Preparation of Biodegradable Polyesters/High-Amylose-Starch Composites by Reactive Blending and Their Characterization

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ABSTRACT: Two different biodegradable polyesters [polycaprolactone (PCL) and poly(3-hydroxybutyrate-*co*-valerate) (PHBV)] were blended with a maize starch that had high amylose content through the use different reactive approaches. The compatibilization of both systems was obtained. PCL/starch composites were obtained by the addition of a third reactive component that was able to act as a coupling agent, and the reactive interface of PHBV/starch composites was improved during blending with an organic peroxide. Thermal, morphological, and mechanical characterization showed that the compatibilized composite materials had better final proprieties than neat materials or composites prepared without compatibilization. Finally, the degradation of all prepared materials by a compost simulation test was investigated. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1432–1442, 2002

Key words: composites; reactive processing; compatibilization; biodegradability

INTRODUCTION

In the last 20 years, the production and use of plastic materials in the world has increased enormously, worsening the problem of waste disposal. Growing interest in the environmental impact of discarded plastics has directed research on the development of plastics that degrade more rapidly in the environment.[1–3]

Usually, degradation can occur both by ultraviolet radiation (photodegradation) and/or microbes (biodegradation).

The term *biodegradable* is used to describe those materials that can be degraded by the enzymatic action of living organisms such as bacteria, yeasts, and fungi; the ultimate end products of these degradation processes are CO_2, H_2O, and biomass under aerobic conditions and hydrocarbons, methane, and biomass under anaerobic conditions.[4]

So, there is considerable interest in the replacement of some or all of synthetic plastics by biodegradable materials in many applications. Some natural polymers (poly(3-hydroxybutyrate) and its copolymers[5]) and aliphatic polyesters [polycaprolactone (PCL)[6] and polylactic acid[7]] are biodegradable, but their high cost compared to petroleum-based plastics prevents larger commercial usage of them.

To increase biodegradability and simultaneously lower the cost and preserve resources, it is possible to blend polymeric materials with natural products.[8,9] Among these, the starches, pro-

duced in enormous quantities (in Europe 5, million tons per year are produced from corn), easily recoverable and chemically or biologically modifiable, are playing an increasing role into the development of new environmentally sound polymeric materials.[10–14]

Starch is a semicrystalline polymer stored in granules as a reserve in most plants. It is composed of repeating 1,4-α-D-glucopyranosyl units: amylose and amylopectin. The amylose is almost linear, the repeating units are linked by α (1-4) linkages; the amylopectin has a α (1-4) linked backbone and about 5% α (1-6) linked branches. The relative amounts of amylose and amylopectin depend on the plant source. Corn starch granules typically contain approximately 70% amylopectin and 30% amylose.[15] Several studies have concentrated on the development of starch-based materials for previously mentioned reasons. On the other hand, the hydrophilicity of the starches is responsible for incompatibility with the most hydrophobic polymers. So, the improvement in the reactive interface between polymers and starch can play a critical role in ensuring that the properties of each component contribute to the bulk properties and in obtaining composite materials with good final properties. Compatibilization between the polymers can occur either by the introduction during blending of a preformed compatibilizing agent or by induction, in appropriate conditions, of reactions between the functional groups of the two incompatible polymers to obtain the formation *in situ* of an interfacial agent.[16]

This article completes the investigation on two preliminary starch-based biodegradable composite systems studied elsewhere.[17,18]

As polymeric matrices, two biodegradable thermoplastic polyesters were selected: PCL and poly(3-hydroxybutyrate-*co*-valerate) (PHBV) containing 5 mol % by hydroxyvalerate (HV). To improve mixing between polymeric matrix and starch, a starch with a high content of amylose (70%) was used.

The major objective of this work was the improvement of the reactive interface between matrix and filler and the study of the influence of interfacial adhesion on the final composite properties.

In the case of the PCL/starch composites, compatibilization was induced by the addition of an anhydride-functionalized PCL phase to the two components. The influence of this phase and its amount on the morphology and properties of the composites was also examined. With regard to the PHBV/starch composites, the improvement of the interfacial adhesion was promoted by means of a reactive blending (RB) of the two components by the addition of a small amount of an organic peroxide.

For both systems, mechanical composites were also prepared to compare their properties to those of the compatibilized materials. Thermal, morphological, and mechanical tests were also carried out. Finally, degradation in compost was analyzed on the systems to evaluate the influence of the starch on the rate of polyester biodisintegration.

EXPERIMENTAL

Materials

Poly(ϵ-caprolactone) [molecular weights (M_w's) = 80,000 and 20,000 Da] was supplied by Solvay (Angera [VA], Italy).

PHBV containing 5 mol % HV was supplied by Monsanto (Italia S.p.A. Milano, Italy).

Starch (amylomaize) with a high content of amylose (70%) was supplied by Cerestar (Italia S.p.A. Milano, Italy).

Pyromellitic anhydride (APM) was supplied by Aldrich Chemical Company (Milwaukee, WI) and was used without further purification.

Bis(*tert*-butylperoxyisopropyl)benzene (AKZO reagent-grade product) was used without further purification.

Composite Preparation

Preparation of PHBV/Starch Composites

PHBV was mixed in the melt with high-amylose starch with a Brabender-like apparatus operating at 190°C for 15 min and at 32 rpm. In the case of RB, 2% of the bis(*tert*-butylperoxyisopropyl)benzene was also added at the same time. Composites containing 80 and 70 wt % PHBV were prepared with and without the addition of the peroxide. Compression-molded samples were prepared with a heated press at 190°C for 5 min under maximum load. The obtained samples and codes in are listed Table I.

Preparation of PCL/Starch Composites

Also in this case, the polyester (PCL) was mixed in the melt with high-amylose starch with a Brabender-like apparatus operating at 80°C for 15

Table I Description of the Composition of the Composites and Relative Codes

Composite Composition (w/w %)	Precompatibilizer (wt %)[a]	Code
PHBV/starch 100/0	0	PHBV 100
PHBV/starch 80/20	0	PHBV 80
PHBV/starch 70/30	0	PHBV 70
PHBV/starch 100/0	2	PHBV 100 R
PHBV/starch 80/20	2	PHBV 80 R
PHBV/starch 70/30	2	PHBV 70 R
PCL/starch 100/0	0	PCL 100
PCL/starch 90/10	0	PCL 90
PCL/starch 70/30	0	PCL 70
PCL/starch 50/50	0	PCL 50
PCL/starch 100/0	2.5	PCL 100 L
PCL/starch 90/10	2.5	PCL 90 L
PCL/starch 70/30	2.5	PCL 70 L
PCL/starch 50/50	2.5	PCL 50 L
PCL/starch 100/0	5	PCL 100 M
PCL/starch 90/10	5	PCL 90 M
PCL/starch 70/30	5	PCL 70 M
PCL/starch 50/50	5	PCL 50 M
PCL/starch 100/0	10	PCL 100 H
PCL/starch 90/10	10	PCL 90 H
PCL/starch 70/30	10	PCL 70 H
PCL/starch 50/50	10	PCL 50 H

[a] For the PCL-based composites the precompatibilizer is related to the weight of the PCL; for PHBV-based composites, the amount of the peroxide refers to the weight of the composites.

[b] L, M, and H refer to low, medium, and high content of precompatibilizer agent, respectively; R refers to the presence of the organic peroxide.

min and at 32 rpm. In the case of compatibilized composites comprising PCL and starch phases, a precompatibilizing agent was added simultaneously in the melting mixer with the same operating conditions.

This precompatibilization agent was obtained as follows: low-molecular-weight PCL (20,000 Da) and APM were placed in a round-bottom flask equipped with a nitrogen inlet. The APM was added in excess mole (20:1) with respect to PCL. The anhydride was dissolved in a minimum amount of tetrahydrofuran, and the solution was added to the melted PCL. The reaction was carried out at 110°C for 24 h under nitrogen flow. The final product was washed in the following way: first, it was dissolved in acetone, and then it was precipitated by the addition of water to the solution. In this way, the APM was removed because of its solubility in the water/acetone mix-

ture. Probably, the added water was responsible for hydrolysis of the nonreacted anhydride groups. Different amounts of precompatibilizer agent were used; the compositions and the codes of all prepared materials are summarized in Table I. For PHB, a series of compression-molded samples for all PCL composites were prepared at 110°C.

Technique

Structural Analyses

Wide-angle X-ray scattering measurements were carried out with a Phillips (Italy) powder diffractomer (PW 1050 model) operating at a Cu Kα wavelength of 1.542 Å and equipped with a rotative sample-holder device. Measurements of the diffracted intensities were performed in the angular range of 4–40° (2θ) at room temperature and at a scanning rate of 1°/min.

The infrared spectra were recorded with a PerkinElmer Paragon 2000 Fourier transform infrared (FTIR) spectrometer (Switzerland). The spectra were performed on the films of the materials prepared for solvent evaporation on a pellet of KBr.

Thermal Analysis

The calorimetric properties of the compression-molded samples were investigated with a differential scanning calorimeter (Mettler TA 3000, Norwalk, CT).

Two series of differential scanning calorimetry (DSC) experiments were performed on about 10 mg of each sample. First, the samples were heated from 30 to 200°C at a scan rate of 10°C/min, cooled to −100°C at a scan rate of 10°C/min, and reheated to 200°C at a scan rate of 10°C/min. Second, the samples were heated from 30 to 200°C at a scan rate of 20°C/min, quenched down to −100°C, and reheated to 200°C at a scan rate of 20°C/min. The observed melting temperature (T_m) was obtained from the maximum of the endothermic peaks. Glass-transition temperature (T_g) was considered to be the temperature at the half-height of the endothermic shift. The degree of crystallinity (X_c) was calculated by the following relation:

$$Xc = \Delta H^*/\Delta H$$

where ΔH^* is the apparent enthalpy of melting per gram the polymeric matrix (PHBV and

PCL) in the blend and ΔH is the heat required to melt 1 g of neat crystalline polymer (ΔH_{PHBV} = 146 J/g, ΔH_{PCL} = 136 J/g).

Morphological Analysis

The surface analyses were performed with a Phillips XL 20 series scanning electron microscope on cryogenically fractured surfaces. Before the observation, the surfaces were coated with an Au–Pd alloy with a scanning electron microscopy (SEM) coating device (unit E5150, Polaron Equipment Ltd., Italy).

Impact Tests

Impact tests were performed with an instrumented Charpy pendulum (Least Autographic Pendulum MK2, Italy) on the compression-molded specimens (6.0 mm wide, 3 mm thick, and 60 mm long) that were cut and notched with a fresh razor blade about 0.2 mm deep. The final value of notch depth was measured after the fracture test with an optical microscope. The impact properties were analyzed according to the linear elastic fracture mechanism (LEFM) approach.

Biodisintegration Analysis

The disintegration of the neat thermoplastic polyesters and starch-based composites was investigated by a compost simulation test. This test was performed in the following conditions: A 3-L reactor was filled with 2 kg of mature compost and set at 55 ± 2°C. The system was continuously aerated with previously water-saturated and thermostated pressurized air. The test specimens with the same initial shape (i.e., the same exposed surface to the biodegradation treatment) were buried inside the reactors. The samples were withdrawn from the compost reactors at different times, washed with distilled water, and dried at 60°C to a constant weight, and the disintegration of the materials was evaluated (referred as percent of weight loss). Centro Ricerche Produzioni Animali (Reggio Emilia, Italy) kindly supplied the mature compost used in this test. It was produced at the Platform of the Composting Plant of Limidi of Soliera (Modena, Italy) from a mixture of residual sludge (from a municipal sewage treatment plant), grass, and wood chips (from the maintenance of civic parks). The compost was stored indoors for several months. Prior to use, the compost humidity was adjusted to 60%.

RESULTS AND DISCUSSION

Starch Characterizations

In this work, maize starch characterized by a high amylose content (70 wt %) was selected as a filler for biodegradable polyesters blends. This choice depended on the lower granule size of the amylomaize with respect to other starch types that allows a better dispersion of the starch into polymeric matrices, as described in literature.[19] Moreover, such starch possesses a greater number of hydroxyl groups on its surface that could increase its reactivity.

To determine the best preparation conditions of the polyester/starch composites, preliminary structural, thermal, and morphological characterizations were performed on the amylomaize starch.

In general, the starch is characterized by a supermolecular organization within the granules that depends on their natural source; four different crystal structures (A, B, C, and V) are associated with it, as revealed by X-ray diffraction analysis.[15]

X-ray analysis performed on the maize starch showed an A-type pattern (Fig. 1). The value of crystallinity was measured according to the method of Hermans and Weidinger,[20] and it was around 16%. This result was related to a low content of amylopectin (30 wt %), which is the crystalline component of the starch.[15]

DSC provided thermal analysis of the starch and showed the presence of an endothermic peak around 130°C. This peak referred to the melting of starch crystallites. Moreover, the broad form of the peak indicated additional thermal phenomena relative to the endothermic desorption of water.

Thermogravimetric analysis was performed to determine the degradation starch temperature and, thus, the best process conditions. This analysis was carried out with a Mettler thermogravimetric Analyzer at a heating rate of 20°C from 30 to 500°C.

The degradation temperature of the high-amylose starch appeared at around 260°C.

The morphological analysis was performed with optical microscopy (OM) and SEM. The SEM analysis revealed that the average diameter of the starch amylomaize granule was about 5–20 μm, and it is characterized a spherical shape (see Fig.2). Finally, by the OM analysis, we observed the presence of birefringence of the starch gran-
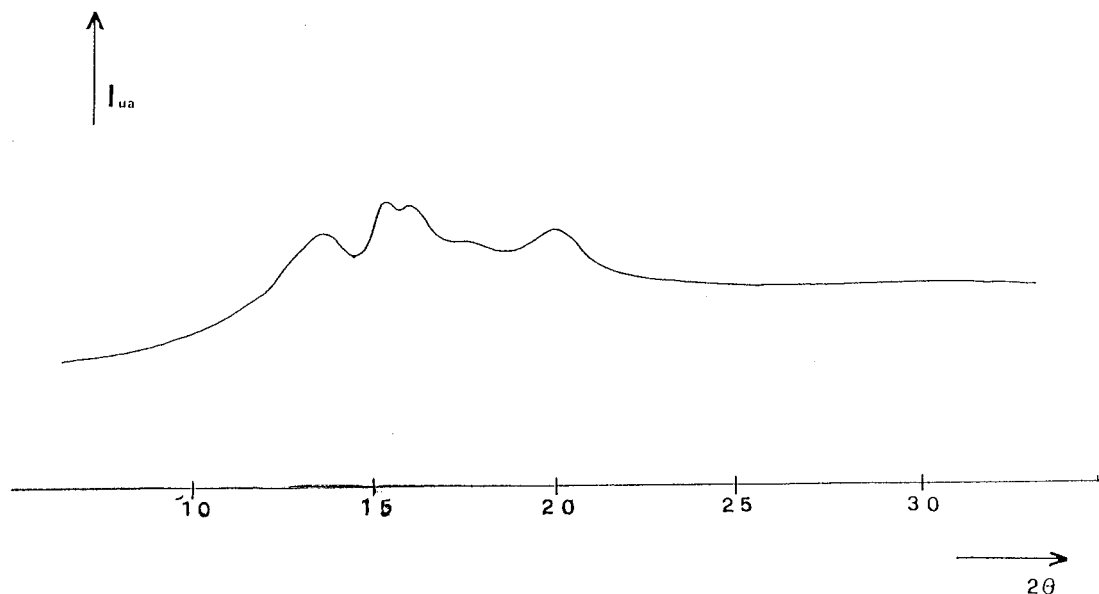
Figure 1 X-ray spectrum of the amylomaize starch.

ules according to their semicrystalline nature (see Fig. 3).

Polyesters/Starch Compatibilization

Generally, polymeric blends can be divided in two categories: miscible and immiscible blends. Compatibilization between the components of these can be improved by the promotion of their interfacial adhesion. In fact, good interfacial adhesion is a key factor to obtain materials with enhanced performances. Two different strategies may be used: the addition of a new phase, the compatibilizing agent, or induction during blending of spe-

cific interactions between the components (RB). These interactions could be strong ionic or covalent bonds, weak hydrogen bonds, or interactions, either ion–dipole or dipole–dipole.[21,22]

The well-known hydrophilicity of the starch renders it incompatible to a wide range of polyesters (hydrophobic in nature), such as PHB and PCL.

The nature of the starch, an unmelting component, with its insolubility in polyester matrices permits us to classify our systems as composites

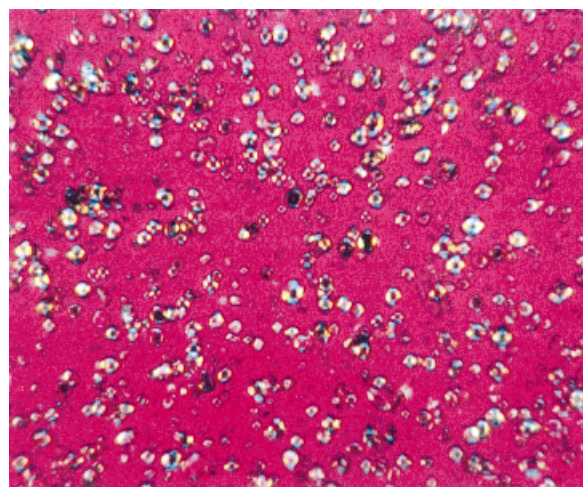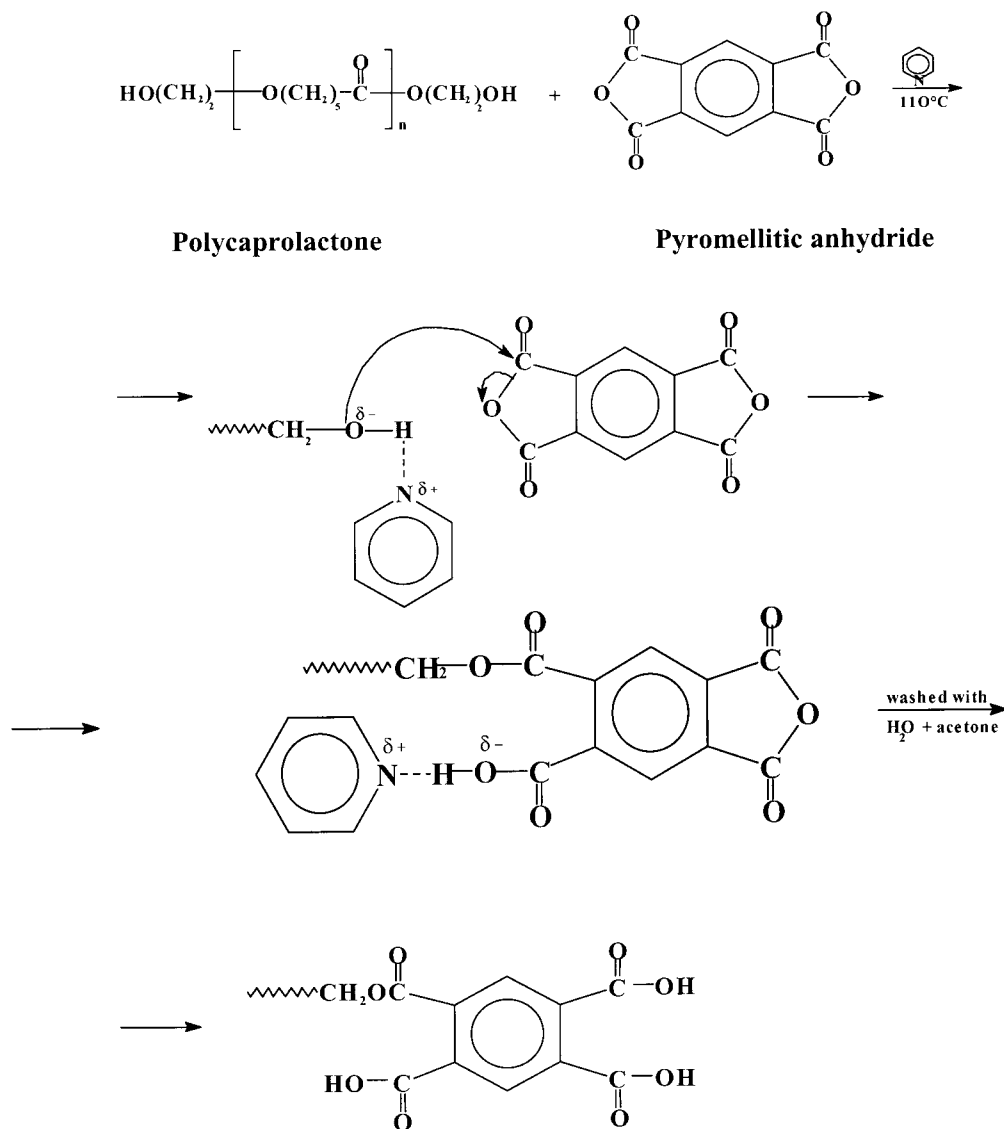**Figure 2** SEM micrograph of the starch amylomaize powder.

Figure 3 OM micrograph of the starch particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Polycaprolactone   **Pyromellitic anhydride**

Scheme 1 Functionalization of low-molecular-weight PCL with APM.

and not blends. Compatibilization between starch and polyester could be affected only by the covering of the starch granules in polymeric matrices.

Thus, to promote compatibilization between the polyester (PHB or PCL) and the starch, two different reactive preparation methodologies were used.

In the case of PCL-based composites, it was possible to prepare a compatibilizing agent with a lower molecular weight PCL, the first strategy previously described.

On the other hand, the PHBV, being a biotechnologically produced polyester with particular properties such as a high molecular weight, it was not possible to use the same preparation method-

ology. In fact, in this case the RB methodology was preferred.

PHBV/Starch Composites

Compatibilization between PHBV and starch was improved with a particular type of blending-denominated RB. This reactive methodology confers chemical reactivity on the polymers that must be blended, promoting in this way their compatibilization. The major qualification needed to use the RB methodology is the presence of reactive groups on the backbone chains of both polymers to create strong interactions between the two incompatible polymers, which produces a lower interfacial energy and a more stable morphology.
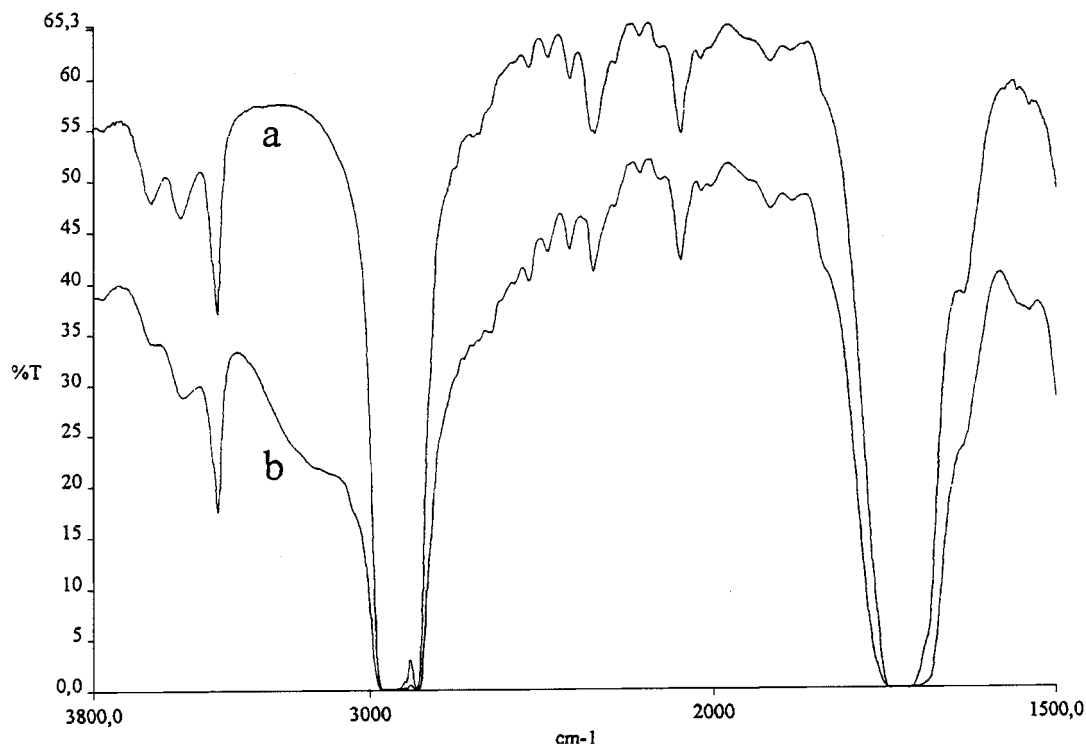
Figure 4 Comparison between FTIR spectra of (a) neat PCL and (b) modified PCL.

PHBV is characterized by the presence of carboxyl groups in the backbone chains that constitute the sites of potential interactions with the starch hydroxyl groups. In particular, chemical interactions between the two composites components were induced by addition of 2 wt % peroxide during the blending. This organic peroxide had a $t_{1/2}$ of about 30 min at 190°C, and the preparation temperature of the composites was about 190°C. In this way, it was possible to prevent too fast a reaction, to keep homogeneous blending, and to avoid completely crosslinking the PHBV. This choice of a starch with a high amylose content depended on a greater number of hydroxyl groups present on its surface, which was responsible for a higher reactivity with the carboxylic groups of the PHBV, and on a lower granule size that allowed a good dispersion of the starch in to PHBV.

PCL/Starch Composites

Compatibilization between starch and PCL was promoted by the addition of a precompatibilizer agent during the blending of the two components.

This agent was prepared through chemical modification of the end groups of a lower molecular weight PCL (M_w = 20,000 Da) with reactive groups able to react with —OH groups of the

starch. A PCL with a lower molecular weight was preferred to obtain a higher concentration of reactive hydroxyl end groups. This chemical modification was performed as described in Scheme 1, the reaction of PCL with an excess of APM.

The excess of APM permitted high conversion and helped us avoid undesirable chain-extension reactions between modified and unmodified PCL.

The reaction was performed in bulk at 110°C, for 24 h with pyridine as the catalyst. These parameters were selected on the basis of reaction monitoring by IR spectroscopy.

In fact, in these conditions the IR analysis showed a decrease in the band relative to the PCL hydroxyl end groups stretching ($\sim$3630 cm^{-1}) and the appearance of a band at 3200 cm^{-1} due to stretching of carboxylic groups, as shown in Figure 4. The intensity of this latter band increased after washing of the product because of partial hydrolysis of the anhydride groups present on the PCL backbone.

Materials Characterizations

Thermal Analysis of the Polyester-Based Composites

The thermal properties (T_m, crystallization temperature, and T_g) of neat PHBV, neat PCL, and

Table II   Thermal Analysis Data

Composite	T_g ($\pm 2°C$)	T_m ($\pm 2°C$)	X_c (± 2)
PHBV 100	4	165	40
PHBV 80	5	160	35
PHBV 70	5	162	34
PHBV 100R	6	163	38
PHBV 80R	5	160	34
PHBV 70 R	6	161	32
PCL 100	−67	62	53
PCL 90	−66	60	52
PCL 70	−65	61	53
PCL 50	−65	59	52
PCL 100L	−67	61	57
PCL 90L	−68	61	57
PCL 70L	−68	59	56
PCL 50L	−67	59	56
PCL 100M	−66	63	64
PCL 90M	−67	64	62
PCL 70M	−66	64	64
PCL 50M	−64	62	63
PCL 100H	−67	62	66
PCL 90H	−69	62	67
PCL 70H	−69	61	66
PCL 50H	−68	60	68

Table III   Impact Properties of PHBV and PHBV/Starch Composites by the Charpy Method

Sample	R (kJ/m^2)
PHBV 100	1.80
PHBV 80	1.20
PHBV 70	0.90
PHBV 80 R	2.10
PHBV 70 R	1.90

their respectively based composites were investigated by DSC to determine the influence of the starch phase on the polymeric matrices. The results are reported in Table II.

The PHBV based composites' thermal properties were very similar to those of neat PHBV, showing that interactions promoted during the PHBV/starch blending were probably only for a low percentage of chains, as reported in literature for other systems prepared by RB.[23,24]

Thermal analysis of the PCL modified with anhydride showed the same T_m as the neat PCL, whereas the T_g shifted by −66°C to −55°C. This could be correlated to reduced segmental chain mobility due to the presence of the pyromellitic groups on the PCL end chains. For the PCL-based composites, only the content of crystallinity was different with respect to neat PCL. In particular, this value changed in relation to the amount of precompatibilizer added and to the presence of a lower molecular weight PCL. In fact, the content of crystallinity increased with decreasing polymer molecular weight.

Impact Behavior and Fractographic Analysis

PHBV-Based Composites. The impact behavior analysis of the neat PHBV, neat PCL, and their

respectively based composites were analyzed according to the LEFM.

The impact analysis performed on PHBV-based composites (PHBV 80 and PHBV 70) showed that the presence of starch was responsible for a significant decrease in PHBV toughness (see Table III). This result is in accord with the morphological analysis performed on the fractured surfaces of the composites. In Figure 5, as an example, the fractured surface of the uncompatibilized PHBV/starch composites with 80 wt % polymeric matrix is reported. The starch granules pulled out their domains after the impact test and showed a poor interfacial adhesion between PHBV and starch.

On the contrary, in the case of PHBV-based *R*-type composites, the starch granules appeared covered by the polymeric matrix even after the mechanical test, (see Fig. 6). This finding indicates that the reactive approach used to prepare these composites allowed a better interaction between the two components, which is responsible for good stress transfer between the matrix and well-dispersed starch domains. This result is in
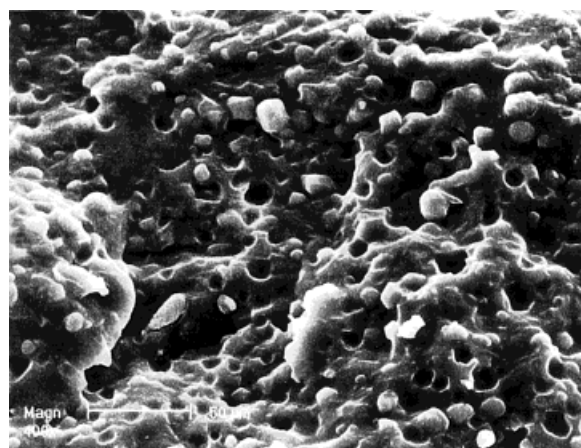

Figure 5   SEM micrograph of the fractured surface of the PHBV/starch 80/20 nonreactive composite.
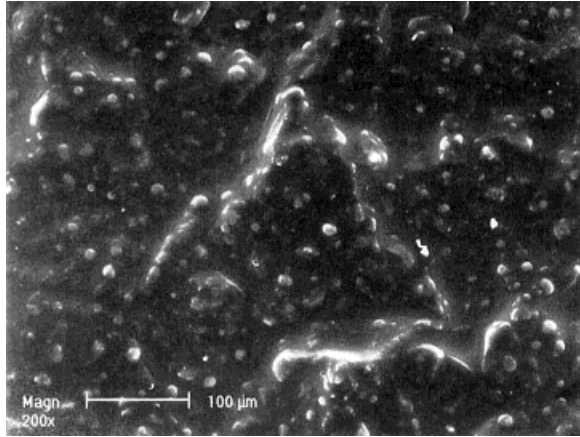
Figure 6 SEM micrograph of the fractured surface of the PHBV/starch 80/20 reactive composite.

accordance with the impact test data. In fact, as shown in Table III, 20% of the starch gave increased PHBV toughness, whereas at 30% the impact strength was similar to that of the polymeric matrix.

The nondeformability nature of the starch, being a rigid filler, did not permit it to reach values typical of rubber-toughened composites despite the presence of a reactive interface matrix/filler.

Impact Analysis of PCL-Based Composites. The values of the fracture parameter R for neat PCL

and the PCL/starch composites with 5 and 10% of compatibilizer calculated as a function of starch content are shown in Figure 7. As shown in this figure, a decrease of R for all samples was observed. Nevertheless, for the samples with the highest starch content (30–50%), the presence of compatibilizer slowed down the decrease in R.

These results on the fracture behavior can be interpreted on the basis of the fractographic analysis performed by SEM on the surface of notched specimens. SEM micrographs were taken near the notch tip in the region of crack initiation. Figure 8 shows the fracture surfaces of PCL/starch composites prepared without [Fig. 8(a)] and with [Fig. 8(b)] the addition of the compatibilizer and the differences are easily seen. In fact, in the first case [Fig. 8(a)], the presence of cavities and voids left by starch grains exhibited a poor adhesion between matrix and filler. In the case of PCL/starch with the compatibilizer [Fig. 8(a)], a fairly smooth fracture surface is evident, almost without the pull out of starch particles, and better interfacial adhesion produced by the compatibilizer can be deduced.

Investigation on Biodisintegration

PHBV, PCL, PHBV/starch 70/30 (compatibilized and not compatibilized), and PCL/starch 70/30 (compatibilized and not compatibilized) samples
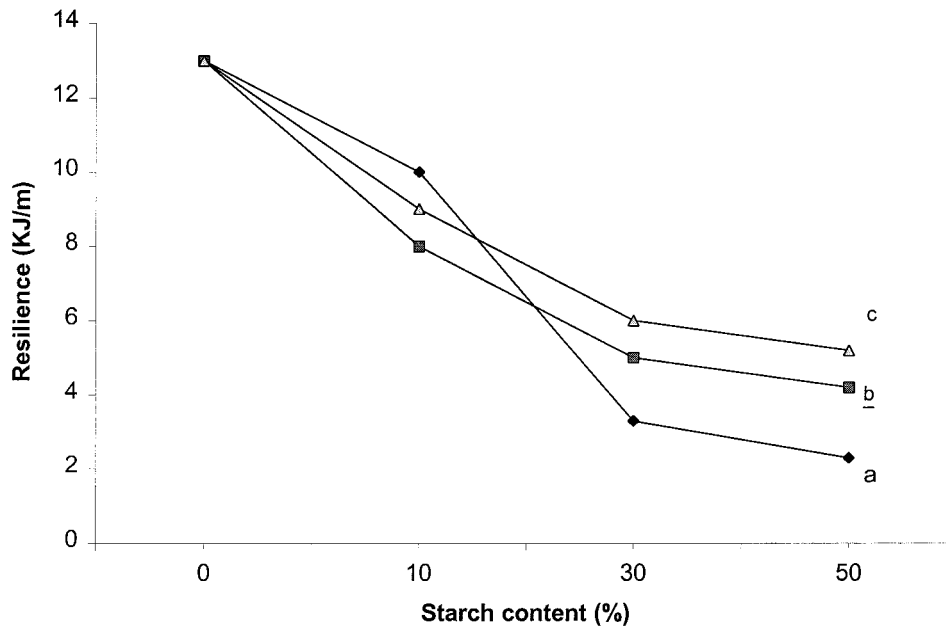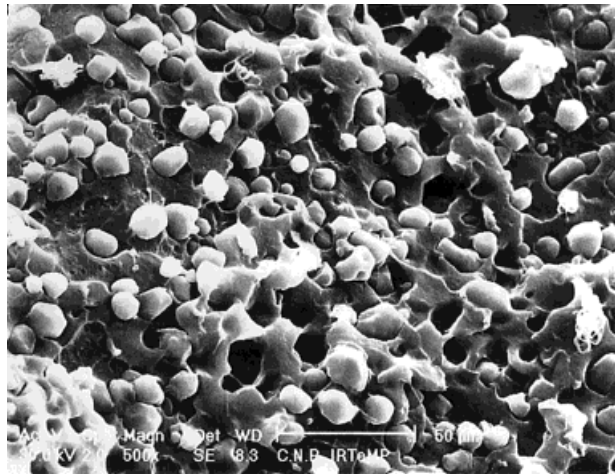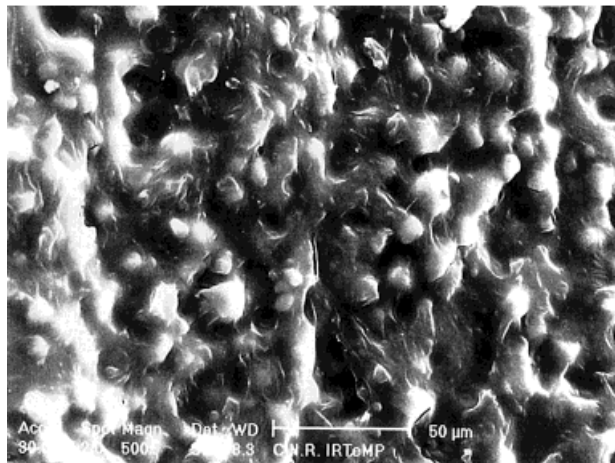

Figure 7 R in function of the percentage of starch content: (a) composites without compatibilizer, (b) composites with 5% of the compatibilizer, and (c) composites with 10% of the compatibilizer.

were subject to compost testing, and the percentage of weight loss was evaluated at different times during the biodegradation process. In Table IV, the results are summarized. From these findings, it is possible to conclude the following:

1. PCL polymer provided, in these conditions, a faster biodeterioration rate than PHBV.
2. The presence of the starch phase was responsible for faster biodeterioration for both the systems with respect to neat polymers.
3. After 20 days of incubation, both PCL/starch and PHBV/starch composites were

Table IV   Percentage of Weight Loss of Neat PCL, Neat PHBV and PCL/Starch and PHBV/Starch Mixtures in the Simulating Compost Test

	Time of Incubation (Days)	
Sample	10	20
Neat PCL	35	60
PCL/starch 70/30 NR	>75	>90
PCL/starch 70/30 R	>75	>90
Neat PHBV	17	41
PHBV/starch 70/30 NR	a	100
PHBV/starch 70/30 R	a	100

The percent of weight loss is the average of 10 specimens.
a Samples completely deteriorated.
R, compatibilized composites; NR, not compatibilized composites.

almost completely biodisintegrated in the compost.
4. These compatibilization procedures did not affect the biodisintegration in the compost. As a matter of fact, compatibilized and uncompatibilized PHBV/starch and PCL/starch composites showed the same percentage weight loss.

CONCLUSIONS

From the previous results, the following can be concluded:

- Compatibilization promoted by RB with the addition of an organic peroxide (PHBV/starch composites) or functionalization of a lower molecular weight PCL with a dianhydride (PCL/starch system) is necessary to obtain a material characterized by a fine starch-phase dispersion into polyester matrices and good performance.
- The performance of the composites are a function of the amount of starch and compatibilizer.
- The compatibilization process does not affect the biodisintegration properties of the neat polymeric matrices (PHBV, PCL), and the presence of the starch phase increases the rate of the degradation process.
- The addition of starch to the PCL and PHBV permits production of biodegradable materi-

Figure 8   (a) SEM micrograph of the fractured surface of the PCL/starch 50/50 composite and (b) SEM micrograph of the fractured surface of the PCL/starch with compatibilizer.

als having lower cost and the required performance of a disposable plastic.

REFERENCES

1. Aminabhavi, T. M.; Balundgi, R. H.; Cassidy, P. E. Polym Plast Technol Eng 1990, 29, 235.
2. Huang, J. C.; Shetty, A. S.; Wang, M. S. Adv Polym Technol 10, 1990, 23.
3. Selke, S. Biodegradation and Packaging; Pira International: Leatherhead, United Kingdom, 1996.
4. Pelissero A. In Le Materie Plastiche e L'Ambiente; Grafis, Ed.; Associazione Italiana di Scienza e Tecnologia delle Macromolecole: Bologna, Italy, 1990; p 129.
5. Dawes, E. A. Microbial Energetic; Blackie: Glasgow, Scotland, 1986.
6. Rutkowska, M.; Dereszewska, A.; Jastrzehska, M.; Janik, H. Macromol Symp 1998 , 130, 199.
7. Doi, Y.; Fukuda, K. Biodegradable Plastics and Polymers; Elsevier: Amsterdam, 1994, p 479.
8. Gould, J. M. In Agricultural and Synthetic Polymers; American Chemical Society: Washington, DC, 1990.
9. Philippa, J.; Hocking, J. P. J Macromol Sci Rev Macromol Chem Phys 1992, 32, 43.
10. Avella, M.; Martuscelli, E.; Pascucci, B.; Raimo, M.; Focher, B.; Marzetti, A. J Appl Polym Sci 1993, 49, 2091.
11. Griffin, G. L. J. In New Approaches to Research on Cereal Carbohydrates; Hill, P. D., Munck, L., Eds.; Elsevier: Amsterdam, 1985; p 201.
12. Koller, I.; Owen, J. Polym Int 1996, 39, 175.
13. Imam, S. H.; Gordon, S. H.; Shogren, R. L.; Greene, R. V. J Environ Polym Degrad 1995, 3, 205.
14. Bastioli, C. Chim Ind 1997, 79, 77.
15. Jarowenko, W. Encyclopedia of Polymer Science and Technology; Interscience, 1970; Vol. 12, p 787.
16. Lin, N. C.; Baker, W. E. Adv Polym Technol 1992, 11, 249.
17. Avella, M.; Errico, M. E. J Appl Polym Sci 2000, 77, 232.
18. Avella, M.; Errico, M. E.; Laurienzo, P.; Martuscelli, E.; Raimo, M.; Rimedio, R. Polymer 2000, 41, 3875,
19. Koenig, M. F.; Huang, J. J. Polymer 1995, 36, 1877.
20. Hermans, P. H.; Weidinger, A. J Polym Sci 1949, 4, 135.
21. Paul, D. R.; Barlow, G. W. J Macromol Sci Rev Macromol Chem 1980, 18, 109.
22. Wang, L. H.; Huang, Z.; Hong, T.; Pater, R. S. J Macromol Sci Phys 1990, 29, 155.
23. Greco, R.; Malinconico, M.; Martuscelli, E.; Ragosta, G.; Scarinzi, G. Polymer 1987, 28, 1187.
24. Avella, M.; Errico, M. E.; Immirzi, B.; Malinconico, M.; Falcigno, L.; Paolillo, L. Macromol Chem Phys 1998, 199, 1901.