

Effect of Thermal Aging on the Biodegradation of PCL, PHB-V, and Their Blends with Starch in Soil Compost

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ABSTRACT: Different proportions of starch were blended with poly(β -hydroxybutyrate)-*co*-poly(β -hydroxyvalerate) (PHB-V) or poly(ϵ -caprolactone) (PCL) by extrusion, and the mechanical (maximum tensile strength, elongation at break and Young's modulus) and thermal properties (by differential scanning calorimetry) were determined. The biodegradability of the blends in soil compost was also assessed after thermal aging for 192, 425, and 600 h at different temperatures. The maximum tensile strength of the PCL50 blend (containing 50% starch) was 35% lower than that of PCL and

that of the PHB-V50 blend was 60% lower than that of PHB-V without thermal aging. PHB-V blends were more biodegradable than PCL blends. For the blends prepared, only the biodegradation of PHB-V25 was affected by thermal aging. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3539–3546, 2003

Key words: aging; blending; biodegradable; poly(β -hydroxybutyrate)-*co*-poly(β -hydroxyvalerate); poly(ϵ -caprolactone)

INTRODUCTION

Waste disposal is an increasing problem as available landfill areas diminish. Plastics currently account for about 7% by weight (18% by volume) of municipal solid waste, with half of this plastic waste derived from plastics used in packaging.¹ Growing environmental concern has created an urgent need to develop new biodegradable materials that have properties comparable with conventional polymeric materials such as polyethylene and polypropylene. The availability of biodegradable polymers is very important for reducing plastic waste.

A great number of biodegradable polymers are derived from synthetic and natural sources,^{2–4} but most of them are relatively expensive. The high cost of biodegradable polymers has limited their wide-scale adoption by industries. In addition, the use of any new material by the manufacturing industry requires that its behavior be well characterized under various conditions of processing, manufacturing, and usage.⁵

Polymeric blends that consist of a mixture of two or more polymers or copolymers that are not covalently linked⁶ are a good alternative for reducing the final

cost of a product. Various blends of conventional and biodegradable plastics have been used.^{7,8} Natural additives such as starch, cellulose, lignin, and other polysaccharides have been used in these formulations.^{9–18}

The use of starch lowers the cost of the finished product and adds some desirable biodegradable characteristics to thermoplastic polymers. Starch and starch derivatives in both granular and nonstructural forms have been blended with various plastics, including polyethylene, poly(vinyl alcohol), poly(vinyl chloride), poly(ethylene-*co*-acrylic acid), and poly(ethylene-*co*-vinyl alcohol),^{12,13} as well as with biodegradable plastics such as poly(β -hydroxybutyrate)-*co*-poly(β -hydroxyvalerate) (PHB-V) and poly(ϵ -caprolactone) (PCL).^{14–16} Previous studies have shown that PCL/starch blends are readily biodegradable.^{4,15,17,18}

In addition to reducing the cost of biodegradable polymers, new alternatives and interventions in treating postconsumer polymers, including thermal aging, may help to reduce the time needed for biodegradation.

In this work PCL and PHB-V, two commercially available biodegradable polymers, were used to prepare blends of these polymers with different amounts of starch. The effect of thermal aging on the biodegradation and mechanical properties of these mixed polymers was then investigated.

EXPERIMENTAL

Materials

Poly(β -hydroxybutyrate)-co-poly(β -hydroxyvalerate): PHB-V was supplied by Copersucar (Cooperativa de

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TABLE I
Composition of Starch/Biodegradable Polymer Blends
Used in the Experiments

Blend designation	Starch content (% w/w)	Polymer content (% w/w)
PCL	0	100
PCL25	25	75
PCL50	50	50
PHB-V	0	100
PHB-V25	25	75
PHB-V50	50	50

Produtores de Cana, Açúcar e Álcool do Estado de São Paulo, São Paulo, SP, Brazil) in powder form. The polymer had a weight-average molecular weight of 150,000 g/mol and contained 5.5% (w/w) valerate, 0.09% nitrogen, and 0.27% ash.

Poly(ϵ -caprolactone): PCL was supplied in pellet form by Union Chemical Carbide Ltd. (P-767) (Cubatão, SP, Brazil) and had a melting index of 1.9 ± 0.3 (ASTM Standard D 1238), a density of 1.14 g/cm³, and a weight-average molecular weight of 80,000 g/mol.

Corn starch type Amidex 3001: The corn starch, was supplied by Corn Products Brazil–Ingredientes Industriais Ltda. (São Paulo, SP, Brazil) and contained 27% (w/w) amylose and 73% of amylopectin, with a weight-average molecular weight of 486,000 g/mol.

Compound blending

Blends containing 0%, 25%, and 50% (w/w) of starch were prepared using Coperion & Werner Pfeiderer (Stuttgart, Germany) twin-screw extruders. The blend compositions used in this work are shown in Table I, and the processing conditions are summarized in Table II.

Film preparation

Injection molding

The films for tensile tests were injection-molded according to ASTM Standard D 638 using a PIC Model 62 (Plastic Injection Command, Chappaqua, NY) injection.

Molding compression

The films were prepared by molding compression using mold temperatures of 205°C for PHB-V and its blends and 95°C for PCL and its blends. The materials were placed in the molds and kept under the appropriate conditions for 3 min. After this, they were transferred to a hydraulic press and submitted to 5 MPa for 2 min. Once removed from the press, the molds were cooled to room temperature. Circular films 37 mm in diameter and 1 mm thick were obtained for each polymer.

Thermal aging

After preparation the films were weighed, placed on aluminum supports, and hung in an oven for thermal aging. The aging temperatures were established based on the melting temperature of the polymers. Two temperatures were chosen for each polymer: 100°C and 140°C for PHB-V and its blends and 30°C and 50°C for PCL and its blends. The exposure times were 192, 425, and 600 h for all polymers and their respective mixtures at each temperature. Each film was weighed again after thermal aging.

Soil compost

The soil compost contained 23% loamy silt, 23% organic matter (cow manure), 23% sand, and 31% distilled water (all w/w). Calcium hydroxide [Ca(OH)₂] was added to give the soil compost a pH of 11.

Mechanical properties

Tensile strength at break, Young's modulus, and elongation at break were measured using a universal testing machine (model DL-2000 NS 5921, EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil). The control program was Mtest LBP version 3.00, and the load cell had a capacity of 200 kgf. The samples were initially 50 mm in length, the crosshead speed was 50 mm/min, and relative humidity was 50%. Five films for each polymer and blend composition were tested according to ASTM

TABLE II
Processing Conditions Used During Blending

Parameter	PCL	PCL25	PCL50	PHB-V	PHB-V25	PHB-V50
Barrel temperature (°C)						
Zone 1	70	81	100	125	130	130
Zone 2	69	85	100	127	130	130
Zone 3	61	81	95	120	128	128
Screw speed (rpm)	120	120	120	250	250	250

TABLE III
Mechanical Properties of Starch/Biodegradable Polymer Blends Before and After 600 h of Thermal Aging

Formulation	Tensile strength at break (MPa)		Elongation at break (%)		Modulus of elasticity (MPa)	
	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging	Before thermal aging	After thermal aging
PCL	16.9 ± 0.5	19.2 ± 0.7	393.0 ± 19.1	330.0 ± 18.0	432.9 ± 20.8	417.0 ± 21.3
PCL25	14.5 ± 0.2	16.3 ± 0.5	302.9 ± 27.4	276.0 ± 12.2	306.0 ± 15.9	278.3 ± 18.0
PCL50	11.0 ± 0.7	13.4 ± 0.3	3.5 ± 0.1	3.3 ± 0.2	520.9 ± 22.5	470.0 ± 20.1
PHB-V	34.2 ± 1.0	37.8 ± 0.9	2.6 ± 0.9	3.9 ± 0.6	3940.6 ± 105.1	3703.4 ± 77.4
PHB-V25	18.9 ± 0.5	16.2 ± 0.7	3.3 ± 0.4	3.5 ± 0.5	1191.8 ± 27.1	1024.3 ± 17.8
PHB-V50	13.8 ± 0.5	13.2 ± 0.8	3.6 ± 0.2	3.9 ± 0.6	924.8 ± 30.5	809.0 ± 22.0

Standard D 638. Stress–strain measurements of the films were obtained before and after thermal aging.

Thermal analysis

Thermal analysis was done with a differential scanning calorimeter (model DSC 204 TASC 414/3A, Netzsch-Gerätebau GmbH, Bavaria, Germany) under a nitrogen atmosphere at a heating rate of 10°C/min. Two heating cycles were used for each film. PHB-V films and their blends were first heated from room temperature to 180°C to eliminate their thermal history and then cooled to room temperature and immediately reheated to 195°C. For PCL the temperatures used were 80°C and 100°C, respectively. The second scan was obtained at the same heating rate.

All DSC experiments were done in duplicate, and the thermograms shown in the results section refer to the second heating. The crystallinity values were obtained by using the following reference melting enthalpies for 100% crystalline materials: for PCL, $\Delta H_{0 \text{ PCL}} = 136.1 \text{ J/g}^{14}$; for PHB-V, the value of PHB, $\Delta H_{0 \text{ PHB-V}} = 146.0 \text{ J/g}^{19}$

Measurement of biodegradability

PHB-V and PCL films and their blends that had or had not been thermally aged were weighed and buried, in triplicate, in soil compost. Biodegradability was as-

sessed every 30 days for approximately 10 months by measuring weight loss. The buried samples were retrieved, washed with distilled water, and dried in the open air before being weighed. The films were buried again in their respective trays after weighing.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of the formulations and pure polymers before and after thermal aging for 600 h are shown in Table III. The temperature of aging was close to 20% below the melting temperature, to accelerate the aging. According to a previous study,²⁰ an aging duration of 600 h resulted in a change in the biodegradation behavior of the materials exposed to UV irradiation for this time. The mechanical properties were measured only in samples thermally aged for 600 h because this was the most severe condition for aging.

The incorporation of starch generally reduced the maximum tensile strength (by 14% for PCL25 and by 45% for PHB-V25). For blends with 50% starch, the reduction was 35% for PCL50 and 60% for PHB-V50 when compared to the values for pure materials (PCL

TABLE IV
Melting Temperatures and Crystallinity of Pure Polymers and Polymer Blends Before and After Thermal Aging

Formulation	Crystallinity (%)			Melting temperature (°C)		
	Pellets	Film	Aging test	Pellets	Film	Aging test
PCL	36.9	34.8	39.1	56.1	56.6	58.8
PCL25	27.6	26.0	32.0	59.1	58.8	59.0
PCL50	19.2	21.8	21.9	57.0	56.7	57.8
PHB-V	44.8	44.5	41.1	167.1	166.2	148.6
PHB-V25	35.1	45.7	42.8	168.7	166.2	144.5
PHB-V50	26.7	24.1	16.5	169.4	167.8	166.7

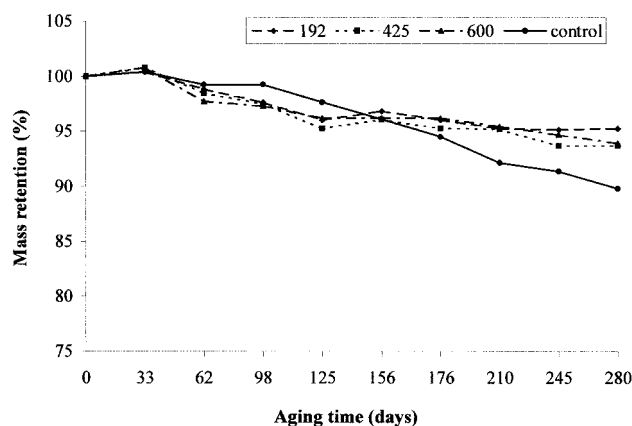


Figure 1 Biodegradation in soil compost of PCL aged thermally at 30°C.

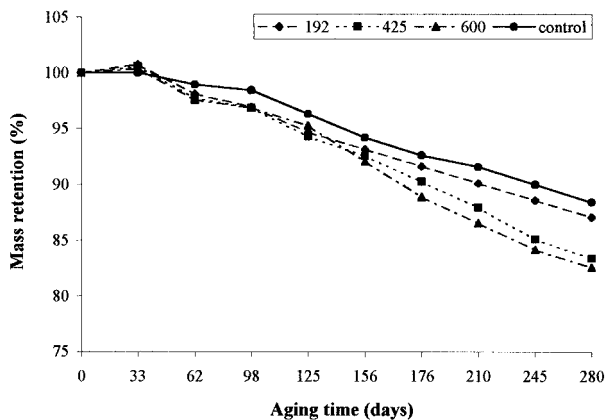


Figure 2 Biodegradation in soil compost of PCL25 aged thermally at 30°C.

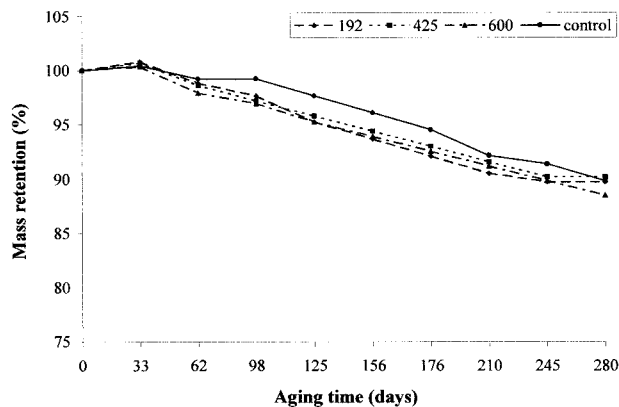


Figure 4 Biodegradation in soil compost of PCL aged thermally at 50°C.

and PHB-V), suggesting incompatibility between the PCL or PHB-V and the starch.²¹

A possible explanation for the decrease in that mechanical property could be the poor miscibility of starch with the polymers studied. This may reflect that the starch used had a large chain size (average molar mass 486,000 g/mol) and a branched structure containing benzene rings (73% of the weight in amylopectin). The inclusion of starch may have reduced the interactions between the chains of polymers and adversely affected the mechanical properties of the blend. A similar behavior was observed for the Young's modulus of elasticity, in which there was a reduction in the elongation at break for blends of PCL (except for PCL50). Thus, a 25% decrease in elongation at break was observed with the incorporation of 25% starch in PCL, whereas an abrupt decrease (99%) in this property occurred in the PCL50 formulation, further emphasizing the poor miscibility of the starch and polymer in the latter composition. In contrast, the

incorporation of starch into the PHB-V blends had little effect on the elongation at break (Table III).

The maximum temperature used in the thermal aging was 50°C for PCL and its blends and 140°C for PHB-V and its blends because these temperatures were approximately 20°C below the melting temperatures of the polymers.

Thermal aging increased the maximum tensile strength of all formulations, except for PHB-V25 and PHB-V50, when compared to the polymers without aging (Table III). In contrast, there was a small reduction in the Young's modulus of all samples and in the elongation at break of PCL and its blends; for PHB-V and its blends there was no effect in elongation at break. For PCL the thermal aging probably caused a small break in the chemical structure, producing small fragments that made the material become more crystalline (Table IV) and consequently reflected an increase in the maximum tensile strength, a reduction in the elongation at break (Table III), and difficulties in PCL biodegradation, as discussed in the next section.

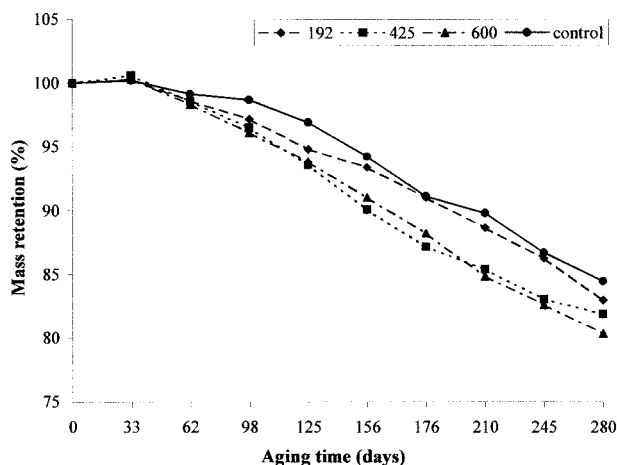


Figure 3 Biodegradation in soil compost of PCL50 aged thermally at 30°C.

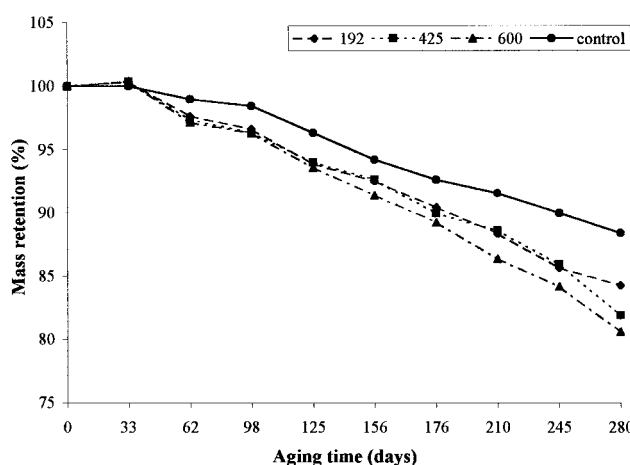


Figure 5 Biodegradation in soil compost of PCL25 aged thermally at 50°C.

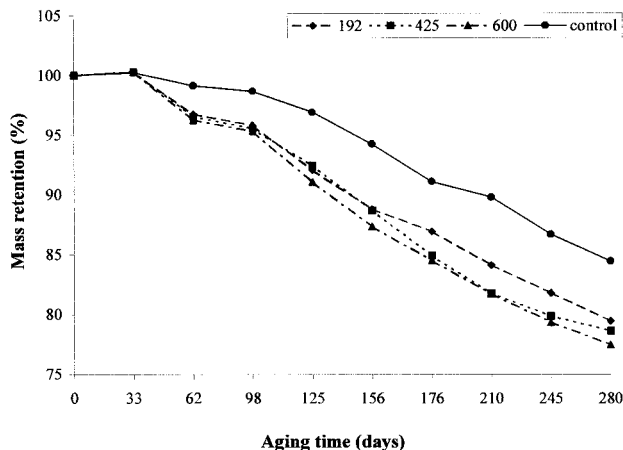


Figure 6 Biodegradation in soil compost of PCL50 aged thermally at 50°C.

Analysis of thermal aging and biodegradability

The biodegradability values of the thermally aged samples compared to the nonaged samples are shown in Figures 1–12. A pH of 11 was chosen for the soil compost because in a previous study with three different pH values (7, 9, and 11), the pH of 11 provided a better condition for biodegradation for PCL and PHB.²⁰ An alkaline pH increased the biodegradation rate of PHB and PCL, with the former showing the greatest weight loss. In this condition the polymers were more suitable to hydrolysis, producing RCOOH groups, which also were able to accelerate ester hydrolysis through autocatalysis²².

The samples of PHB-V degraded more than those of PCL because after about 62 days of aging in soil compost, the first polymer had biodegraded almost 100% (Figs. 3–4). This greater susceptibility reflected the chemical structure of PHB-V, which, in addition to having ester groups, is highly branched and consequently contains a large quantity of tertiary carbons

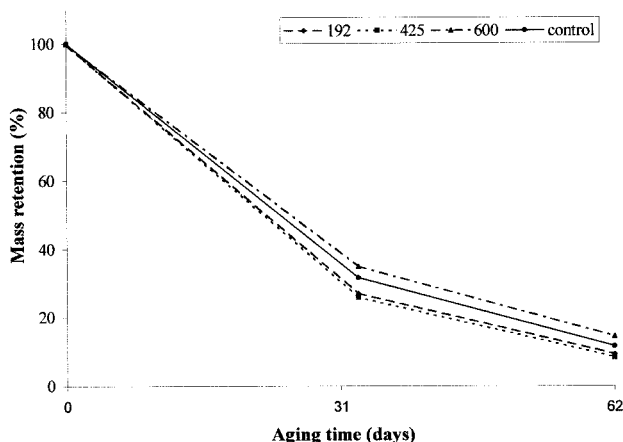


Figure 7 Biodegradation in soil compost of PHB-V aged thermally at 100°C.

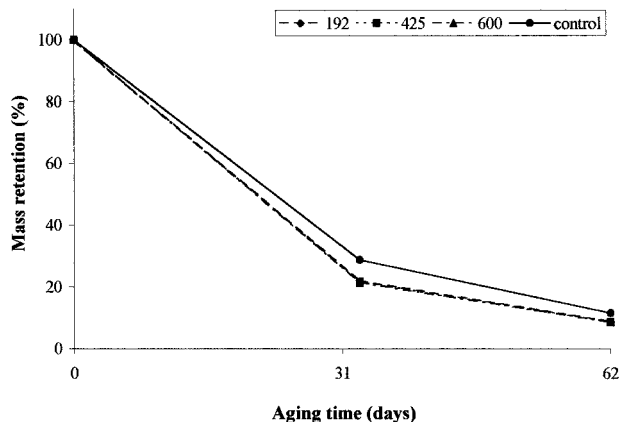


Figure 8 Biodegradation in soil compost of PHB-V25 aged thermally at 100°C.

that facilitate the hydrolysis and cleavage of the films.²³

The addition of starch to PCL slightly increased the loss of mass during biodegradation. Thus, after 280 days of aging, the PCL samples containing starch, that is, the PCL25 and PCL50 formulations, lost 11.6% and 15.6%, respectively, of their mass compared to 6.6% for pure PCL (Figs. 2, 3, 5, and 6). This increase in biodegradation perhaps reflected the reduced crystallinity in the blends of PCL (Table IV). The inclusion of starch added branched polymeric chains (amylopectin) to the blend mixture, decreased the organization of the chains, and reduced the crystalline regions. For PHB-V the addition of 50% starch made the blend more susceptible to biodegradation, with PHB-V50 totally degraded in only 33 days (Figs. 9 and 12). This represented a reduction of approximately 50% in the time to degrade when compared to samples of PHB-V without starch (Figs. 7 and 10). Thus, the incorporation of starch reduced the crystallinity of the polymers and increased the amorphous phase of the blends,

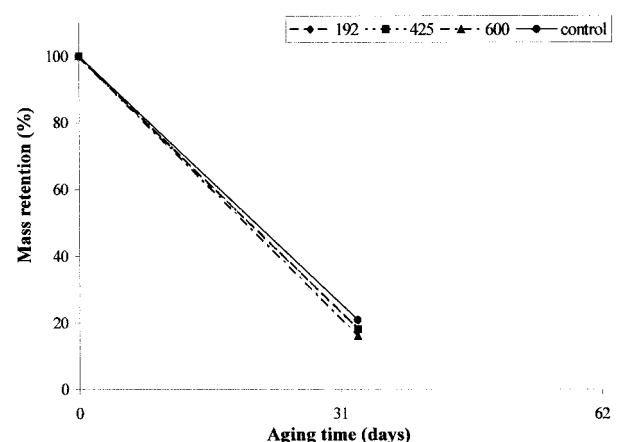


Figure 9 Biodegradation in soil compost of PHB-V50 aged thermally at 100°C.

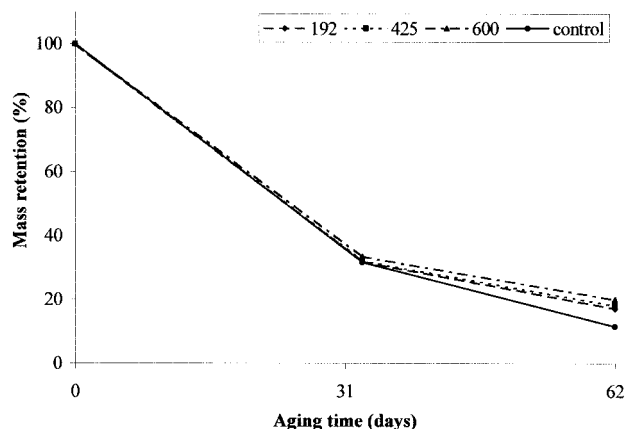


Figure 10 Biodegradation in soil compost of PHB-V aged thermally at 140°C.

making them more susceptible to biodegradation (Table IV).

Because the biodegradation of PHB-V was very fast, it was not possible to assess the effect of thermal aging on mass loss during the biodegradability test. An exception was the PHB-V25 blend, which, after thermal aging at 140°C, had the same level of biodegradation as the PHB-V50 blend (Figs. 11 and 12).

Although thermal aging had little or no apparent effect on PHB-V, PHB-V25, and PHB-V50, DSC showed a decrease in the crystalline melting temperature of these materials (Figs. 13–15). The DSC results suggested that thermal aging caused thermooxidation with consequent bond rupture in the polymeric chains to produce low-molecular-weight fragments.²³ Evidence of this can be seen in the formation of a shoulder at lower temperatures in the thermal curves of DSC.

The thermooxidation of PHB-V produced lower stereoregular structures, which made organization of the chains more difficult. This in turn reduced the crystallinity and made the blend more susceptible to biodeg-

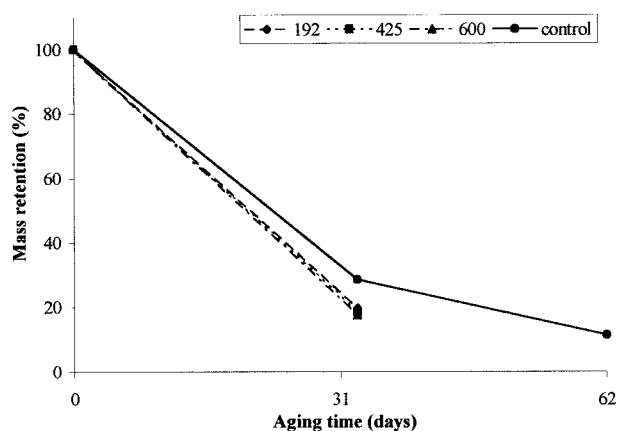


Figure 11 Biodegradation in soil compost of PHB-V25 aged thermally at 140°C.

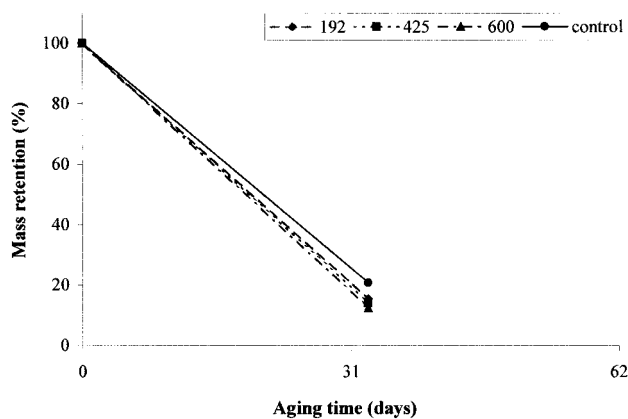


Figure 12 Biodegradation in soil compost of PHB-V50 aged thermally at 140°C.

radation. This effect was not seen in PCL because thermal aging did not cause significant thermal degradation in this material. In agreement with this were the results for the melting temperatures of PCL and its blends, which were practically unchanged (Table IV and Figs. 16–18). Thermal aging increased the crystallinity of these formulations, perhaps through an annealing effect. The unaltered melting temperatures meant there was no scission of the polymeric chains and hence little hydrolysis and biodegradation.

For the samples PCL25 and PCL50, thermal aging slightly increased the loss of mass, to nearly 6.6% for samples aged at 30°C and 8.8% for those aged at 50°C. The duration of aging had no effect on mass loss. The small increase in biodegradation in soil compost probably reflected the small variation in the thermal properties of PCL25 and PCL50 shown in Figures 17 and 18, respectively.

CONCLUSIONS

The addition of starch to pure polymers generally reduced the maximum tensile strength of the prod-

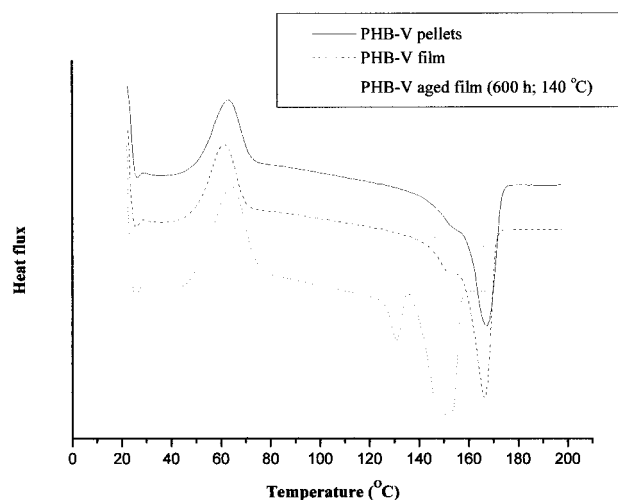


Figure 13 DSC curves for PHB-V pellets, film, and aged film.

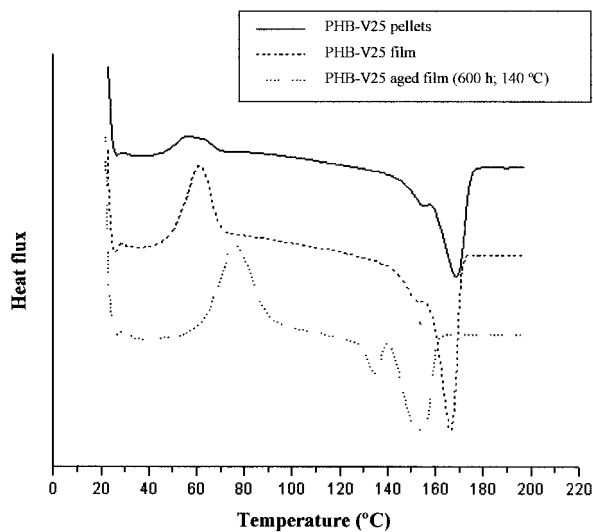


Figure 14 DSC curves for PHB-V25 pellets, film, and aged film.

ucts, suggesting that these materials were immiscible. This behavior was not observed for the elongation at break in the PHB-V blends.

PHB-V films were more biodegradable than PCL films, and the addition of starch increased the biodegradation of PHB-V50 even more. In contrast, a significant reduction was observed for PCL after the inclusion of starch.

For PHB-V formulations thermal aging affected only PHB-V25 at 140°C, independent of the duration of exposure to heat. No significant change in weight loss was detected in other formulations of this polymer because of the rapid biodegradation of these materials. Thermal aging for 280 days did not affect the biodegradability of formulations containing PCL.

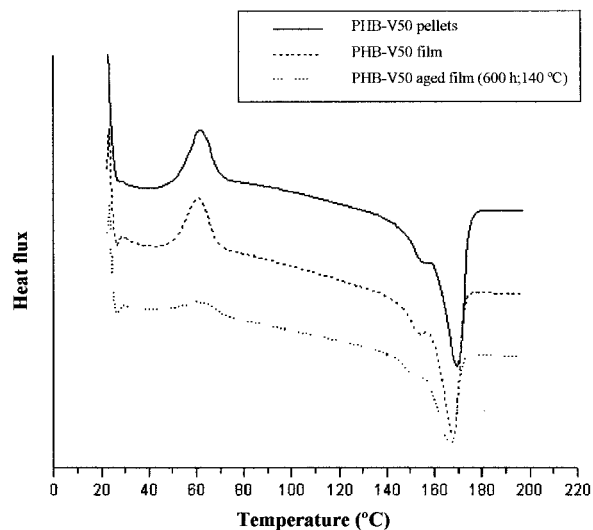


Figure 15 DSC curves for PHB-V50 pellets, film, and aged film.

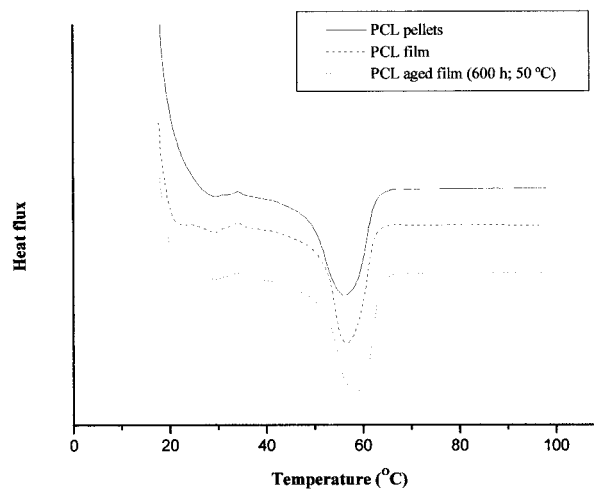


Figure 16 DSC curves for PCL pellets, film, and aged film.

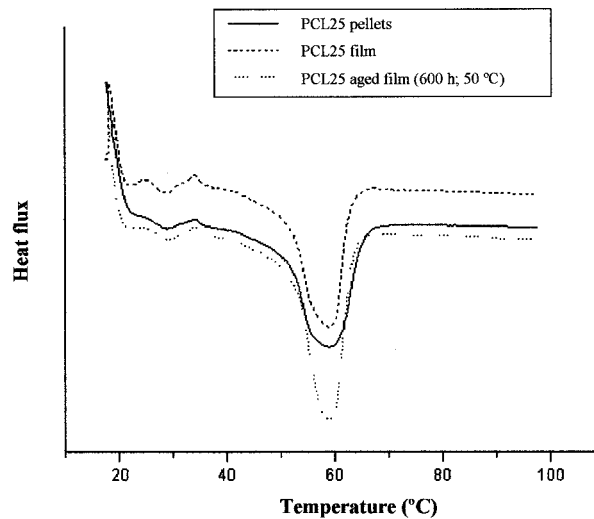


Figure 17 DSC curves for PCL25 pellets, film, and aged film.

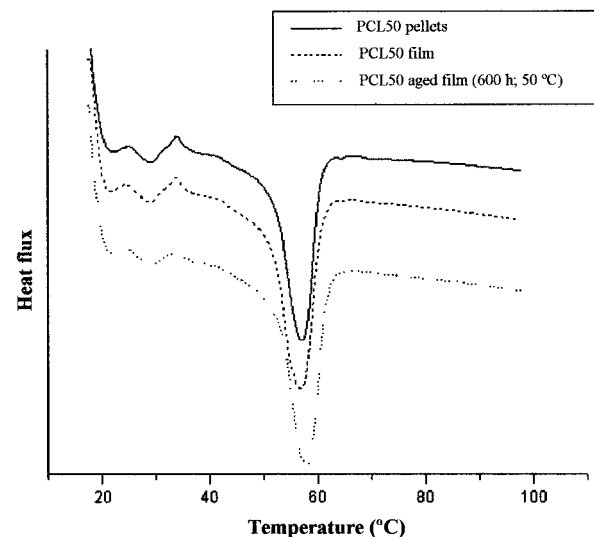


Figure 18 DSC curves for PCL50 pellets, film, and aged film.

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References

1. Thayer, A. M. *Chem Eng News* 1990, 25, 7.
2. Kaplan, D. J.; Mayer, J. M.; Ball, D.; McMassie, J.; Allen, A. L.; Stenhouse, P. In *Fundamentals of Biodegradable Polymers*; Technomic Publication: Basel, Switzerland, 1993; Chapter 1.
3. Chiellini, E.; Solaro, R. *Adv Mater* 1996, 8, 305.
4. Amass, W.; Amass, A.; Tighe, B. *Polym Int* 1998, 47, 89.
5. Sen, A.; Bhattacharya, M. *Polymer* 2000, 41, 9177.
6. Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1999.
7. Yam, W. Y.; Ismail, J.; Kammer, H. W.; Lechener, M. D.; Kummerlöwe, C. *Polymer* 2000, 41, 9073.
8. Guo, Q.; Zheng, H. *Polymer* 1999, 40, 637.
9. Bagley, E. B.; Fanta, G. F. E.; Burr, R. C. *Polym Eng Sci* 1977, 17, 311.
10. Barham, P. J.; Keller, A.; Otun, E. L.; Holmes, P. A. *J. Mater Sci* 1984, 19, 2781.
11. Gogolewski, S.; Janvanovic, M.; Perren, S. M.; Dillon, J. G.; Hughes, G. *Polym Degrad Stab* 1993, 40, 313.
12. Rutenberg, M. V.; Solarek, D. *Starch Chemistry and Technology*; Academic Press: New York, 1984.
13. Peanasky, J. S.; Long, J. M.; Wool, R. P. *J Polym Sci, Part B: Polym Phys* 1991, 29, 565.
14. Chun, Y. S.; Kim, W. N. *Polymer* 2000, 41, 2305.
15. Avella, M.; Errico, M. E.; Laurienzo, P.; Martuscelli, E.; Raimo, M.; Rimedio, R. *Polymer* 2000, 41, 3875.
16. Averous, L.; Moro, L.; Dole, P.; Fringant, C. *Polymer* 2000, 41, 4157.
17. Bastioli, C.; Cerutti, A. L.; Guanella, I.; Romano, G. C.; Tosin, M. *J Environ Polym Degrad* 1995, 3, 81.
18. Pranamuda, H.; Tokiwa, Y.; Tanaka, H. *J Environ Polym Degrad* 1996, 4, 1.
19. Lüpke, T.; Radusch, H. J.; Metzner, K. *Macromol Symp* 1998, 127, 227.
20. Rosa, D. S.; Calil, M. R.; Guedes, C. G. F.; Santos, C. E. O. *J Polym Environ* 2001, 9, 111.
21. Paul, D. R.; Bucknall, C. B. *Polymer Blends: Performance*; John Wiley: New York, 1999.
22. Pitt, C. G.; Gratzl, M. M.; Kimmel, G. L.; Surles, J.; Schindrer, A. *Biomaterials* 1981, 2, 215.
23. Scott, G.; Gilead, D. *Degradable Polymers*; Chapman & Hall: London, 1995.