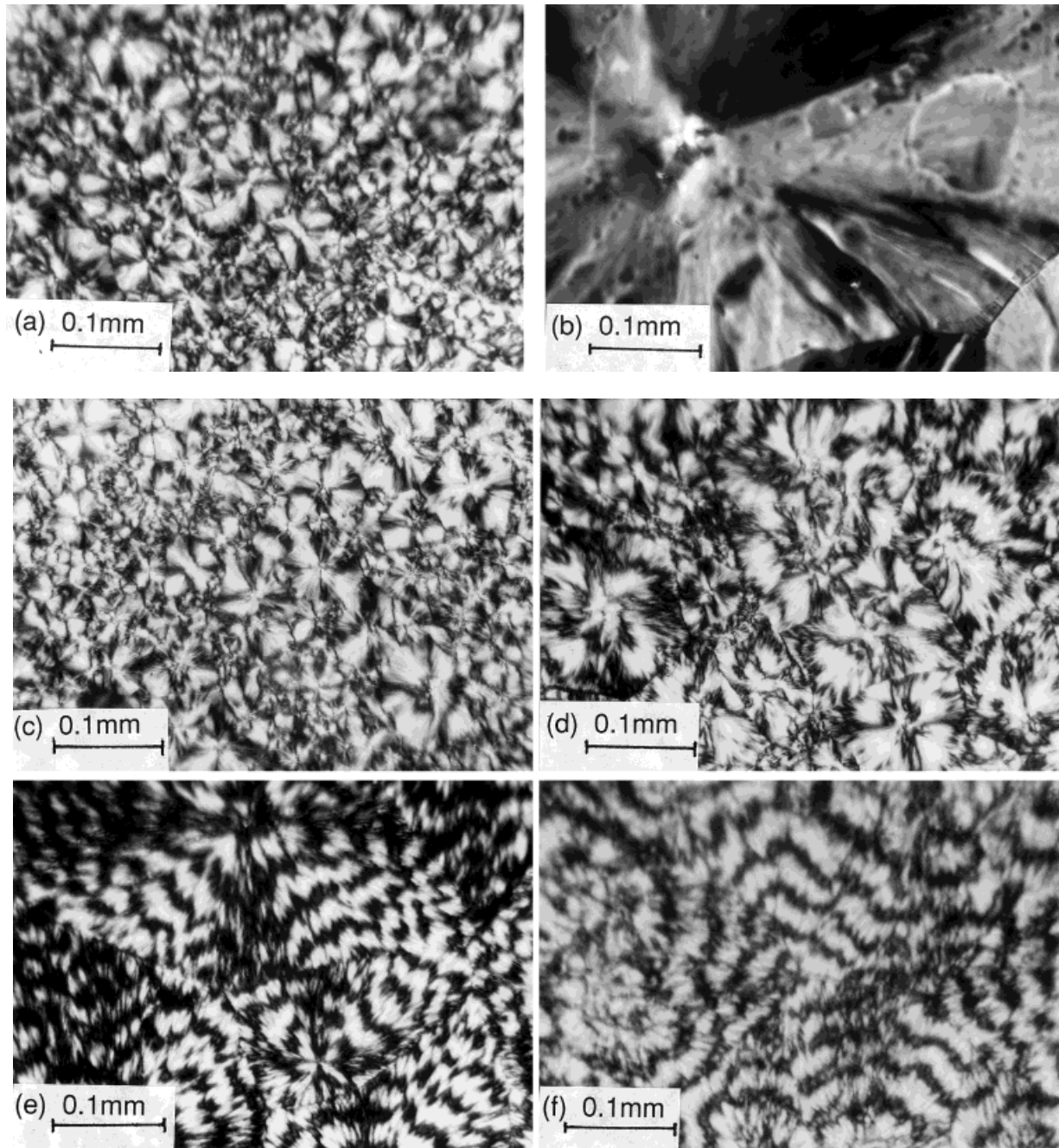


Figure 3 Polarized micrographs of (a) PLA, (b) PEG, (c) PLA/PEG-90/10, (d) PLA/PEG-70/30, (e) PLA/PEG-50/50, and (f) PLA/PEG-30/70 cooled from 130°C at 0.2°C/min.

degradation. To determine the weight loss of PLA and dissolution of PEG component individually, a composition analysis for PLA/PEG blends before and after degradation was carried out by proton NMR spectroscopy. The compositions of the 90/10 and 70/30 blends were determined after 48 h of degradation, and those for the 50/50 and 30/70 blends after 8 h of degradation. It was not possible

to carry out NMR studies for the 50/50 and 30/70 blends beyond 8 h of degradation, as the weight loss was very high and it was difficult to maintain an adequate solution concentration for NMR analysis. Figure 7 shows the NMR spectra of pure PLA, pure PEG, and the 50/50 blend (as processed). Table III summarizes the percentage weight loss, the normalized weight loss, composi-

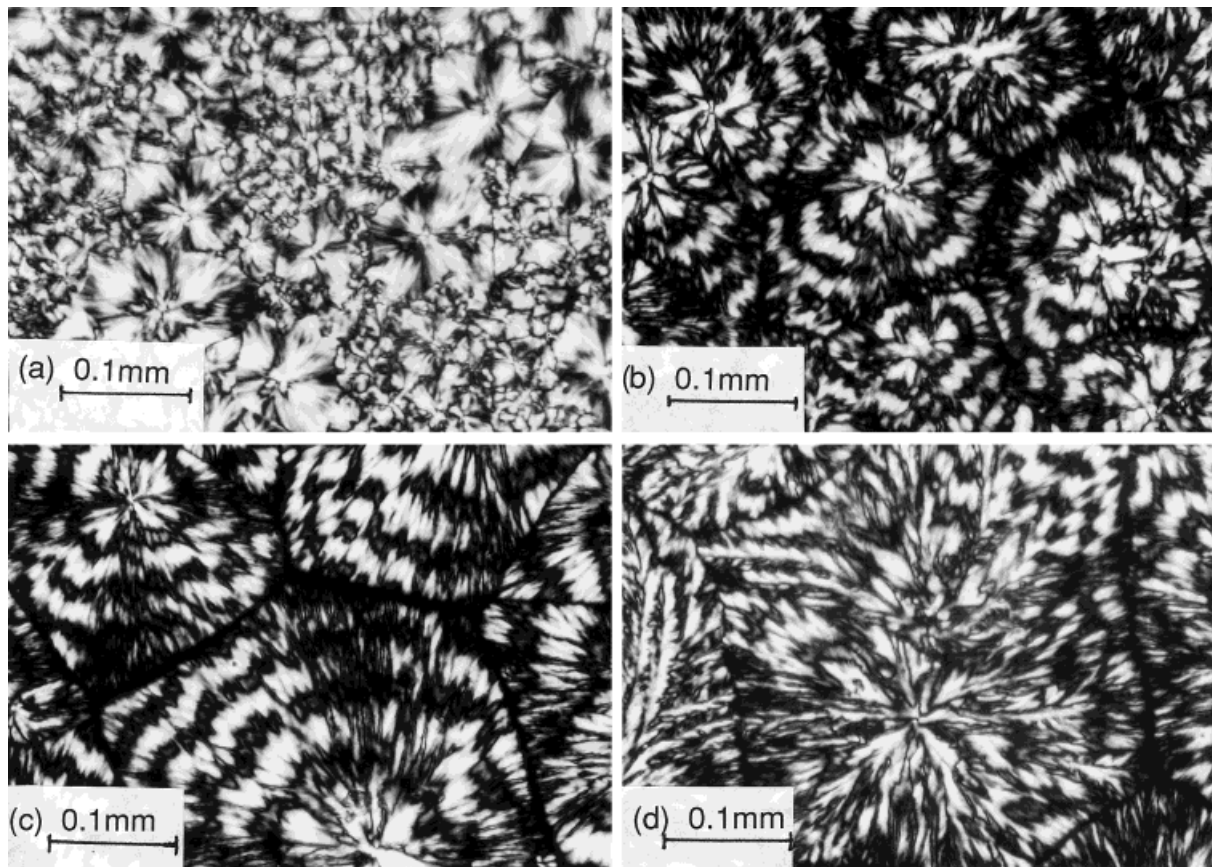


Figure 4 Polarized micrographs of (a) PLA/PEG-90/10, (b) PLA/PEG-70/30, (c) PLA/PEG-50/50, and (d) PLA/PEG-30/70 cooled from 130°C at 0.2°C/min and heated to 80°C.

tion before and after degradation, and the normalized weight loss of the individual components of the PLA/PEG blends. Normalized weight loss ($\mu\text{g}/\text{mm}^2$) of individual components (i.e., PLA and PEG) was calculated from total normalized weight loss based on change in composition after degradation. The method of calculating the composition from the NMR results and that of calculating normalized weight loss of individual components are described in the Appendix.

Pure PLA degraded by 20% of its total weight after 48 h of enzymatic degradation. Weight loss of PLA under the control degradation conditions, i.e., degradation without enzyme, was 1.6%. This difference in weight loss indicates that the PLA degradation is dominated by the enzyme Proteinase K. The weight loss for the 90/10 blend was approximately 27% after 48 h of degradation. From the NMR results, it was observed for this blend that the actual composition before and after degradation was 88/12 (Table III). The total weight loss was $18.75 \mu\text{g}/\text{mm}^2$ and the weight loss due to degradation of PLA was $17.25 \mu\text{g}/\text{mm}^2$.

The normalized weight loss of PEG was $1.5 \mu\text{g}/\text{mm}^2$. Therefore, for the PLA/PEG 90/10 blend, the dissolution of PEG was approximately 8% of total weight loss. This indicates that weight loss occurred mostly due to enzymatic degradation of PLA for this particular blend. This composition was shown from the thermal analysis to possess a T_g which is above the 37°C degradation-study temperature, indicating that when the miscible blend is in the glassy state, below T_g , there is no preferential dissolution of the PEG.

For the 70/30 blend, the weight loss was approximately 70% after 48 h. The actual composition of the blend before degradation was 71/29, and after degradation the composition changed to 84/16 PLA/PEG (Table III). This change in composition shows that there was some preferential dissolution of PEG. The total weight loss for this blend was $65 \mu\text{g}/\text{mm}^2$, out of which $41 \mu\text{g}/\text{mm}^2$ weight loss occurred due to enzymatic degradation of PLA. PEG was dissolved by approximately $24 \mu\text{g}/\text{mm}^2$, which represents 35% of the total weight loss. It is interesting to note that the

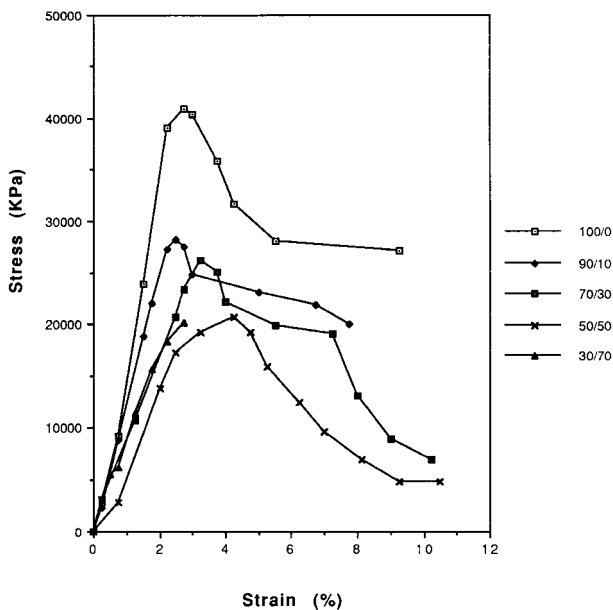


Figure 5 Stress-strain curves of the PLA/PEG blends.

final composition of this 70/30 blend became 84/16 PLA/PEG, corresponding to the composition of the miscible blend, which has a T_g corresponding to the test temperature of 39°C. In other words, as the PEG preferentially dissolves from the miscible blend the T_g of the blend will increase. This preferential dissolution will cease when the glassy state is reached, i.e., when the T_g of the miscible blend reaches the test temperature of 37°C.

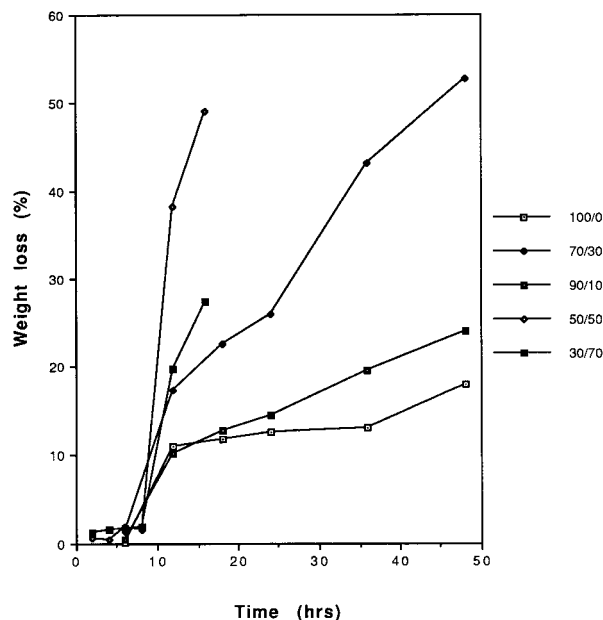


Figure 6 Net weight loss of the PLA/PEG blends due to enzymatic degradation.

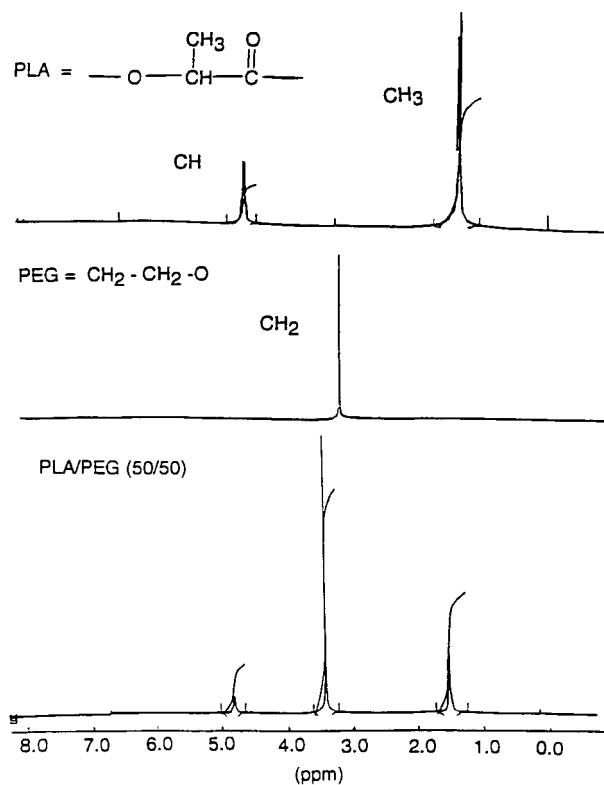


Figure 7 Proton NMR of pure PLA, pure PEG, and PLA/PEG-50/50 blend.

The weight loss after 8 h for the PLA/PEG 50/50 blend was approximately 38% of its original weight. Composition of this blend before degradation was 56/44 and after degradation it changed to 88/12. This change in composition indicates that a large portion of the PEG was preferentially dissolved during the degradation study. After 8 h, the total weight loss was approximately 22 $\mu\text{g}/\text{mm}^2$. The weight loss of PLA was 2.6 $\mu\text{g}/\text{mm}^2$ and that of PEG was 19 $\mu\text{g}/\text{mm}^2$. This indicates that the PEG was dissolved by 87% of the total weight loss. It is again interesting to note that the final composition of this 50/50 blend became 88/12 PLA/PEG which, again, corresponds to the composition of the miscible blend which has a T_g corresponding to the test temperature of 37°C.

The PLA/PEG 30/70 blend degraded by 53% of its original weight. There was a major change in composition of this blend after degradation. Composition of this blend before degradation was 35/65 and after degradation it changed to 71/29. Total weight loss for this blend after 8 h was 32.68 $\mu\text{g}/\text{mm}^2$. Degradation of PLA was only 1 $\mu\text{g}/\text{mm}^2$. Approximately 31 $\mu\text{g}/\text{mm}^2$ of PEG dissolved during the degradation study. This indicates that approximately 97% of total weight loss was due to

Table III Summary of Enzymatic Degradation Study of PLA/PEG Blends

PLA/PEG Blend	Weight Loss (%)	Normalized Weight Loss ($\mu\text{g}/\text{mm}^2$)	Composition		Normalized Weight Loss	
			Before Degradation	After Degradation	PLA ($\mu\text{g}/\text{mm}^2$)	PEG ($\mu\text{g}/\text{mm}^2$)
100/0 Enzymatic	19.51	16.275	—	—	—	—
100/0 Control	1.6	1.34	—	—	—	—
90/10 Enzymatic	27.32	18.75	88/12	88/12	17.25	1.5
90/10 Control	3.25	2.175	—	—	—	—
70/30 Enzymatic	72.41	65.575	71/29	84/16	41.235	24.34
70/30 Control	19.60	17.25	—	—	—	—
50/50 Enzymatic	38.18	21.9	56/44	88/12	2.63	19.27
50/50 Control	36.55	20.3	—	—	—	—
30/70 Enzymatic	54.75	32.68	35/65	71/29	1	31.675
30/70 Control	52.89	31.275	—	—	—	—

dissolution of PEG. This confirms that when PEG content was 30% or higher, weight loss occurred mainly due to dissolution of PEG in the buffer solution. It is again interesting to note that the final composition of this 30/70 PLA/PEG blend became 71/29. This is again attributed to the corresponding T_g of the miscible blend, although there is a higher percentage of PEG than was seen in the other blends. This increase is possibly due to some entrapped crystalline PEG domains remaining undissolved.

Figure 8(a,b) summarize the normalized weight loss (i.e., total and individual components)

of the blend as a function of PEG content after 48 and 8 h of degradation time, respectively. It is evident that when the PEG content was approximately 10%, the weight loss occurred mainly by the degradation of PLA. As the PEG content increased to 30%, the weight loss occurred due to the degradation of PLA and the dissolution of PEG. At higher PEG contents (i.e., 50% and 70%), the weight loss was observed predominantly due to the dissolution of PEG. The degradation of PLA decreased when the blends contained higher amounts of PEG, possibly due to the increased crystallinity of the PLA.

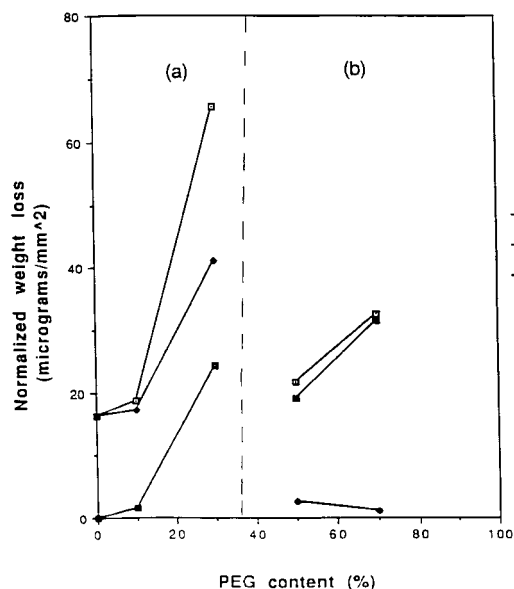


Figure 8 Normalized weight loss of the PLA/PEG blends as a function of PEG content: (a) after 48 h of degradation; (b) after 8 h of degradation.

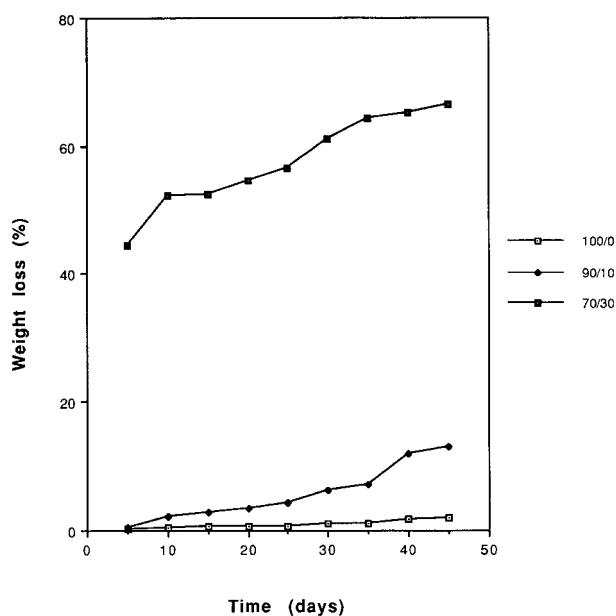


Figure 9 Weight loss as a function of time for the PLA/PEG blends due to hydrolytic degradation.

Table IV Summary of Hydrolytic Degradation Study of PLA/PEG Blends

PLA/PEG Blend	Weight Loss (%)	Normalized Weight Loss ($\mu\text{g}/\text{mm}^2$)	Composition		Normalized Weight Loss	
			Before Degradation	After Degradation	PLA ($\mu\text{g}/\text{mm}^2$)	PEG ($\mu\text{g}/\text{mm}^2$)
100/0	1.97	1.65	—	—	—	—
90/10	12.91	9.23	88/12	88/12	8.307	0.923
70/30	66.39	63.19	71/29	89/11	36.25	28.07

Hydrolytic Degradation Study

The hydrolytic degradation study was carried out on PLA/PEG 100/0, 90/10, and 70/30 blends for 45 days. Figure 9 shows the plot of weight loss (%) as a function of time for PLA/PEG blends. Table IV summarizes the composition analysis of the hydrolytically degraded PLA/PEG blends before and after degradation. For the 90/10 blend, weight loss after 45 days was 12%. As shown by the NMR results, there was no change in composition before and after degradation (Table IV). Total weight loss for this blend was $9.23 \mu\text{g}/\text{mm}^2$. Weight loss due to degradation of PLA was $8.307 \mu\text{g}/\text{mm}^2$ and that of PEG was $0.923 \mu\text{g}/\text{mm}^2$. This shows that weight loss occurred mainly due to degradation of PLA. The composition of the 70/30 blend changed significantly after degradation, as shown by the NMR results (Table IV). The weight loss of PEG was approximately 67% of the original weight. Weight loss of PEG was $28.07 \mu\text{g}/\text{mm}^2$ after degradation, which was approximately 44% of total weight loss. This confirms that when PEG content was up to 30% in the blend, weight loss occurred as a result of hydrolytic degradation and also due to dissolution of PEG.

CONCLUSIONS

Based on the thermal analysis performed it is concluded that PLA and PEG form miscible blends in compositions less than 50/50. Both components in the blends were able to crystallize and the presence of the PEG was found to enhance the crystallization of the PLA, however the crystallinity of PEG seemed to be suppressed in the blends. DMA results indicated that all the blends showed some level of plasticization due to partial miscibility and that the transition occurred over a broad range of temperature.

For all of the PLA/PEG blends, the tensile strength was found to decrease with increases in the PEG content. When the PEG content was 50%

or lower in the blend, the modulus was found to decrease and the strain was found to increase with an increase in PEG content. Above 50% PEG content the blend crystallinity was found to increase, resulting in an increased modulus and a drastic decrease in elongation at break.

The results obtained from enzymatic degradation show that the weight loss for all of the blends was higher than that for pure PLA. When PEG content was 30% or lower, the weight loss was due to primarily to the enzymatic degradation of PLA. Above 30% PEG content the weight loss occurs mainly due to dissolution of PEG. In the hydrolytic degradation study when the PEG content was 30% or lower, the weight loss was found to occur as a combination of degradation of PLA and dissolution of PEG.

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APPENDIX

Calculation of Composition from NMR Results for PLA/PEG (90/10) Blend Before Degradation

- Mole ratio:

$$\begin{aligned} \text{Mole} &= \text{weight fraction/molecular weight} \\ &= 0.9/137,000 \\ &= 6.56 \times 10^{-6} \text{ mole of PLA} \\ &= 0.1/20,000 = 5 \times 10^{-5} \text{ mole of PEG} \\ \text{Mole ratio} &= 6.56 \times 10^{-6}/5 \times 10^{-5} = 0.13 : 1 \end{aligned}$$

- Proton ratio:

$$(\text{Proton in PLA/Proton in PEG}) \times \text{mole ratio}$$

$$(5,832/1,816) \times 0.13/1 = 0.42 : 1$$

- Actual proton ratio from NMR results:

Ratio of integrated area for the proton
in PLA to that in PEG = 3.43 : 1

- Actual mole ratio: Suppose mole ratio is Y .

$$(5,832/1,816) \times Y = 3.43/1$$

$$\text{Actual mole ratio} = 1.06/1$$

- Actual weight ratio:

Mole \times molecular weight of polymer

$$= 1.06 \times 137,000 = 146,323 \text{ gm}$$

$$= 1 \times 20,000 = 20,000 \text{ gm}$$

$$\text{Weight ratio} = 146,323/20,000 = 7.3/1$$

- Actual composition of the blend:

$$\begin{aligned} \text{PLA in the blend (\%, w/w)} &= 7.3/(1 + 7.3) \\ &= 88 \end{aligned}$$

$$\begin{aligned} \text{PEG in the blend (\%, w/w)} &= 1/(1 + 7.3) \\ &= 12 \end{aligned}$$

Similarly, composition of PLA/PEG-90/10 blend after degradation was calculated from the NMR results.

Calculation of Normalized Weight Loss of Individual Component for PLA/PEG-90/10 Blend

$$\text{Composition before degradation} = 88/12$$

$$\text{Composition after degradation} = 88/12$$

$$\text{Weight of the sample before degradation} = 28.48$$

$$\text{Weight of the sample after degradation} = 20.64$$

PLA in the blend before degradation:

$$0.88 \times 28.48 = 25.06 \text{ mg.}$$

PLA in the blend after degradation:

$$0.88 \times 20.64 = 18.16 \text{ mg}$$

$$\begin{aligned} \text{Weight loss of PLA} &= 25.06 - 18.16 \\ &= 6.9 \text{ mg} \end{aligned}$$

Normalized weight loss of PLA

$$\begin{aligned} &= (6.9 \times 1000)/ \\ &\quad (20 \times 10 \times 2) \\ &= 17.25 \mu\text{g}/\text{mm}^2 \end{aligned}$$

Normalized weight loss of PEG

$$\begin{aligned} &= \text{Total weight loss} \\ &\quad - 17.25 \\ &= 1.5 \mu\text{g}/\text{mm}^2 \end{aligned}$$

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