# Biodegradation Study of a Coextruded Starch and Poly(lactic acid) Material in Various Media

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**ABSTRACT:** The biodegradation of a coextruded starch/poly(lactic acid) polymeric material was studied in a liquid, in an inert solid, and in composting media. Mineralization of the material's carbon content was followed using the appropriate ASTM standard experimental methods. The final percentage of biodegradation depended on the nature of the medium used. The percentage of mineralization (Cg) was better with the liquid medium (65%) than with either the compost medium (64%) or the inert medium (59%0. To understand the workings of the biodegradability of the polymer material, a measurement of the carbon balance seemed essential A repartitioning of the material's carbon between the various degradation products to biomass carbon (Cb), to carbon dioxide carbon (Cg), to dissolved organic carbon (Cs), and to residual insoluble material carbon (Cnd) produced was quantified throughout the experimental runs. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 825–831, 2003

**Key words:** starch; poly(lactic acid); coextrusion; carbon; mineralization; partition; biodegradation

## INTRODUCTION

Interest in biodegradable and compostable plastics has grown considerably during the last decade. Although only a few biodegradable plastic materials were available at the beginning of the 1990s,[1] today several new materials have been developed and begun to marketed.[2,3] Industrial development of new biodegradable plastics has been accompanied by the parallel development of suitable standards and criteria for defining the biodegradability of man-made materials. Many methods have been proposed to evaluate the biodegradability of a material, and some are standardized, either for liquid medium[4,5] or in a composting medium.[6,7] All measurements are based on respirometric methods for the determination of the evolution of net $CO_2$. For a controlled composting test, a mature compost is used as a solid matrix, as a source of microorganisms (inoculum), and as a source of nutriments.

However, compost is a very heterogeneous and complex matrix, and the production of $CO_2$ from the main product of the biodegradation reaction should match the disappearance of polymer, which is the original substrate; so, experimentally, the determination of net $CO_2$ evolution is the $CO_2$ evolved from a mixture of polymer–compost minus the $CO_2$ evolved from the unamended compost (blank) tested in a different reactor. It is also important to assess the production of low-molecular-weight substances and of carbon trapped in newly generated biomass. This is a reason to realize a carbon balance. But it is very difficult to detect a test material's residues of metabolic compounds produced during degradation, and it also is very important to take into account the other components involved in the biodegradation reaction. This can be accomplished by measuring the evolution of the $^{14}CO_2$ from $^{14}$C-radiolabeled test materials.[8–10] However, this is an expensive and laborious method because of the need for $^{14}$C-labeling each specific test material. Detection of a test material's residues and metabolic compounds produced during degradation could be more easily accomplished using liquid test systems, such as the Sturm test,[11,12] but this test does not simulate a real composting environment. Therefore, a test method simulating the composting environment and suitable for extraction purposes, and that could perform solid-state fermentation using vermiculite as a mineral solid bed, would be highly useful in this field. Vermiculite is known to be particularly suitable as a microbial carrier, allowing the survival and full activity of microbes, and its fermentation conditions are typical of a composting environment, generating an active environment that can be used to test new polymers.

Starch, an easily biodegradable polymer, cannot be used as a packaging material because of its hydrophilic character. The quest for biodegradable packaging materials has led to more complex mixtures. These materials are often made up of several compounds associated together, either as a homogeneous blend or in a multilayer form. The first research in this field

TABLE I
Main Characteristics of the A (PLA) and B (Starch) Parts of the Coextruded FILM A/B/A

| | Proportion (in weight) | Thickness (mm) | Humidity (%) | Elementary analysis (%) | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | | Carbon | Hydrogen | Nitrogen |
| A (PLA) | 19.4 ± 0.3 | 0.66 ± 0.05 | 5.4 ± 0.2 | 48.96 ± 0.10 | 5.00 ± 0.06 | 0.20 ± 0.002 |
| B (starch) | 80.6 ± 0.5 | 0.87 ± 0.06 | 10.5 ± 0.3 | 38.57 ± 0.15 | 6.74 ± 0.04 | 0.10 ± 0.01 |

conducted with blends of starch with synthetic polymers was done by Griffin in 1973[13] and Otey et al. in 1977.[14] The materials that initially were considered biodegradable were found to actually biofragment, leaving polymer residues to remain.[15] At best, starch biodegradation stimulates chemical degradation and fragmentation of the synthetic fraction.[16,17] Starch biodegradation is reduced in such blends, probably because of the inaccessibility of the appropriate enzyme to the substrate.[18]

To avoid this problem, the use of coextruded materials recently has been considered. Coextrusion produces multilayered materials comprised of two or more separate polymers. In one case, the middle layer was comprised of low-cost thermoplastic starch, and the two external layers were made of another biopolymer such as poly(lactic acid).[19] This arrangement decreased the water sensitivity of starch and improved the mechanical properties of the film. However, before using such a material, it is desirable to check both its chemical degradability and biodegradability. The purpose of the studies reported here was to investigate both the physicochemical properties of such a coextruded material and to test its biodegradability in different media according to the correspondent ASTM standard methods, as well as to carry out carbon balances during the degradations and verify if the vermiculite could be used in place of the mature compost as a solid substrate in respirometric tests.

## EXPERIMENTAL

### Extruded material

In Part A Poly(lactic acid) was first plasticized with 10 wt % poly(ethylene glycol). At the same time, a starch-based formulation was prepared containing 65% starch and 35% glycerol (Part B). Then these two components were coextruded using two S2032 single-screw extruders (SCAMIA) to form an A/B/A-type film. The various parameter values for Parts A and B, listed in Table I, were measured after delamination of an entire film. Percentage of moisture content was measured after storage for 1 week at 23°C at a relative humidity of 50% on a crushed sample using the Karl Fischer method (NF VO3-625). Elemental analyses were carried out on crushed samples that had been dried at 105°C for 24 h.

### Degradation test conditions

Degradation was monitored and U.S. procedures applied, imposing the following temperature profile during the trial: Day 1, 35°C; Days 1–5, 58°C; Days 6–28, 50°C; and Days 28–45, 35°C, in accord with the ASTM-D 5209-92[4] and 5338-92[6] standards. Assessment of material degradation was made on plates 1 cm$^2$ in area using the method of Derradji et al., 1996.

### Liquid medium

The support medium did not contain any organic or inorganic carbon. Every 5 L was composed of CaCl$_2$·2H$_2$O (0.65 g), Na$_2$HPO$_4$·2H$_2$O (34.85 g), KH$_2$PO$_4$ (18.75 g), (NH$_4$)$_2$SO$_4$ (20.0 g), MgSO$_4$·7H$_2$O (1.0 g), FeSO$_4$·7H$_2$O (0.0135 g), MnSO$_4$·7H$_2$O (0.005 g), ZnSO$_4$·7H$_2$O (0.005 g), H$_3$BO$_3$ (0.005 g), KI (0.005 g), and (NH$_4$)$_6$ Mo$_7$O$_{24}$·4H$_2$O (0.005 g).

Each bioreactor was first seeded with 15 mL of compost extract in 1.5 L of the liquid support medium, prepared as described in a previous article. Following this, 13.7 g of film containing 5.2 g of carbon was introduced into the bioreactor.

### Composting medium

The composting medium was prepared from the organic fraction of a 2-month-old mature compost made from municipal refuse (Arras 62, France). It was sieved through a 1-cm sieve prior to use. Its physicochemical characteristics, as presented in Table II, were in accord with the European standard ISO/CEN 14855.[7] This compost (560 g) was placed in a bioreactor contained by a 2-cm$^2$ mesh screen and net (AT 14/10, 0.75 × 0.50 mm$^2$, Huck-Occitania) above a liquid level maintained at 150 mL with distilled water.

TABLE II
Comparison of Physical and Chemical Characteristics of the Compost with the Values Recommended by the ISO/CEN 14855 Norm

| Recommended values | Initial values | Values after 10 days in reactors |
| --- | --- | --- |
| 50% < dry matter > 55% | 52.7 ± 1.5% | 51.1 ± 1.2% |
| Organic matter > 30% | 65.8 ± 0.8% | 60.7 ± 1.5% |
| 10 < C/N < 40 | 28.9 ± 0.8 | 19.6 ± 0.6 |
| 7 < pH < 9 | 8.0 ± 0.1 | 8.2 ± 0.1 |

Air was bubbled through the distilled water to maintain a relative humidity of at least 70% in the compost. Some 36.4 g of film containing 14.0 g of carbon was introduced into the solid compost.

### Inert solid medium

The inert solid medium used was an aluminum–magnesium–iron silicate whose chemical composition was $(Mg, Fe, Al)_3 5Al, Si_4O_{10}(OH)_2 š4H_2O$. This product (Sigma-Aldrich vermiculite grade 3) maintains its water content well. Consequently, the relative humidity (*Aw*) of the medium was 100% when the water content reached 70 wt %.[21] This inert solid medium (180 g) was added to 410 mL of the previous liquid medium together with 15 mL of compost extract. Finally, a piece of film weighing 20.1 g and containing 7.7 g of carbon was placed into this mixture.

### Protein content

The total protein content of the media was measured with the micromethod described by Spitzer and Coll,[22] using the Kit I for DC protein assay developed by Bio-Rad Laboratories. Optical density measurements were made at 750 nm with a UV-visible spectrophotometer (Uvikon-932, Kontron).

### Dissolved organic carbon

The analysis of soluble degradation products was performed with an organic carbon analyzer (1010 model, OI Analytical brand). Before the analyses, samples extracted from the different media were filtered through a cellulose acetate membrane with pores 0.2 $\mu$m in size (Osmonics, USA). Following this, the organic carbon of the sample was oxidized chemically into carbon dioxide in the carbon analyzer. This measure corresponds to dissolved organic carbon (DOC). The dissolved inorganic carbon (DIC) was previously measured and was found to be negligible in comparison with the DOC (<20 mg/L).

### Degradation residues analysis

Starch hydrolyzates were analyzed for sugars by HPLC (Model 8880, TSP, Les Ulis, France) using the same procedure outlined by Coma.[23] The lactic acid was also analyzed by HPLC using the same apparatus but with an Aminex HPX 87H column, 300 mm × 7.8 mm (Bio-Rad, Ivry/Seine, France), maintained at 35°C. The mobile phase (0.02 mol/L of sulfuric acid) was degassed by passing through a filter with pores 0.2 $\mu$m in size. A flow rate of 0.6 mL/min was maintained at 900 psi pressure. Lactic acid was measured using a UV detector (TSP 8880, Les Ulis, France). The injection volume of the sample was 20 $\mu$L. Prior to injection the samples were filtered through filters that had 0.22 $\mu$m pores (Millipore Corporation, USA). Three filtered solutions corresponding to three replicated experiments were combined. A calibration curve was established beforehand using different concentrations of lactic acid (Sigma Chemical Co., St. Louis, MO).

### Residual materials study

Weight loss estimation

Samples were dried at 25°C and 50% relative humidity to a constant weight. Recovered pieces of film, which had been stored for 45 days under these conditions, were weighed with a precision balance (Mettler Toledo AB104, Switzerland).

Thermal properties

Thermal properties were determined with a modulated differential thermal analyzser (Universal V1.9D TA Instrument, USA) frozen by liquid nitrogen circulation. The analyses were carried out on film samples recovered during experiments and stored at 25°C and 50% relative humidity. Samples 15 mg in size were then placed in hermetically sealed aluminum dishes. Two temperature scans at 10°C per minute from 20°C to 200°C were performed. The first scan was used to eliminate the thermal history of the material.

### Molecular weight distribution of PLA films

Gel permeation chromatography (GPC) testing was performed an samples of PLA films using a Thermo Separate products model 300 high-performance liquid chromatograph (Les Ulis, France). Tetrahydrofuran (THF) was pumped at 1 mL/min, and an injection volume of 200 $\mu$L was used for HPSEC analysis. A PLA sample of 0.1 g was dissolved in 5 mL of THF. A refractive index detector (Shodex RI 71) was interfaced to a PIII personal computer. PL Caliber software and interface PL-DCU (Polymer Laboratories) enabled chromatograms to be numerically recorded. The Plgel 5 $\mu$m MIXTE-C column (Polymer Laboratories) was used.

A molecular weight calibration curve was constructed based on 10 narrow-molecular-weight-distribution polystyrene standards (Easical), with MW peaks ranging from 580 to 7,500,000 g $mol^{-1}$

### RESULTS

### Degradation products

To confirm complete biodegradation, it is necessary to conduct a carbon balance. The carbon content of a polymer ($C_{polymer}$) was converted by microorganisms to biomass carbon (Cb), to carbon dioxide carbon (Cg), to dissolved organic carbon (Cs), and to residual in-
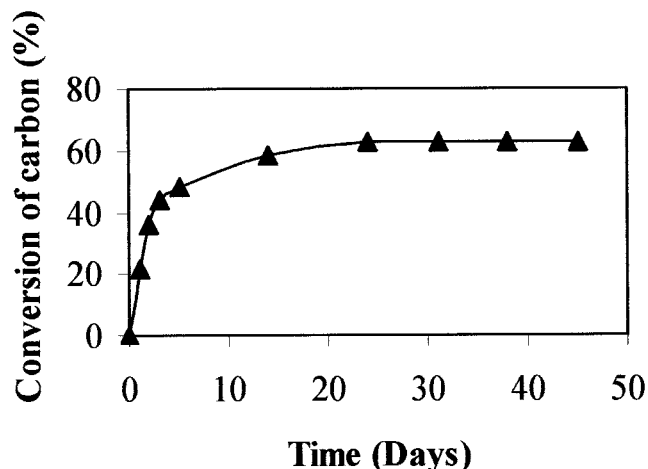
**Figure 1** Mineralization of the coextruded material in compost medium according to the ASTM D-5338-92 norm.



**Figure 2** Carbon balance during coextruded film degradation in liquid medium according to the ASTM D-5209-92 norm [▲: Cg, ■: Cs, ◆: Cb, ●: Cd, from eq. (2)].

soluble material carbon (Cnd). Therefore, the equation representing the carbon balance for a biodegradation test is:

$$C_{polymer} = Cb + Cg + Cs + Cnd \qquad (1)$$

where Cg = ($C_{CO2\ ingoing\ air}$ − $C_{CO2\ outgoing\ air}$). All the degraded carbon corresponds to:

$$Cd = Cb + Cg + Cs \qquad (2)$$

**Composting medium**

In the composting medium only the study of the mineralization of the material is allowed because a complete carbon balance can be realized.

The carbon degradation curve plotted in Figure 1 shows three steps:

1. latency period of 1 day;
2. inflection over the entire curve; and
3. a final mineralization percentage of 64%.

**Liquid medium**

Mineralization

The mineralization rate curve (Cg) reported in Figure 2 shows the total mineralization of coextruded material (PLLA and starch). No period of latency was observed. Over the first day the material disintegrated. The two components, starch and poly(lactic acid), were separated. Then the starch became accessible to microorganisms, whereas the poly(lactic acid) layer remained in sheet form. Figure 2 shows the conversion of starch, which mineralized quickly so that it was completed by the end of the fifth day. Its final carbon percentage represented 55% of the material's initial carbon content. After about 15 days the
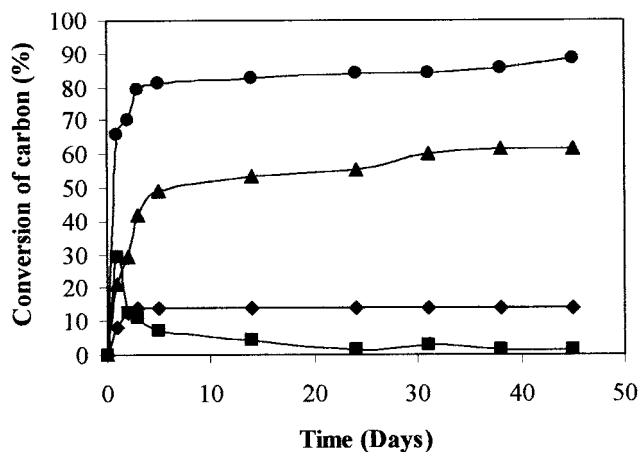
slope of the curve indicated mineralization of another compound had commenced—presumably that of poly(lactic acid). Finally, at the end of the experiment the percentage mineralization reached 65%.

What is shown in Figure 3 confirms the later degradation of poly(lactic acid). In fact, the mineralization rate curve reported in Figure 3 shows a conversion of 17% after 45 days of degradation.

DOC

In Figure 2 the DOC (Cs) after 1 day of the experiment represented 30% of the material's initial carbon. From then on, this proportion continuously decreased, reaching 15% at the end of the second day, and constituted only 2% at the end of the experiment.

HPLC analysis of this dissolved carbon fraction (Fig. 4) showed glucose to be the major degradation product of the coextruded poly(lactic acid) substrate. The maximum quantity of released glucose occurred at the same time as the maximum in the (DOC) Cs value, during the first and second days. In other re-
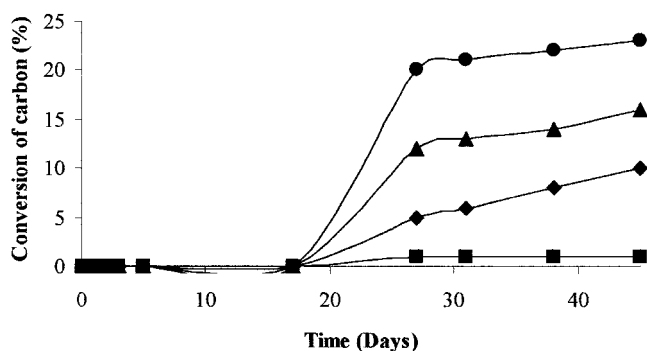


**Figure 3** Carbon balance during the PLA part of coextruded film degradation in liquid medium according to the ASTM D-5209-92 norm [▲: Cg, ■: Cs, ◆: Cb, ●: Cd; from eq. (2)].
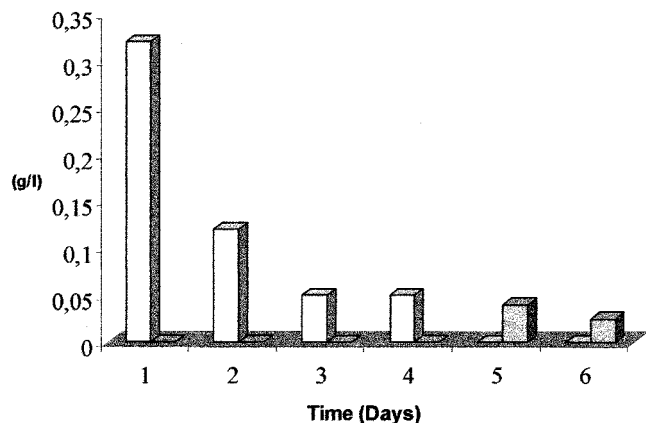
**Figure 4** Evolution of some soluble released products during the degradation of the coextruded material in liquid medium according to the ASTM D-5209-92 norm ( □ : glucose, ■ : lactic acid).

spects, lactic acid appeared as soon as the 15th day, when the degradation of the starch fraction had been completed. This confirms the successive degradation of the two components of the material.

### Biomass

Biomass formed at the expense of the plastic film material (Cb) increased during the first 2 days and represented 16% of the initial carbon. Then this production slowed down, and only 14% of the material carbon had been bioassimilated after 45 days (Fig. 2).

### Biodegraded carbon

The biodegraded carbon (Cd), calculated by eq. (2), represented 95% of the total initial carbon as early as 5 days into the experiment (Fig. 2). But the Cd of starch represented 100% of the initial carbon of starch as early as 5 days into the experiment (Fig. 5) and the Cd of poly(lactic acid) represented 17% of the initial carbon of poly(lactic acid) after only 25 days of biodegradation.
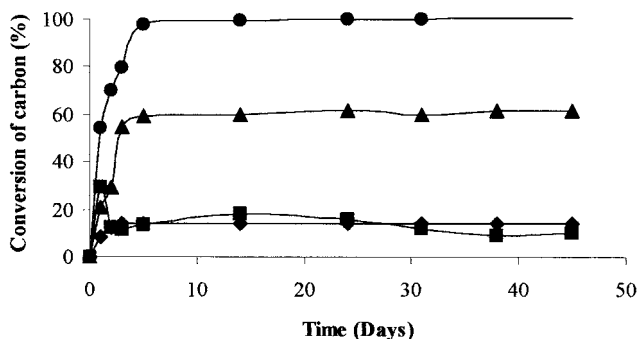


**Figure 5** Carbon balance during the starch part of coextruded film degradation in liquid medium according to the ASTM D-5209-92 norm [▲: Cg, ■: Cs, ◆ : Cb, ●: Cd; from eq. (2)].
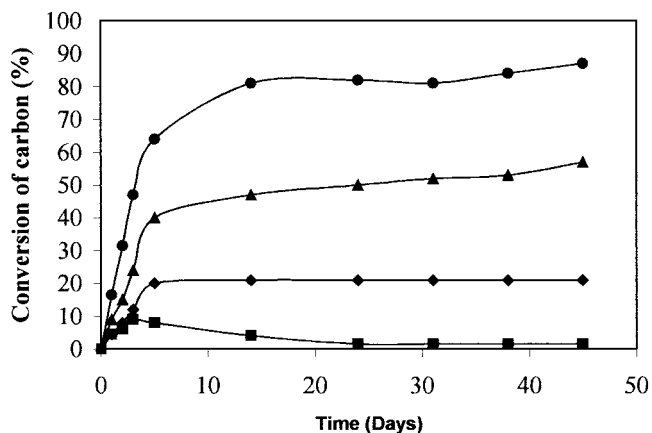


**Figure 6** Carbon balance during coextruded film degradation in vermiculite medium according to the ASTM D-5338-92 norm [▲: Cg, ■: Cs, ◆ : Cb, ●: Cd; from eq. (2)].

The final result value of Cd (95%) compared with the insoluble residual material, Cnd (6%), shows, thanks to eq. (1), that all the degradation products were well identified at the end of the experiment.

## Vermiculite medium

### Mineralization

The mineralization (Cg) of the substrate in this medium exhibited, like compost, a 1-day latency period (Fig. 6). Following this, the curve did present an inflection point over the course of the experiment. This indicated the beginnings of degradation of poly(lactic acid) after the end of starch degradation. The Cg final percentage mineralization (59%) was lower than that in the liquid medium.

### DOC

In this inert solid medium, the DOC (Cs) percentage did not exceed 7% of the initial carbon. Then this production slowed down, and only 1% of the material carbon corresponded to the dissolved organic carbon after 45 days.

### Biomass

The biomass (Cb) increased mainly at the beginning of the experiment, while the starch fraction degraded. The Cb final percentage mineralization was 23.3%.

### Biodegraded carbon

After 45 days of the experiment, all the degraded carbon (Cd) represented 85% of the initial substrate carbon, of which 80.6% was the resultant of starch biodegradation and 4.9% the resultant of poly(lactic acid) biodegradation.
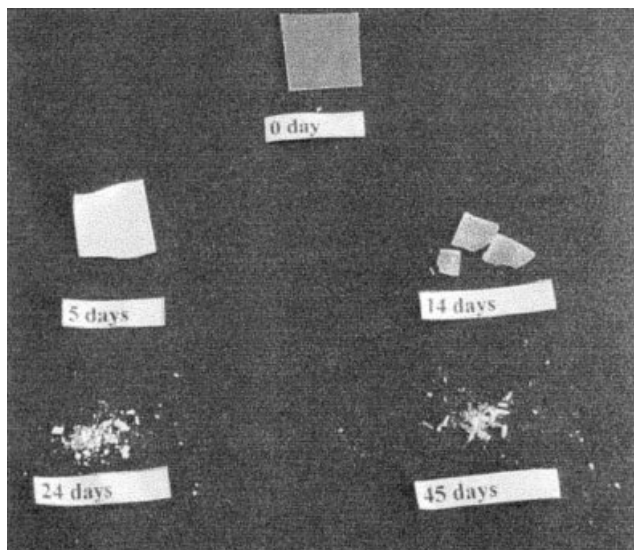
**Figure 7**  Evolution of the physic state of the PLA film pieces during their degradation in liquid medium according to the ASTM D-5209-92 norm.

## Residual material studies

All the starch had disappeared from the samples in the liquid medium by the end of the first day. The poly-(lactic acid) sheets had separated and rolled up (Figs. 7 and 8). These had fragmented by the 14th day and become finer and finer powders. The same physical evolution was observed in the vermiculite medium, but poly(lactic acid) film fragmentation had only just begun by the end of the experiment.
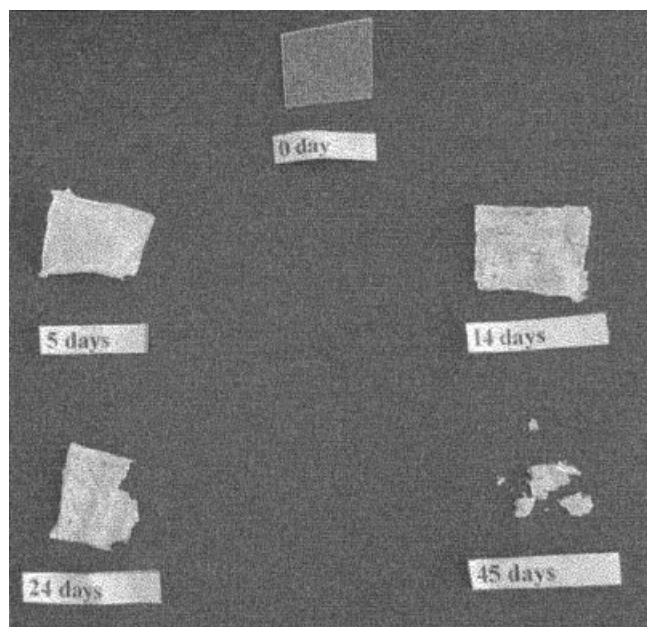


**Figure 8**  Evolution of the physic state of the PLA film pieces during their degradation in liquid medium according to the 14852 ISO/CEN norm [▲: Cg, ■: Cs, ♦: Cb, ●: Cd; from eq. (2)].
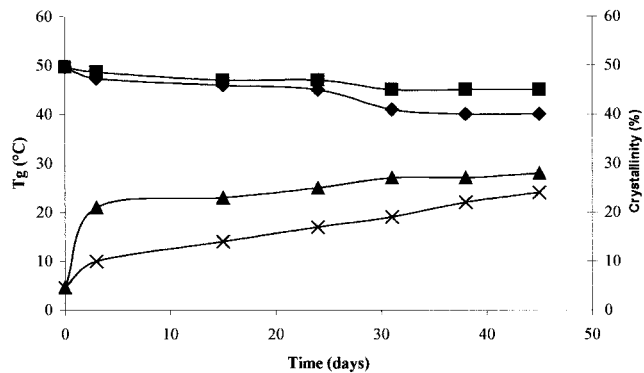


**Figure 9**  Evolution of the glass-transition temperature ($T_g$) and crystallinity percentage ($X_m$) of the coextruded material during its degradation in liquid and vermiculite media ($T_g$—♦: liquid medium, ■: vermiculite; $X_m$—▲: liquid medium, X: vermiculite).

## Thermal analysis

DSC thermograms (Fig. 9) of the initial coextruded material showed a glass-transition temperature ($T_g$) of 49.7°C and a crystallinity percentage of 4.6% (Fig. 8).

During the material's degradation in liquid medium, the $T_g$ value decreased because of a change in the material's degree of plasticization due to water penetration between the polymer chains, thereby increasing their mobility. The reduction in $T_g$ went slowly over the first 20 days, and its final value was stabilized at a constant value, 40°C.

During the material's degradation in inert solid medium, the $T_g$ decreased slowly, too. But the final value was stabilized at a constant value, 45°C, because water percentage of the vermiculite is weaker. In parallel, the crystallinity increased all along the degradation and was higher in the liquid medium because of a better reorganization of the polymer chains.

## Molecular weight distribution

Figure 10 shows the changes in average molar mass as deduced from SEC chromatograms. The initial de-
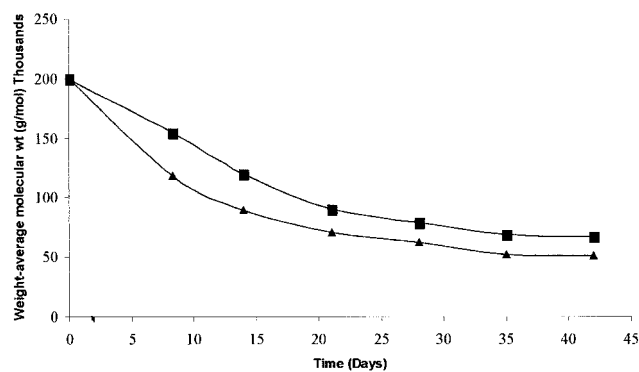


**Figure 10**  Evolution of the molecular weight (g/mol) of PLA plastic films in liquid medium (▲) and vermiculite medium (■). Each point is the average of three replicates.

crease of weight average molar mass was smaller for the vermiculite medium than for films with the liquid medium. For instance, molecular weight dropped down to 65% of its initial value after 2 weeks and 75% at 7 weeks for films exposed to the liquid medium. The effects of temperature and relative humidity on the degradation of PLA were equally observed but decreased with an inert medium. The molecular weight dropped down to 60% of its initial value after 2 weeks and to 67% after 7 weeks.

## CONCLUSIONS

The final mineralization percentages for the coextruded material in liquid, inert solid, and composting media were, respectively, 65%, 59%, and 63%. These values allow the conclusion that coextruded materials of the type studied may be considered biodegradable whatever the medium because according to the established standards, the minimum required degradation percentage is only 60%.

Classification of media by increasing degree of degradation observed was: liquid medium > composting medium > inert solid medium.

We have shown in this study that in liquid media, up to 95%, or in an admixture with inert solids, up to 85% of the material's initial carbon appears as various degradation products. Depending on the degradation medium or procedure employed, the results may be quite different. To understand the workings of the biodegradability of the polymer material, a measurement of the carbon balance seems to be essential.

The carbon balance depended on the nature of the microbial growth, which was principally bacterial in liquid media and principally fungal in solid admixture with vermiculite. Moreover, the degradation was monitored and imposed U.S. procedures were applied for the following temperature profile during the trial: Day 1, 35°C; Days 1–5, 58°C; Days 6–28, 50°C;, and Days 28–45, 35°C, in accordance with ASTM-D 5209-92 and 5338-92 standards. The variation of temperature incites specific microbial growth at different time.

The nature of the components of materials is very important because starch is degraded by strains of either bacteria or fungi, whereas poly(lactic acid) is preferentially degraded by fungal strains.

We also observed the high temperature and relative humidity needed to initiate the hydrolytic degradation of this polyester before the action of microorganisms commences. In fact, the higher water content of the liquid medium facilitated a greater degree of hydrolysis and therefore a higher ultimate degradation percentage. Moreover, DSC and GPC analysis of the poly(lactic acid) fraction of the material during degradation confirmed this because the degree of $T_g$ and average molar mass decrease was greater for experiments conducted in liquid media. And, finally, the presence of starch in the coextruded material facilitated degradation of the poly(lactic acid) fraction. This result was in accord with previous work by Bastioli and Coll.[24]

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