Influence of Low Molecular Weight Lactic Acid Derivatives on Degradability of Polylactide

MINNA HAKKARAINEN, SIGBRITT KARLSSON, ANN-CHRISTINE ALBERTSSON

Department of Polymer Technology, The Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden

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ABSTRACT: The presence of low molecular weight lactic acid derivatives in films enhanced the degradability of polylactide in a biotic medium. Two different biotic and abiotic series were investigated. The films used for the first abiotic and biotic series (a-1 and b-1 films) initially contained some lactic acid and lactoyl lactic acid, while the films used for the second abiotic and biotic series (a-2 and b-2 films) did not originally contain them. The b-1 films decreased in molecular weight during 3 weeks in the biotic medium, while no molecular weight decrease was seen in the a-1 films aged in a corresponding abiotic mineral medium. The molecular weight for the a-2 and b-2 films without lactic and lactoyl lactic acid remained almost constant. Scanning electron microscopy micrographs showed a larger amount of bacteria and fungi growing on the surface of b-1 films compared to b-2 films; thus, the presence of easily assimilated lactic acid and lactoyl lactic acid in the films improved the initial growth of microorganisms on the film surfaces. Gas chromatography and mass spectrometry analysis showed that lactic acid and lactoyl lactic acid were rapidly assimilated from the films aged in a biotic medium. New degradation products (e.g., ethyl ester of lactoyl lactic acid, acetic acid, and propanoic acid) were formed during aging in a biotic medium. Acetic acid and propanoic acid were formed as intermediate degradation products during the initial stages, but they were no longer detected after prolonged aging. The concentration of the ethyl ester of lactoyl lactic acid increased with aging time. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 228–239, 2000

Key words: polylactide; degradation; low molecular weight products

INTRODUCTION

Environmental concern has led to escalated interest in polylactide (PLA) and other biodegradable polymers as alternatives to traditional commodity plastics. PLA has the advantage of being both degradable and renewable. The physical properties and melt processing of PLA are similar to conventional packaging resins. It may thus be used as a commodity resin for general packaging applications. Possible applications are disposables such as food packaging, diapers, and contaminated hospital waste, which are not suitable for collecting and recycling.

The effect of temperature, pH, molecular weight, and copolymerization on the hydrolysis rate of PLA has been studied.[1–7] Impurities, residual monomer,[8,9] and peroxide modification[10] all increase the hydrolysis rate. In the large size devices the rate of degradation is larger inside than at the surface of the device, because of the catalyzing effect of the carboxylic acid groups trapped inside the device.[11–13]

Some polymers degrade by biological attack from the very beginning up to complete assimilation; in other cases the polymer initially degrades

Correspondence to: A.-C. Albertsson.

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by an abiotic chemical attack, which is followed by bioassimilation or mineralization of the intermediate degradation products. It is generally believed that PLA is initially degraded by hydrolysis in mammalian bodies, but after soluble oligomers are formed they can be metabolized or mineralized by cells and enzymes. Whether there are microorganisms in nature that are able to biodegrade PLA is still under discussion. There were only a few studies where PLA or PLA oligomers were subjected to selected microorganisms.[14–18] In general these studies state that the molecular weight was initially decreased by abiotic hydrolysis, but after the initial abiotic decrease the molecular weight of the samples aged in a biotic medium decreased faster than the molecular weight of the samples aged in an abiotic medium. The presence of certain enzymes (e.g., pronase, proteinase K, and bromelain) increases the degradation rate of PLA, but no results or negative results were obtained with other enzymes (e.g., esterase and lactate dehydrogenase).[19,20]

In a recent study the degradation rate of PLA was greatly enhanced by the presence of a mixed culture of compost microorganisms.[21] We further studied the influence of low molecular weight lactic acid derivatives on the degradability of the films. The changes in the polymer matrix were characterized by size exclusion chromatography (SEC), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). The low molecular weight products were followed by gas chromatography and mass spectrometry (GC-MS).

EXPERIMENTAL

Materials and Degradation Procedure

The material was pure poly(L-lactide) (PLLA) without additives made by Neste Oy, Finland. The film samples were 45-μm thick. Each series contained about 3 g of the polymer cut into 20 pieces. In the a-1 and b-1 series the polymer films were used as received. For the a-2 and b-2 series the films were first aged for 7 days at 80°C. The abiotic and biotic aging was performed in 250-mL Erlenmeyer flasks containing 150 mL of mineral medium. The mineral medium consisted of (per liter of deionized water) 5 g of $(NH_4)C_4H_4O_6$, 1 g of KH_2PO_4, 1 g of $MgSO_4 \cdot 7H_2O$, 0.85 mL of $FeCl_3 \cdot 6H_2O$ (1% solution), and 7.5 mL of $ZnSO_4 \cdot 7H_2O$ (1% solution). A mixed culture of microorganisms from compost was added to the b-1 and b-2 series. Five milliliters of 0.02% NaN_3 was added to the a-1 and a-2 series to prevent microbial growth. The series were held in a shaking oven at 37°C.

Extraction Procedure

After 0, 1, 2, and 3 weeks the low molecular weight products were extracted from the films. At each time period three 100-mg pieces of polymer were removed from the abiotic and biotic media for the extraction. Each film piece was put into 1 mL of diethyl ether for 1 h to extract the low molecular weight products. At the same time intervals the water soluble products were extracted from the mineral medium. ENV+ solid phase extraction (SPE) columns (100 mg) from Sorbent AB were used to extract the products from the buffer solution. The column was first activated with 1 mL of methanol and then equilibrated with 1 mL of water where the pH was adjusted to 2 by adding HCl. The pH of the mineral medium with the degradation products was also adjusted to 2 before it was applied to the SPE column. After light drying of the column, the analytes retarded into the column were eluted with 1 mL of acetonitrile and analyzed with GC-MS. Triple extractions were done from the films and double extractions were done from the mineral medium.

GC-MS

The low molecular weight products were identified by a Finnigan GCQ gas chromatograph-mass spectrometer. The gas chromatograph was equipped with an RTX-5MS column. Helium was used as a carrier gas. The column was first held at 40°C for 1 min, then programmed to 250°C at 8°C/min, and finally held at 250°C for 13 min. The injector temperature was held at 225°C.

SEC

The change in molecular weight during the inoculation was analyzed by SEC. The SEC instrument was equipped with a Waters 6000A pump, a refractive index detector, a PL-EMD 960 light scattering evaporative detector, and two PL gel 10-μm mixed-B columns (300 $\times$ 7.5 mm) from Waters. Dimethylformamide was used as the mobile phase. The flow rate was 1 mL/min. Polyethylene oxide standards in the molecular weight range of 10,600–645,600 g/mol were used for cal-

ibration. The molecular weight of three different samples was analyzed after each time, and the given molecular weight is an average of these values.

SEM

The surface structures of the films after culture were observed with a Jeol scanning electron microscope (model JSM-5400) using an acceleration voltage of 15 kV. The samples were gold-palladium sputtered with a Denton Vacuum Desk II cold sputter etch unit for 2×30 s.

DSC

The melting behavior of the samples was studied using a Mettler Toledo DSC 820 Calorimeter at a heating rate of 10°C/min in a nitrogen atmosphere. The heat of fusion and melting temperature were given for the first and second scans. The degree of crystallinity was calculated from the first scan to eliminate the effects of degradation during the first heating. The reference value for the heat of fusion in calculating the crystallinity was 93.6 J/g. The apparatus was calibrated with indium standards. Triplicate samples were analyzed after each time interval.

RESULTS AND DISCUSSION

Low Molecular Weight Lactic Acid Derivatives Extracted from Films

Figures 1 and 2 show chromatograms obtained after extractions from unaged films and films aged in abiotic and biotic media. Only the beginning of each run is shown to more clearly show the changing amounts of the main products. The area with the trimer, tetramer, and pentamer peaks is not shown, because the concentrations of these products were very low and remained almost constant. Lactic acid, lactoyl lactic acid, lactide, and small amounts of trimer, tetramer, and pentamer were present in the unaged films used for the 1 series. During the aging in the sterile mineral medium the amount of lactic acid in the a-1 films increased rapidly due to formation of new lactic acid by abiotic hydrolysis. At the same time the amount of lactic acid in the b-1 films remained almost constant. Because new lactic acid is formed through abiotic hydrolysis even in the biotic environment, the constant amount implies that the lactic acid assimilation proceeds at the same rate as new lactic acid is formed. The amount of lactoyl lactic acid decreased in both the b-1 and a-1 films, but the decrease was much faster in the b-1 films. After 3 weeks all lactoyl lactic acid had been removed from the films aged in a biotic medium.

The films used for the 2 series were thermally aged at 80°C before they were subjected to abiotic or biotic environments. This thermal treatment removed lactic acid and lactoyl lactic acid from the films and decreased the amount of lactide. However, during the aging in sterile and biotic mineral media new lactic acid and lactoyl lactic acid were formed due to abiotic hydrolysis. Opposite of the 1 series, the amount of lactic acid was almost similar in the b-2 and a-2 films. The amount of lactoyl lactic acid was slightly higher in the a-2 films compared to the b-2 films. The amount of lactide decreased somewhat in all cases (i.e., in a-1, b-1, a-2, and b-2 films due to hydrolysis or solvation into the mineral medium). The decrease was slightly larger in the films aged in the biotic medium.

A new product, ethyl ester of lactoyl lactic acid, was formed during the aging in the biotic medium. Traces of the ester could be detected already after the first week and the amount increased with prolonged aging time. In accordance with the other results a larger amount of ethyl ester of lactoyl lactic acid was formed in b-1 films than in b-2 films. Ethyl ester of lactoyl lactic acid cannot be formed by abiotic hydrolysis and it was absent in the abiotic chromatograms. Figure 3 shows the relative amounts of lactide, lactic acid, lactoyl lactic acid, and ethyl ester of lactoyl lactic acid for all series as a function of aging time.

Low Molecular Weight Products Extracted from Mineral Medium

Figure 4 shows the products extracted from the b-1 and a-1 mineral media after 7 days. Acetic acid and propanoic acid were extracted from the mineral medium of both biotic series. The amount of acetic acid was large in both series, but more propanoic acid was extracted from the b-1 series than from the b-2 series. No products were detected in the extractions from the abiotic mineral media. After 14 days acetic and propanoic acid were no longer detected due to further assimilation.

The acetic and propanoic acid detected in the biotic mineral medium are well-known fermentation products formed by heterolactic fermenters

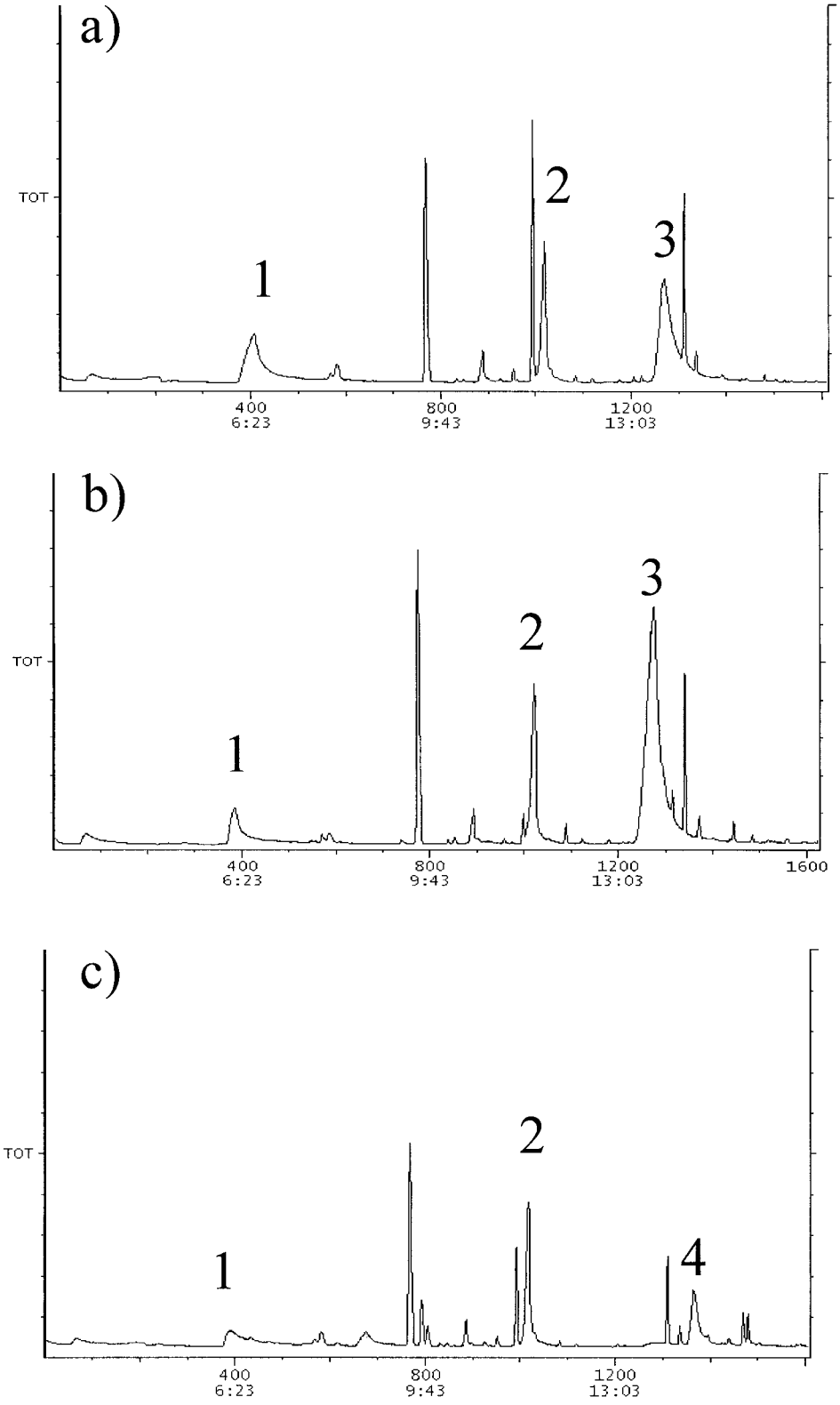

Figure 1 The GC-MS chromatograms after extractions from the films of the 1 series: (a) unaged PLLA, (b) after 21 days in sterile medium, and (c) after 21 days in biotic medium. Peak 1 is lactic acid, peak 2 is lactide, peak 3 is lactoyl lactic acid, and peak 4 is ethyl ester of lactoyl lactic acid.

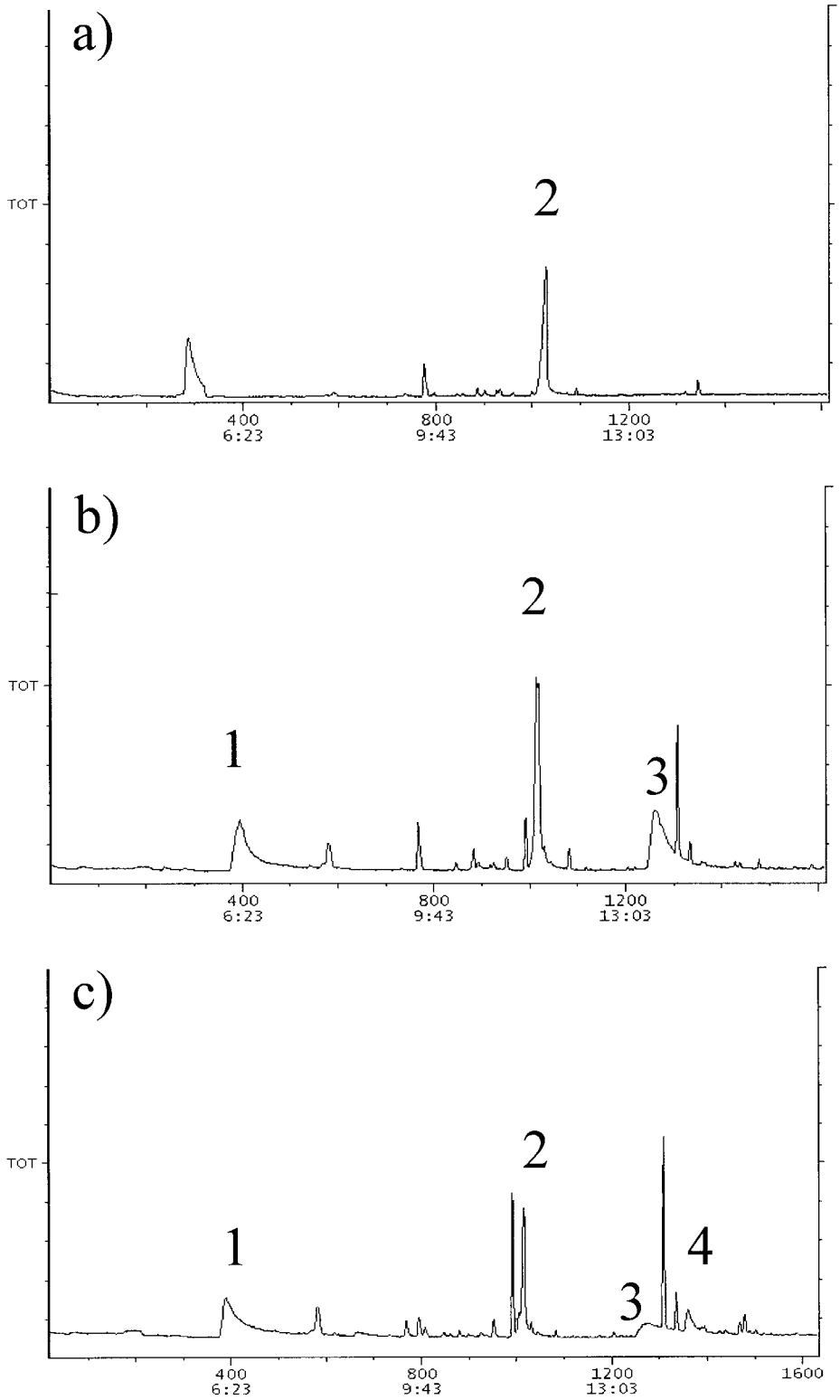

Figure 2 The GC-MS chromatograms after extraction from the films of the 2 series after (a) 7 days at 80°C, (b) 21 days in sterile medium, and (c) 21 in biotic medium. Peak 1 is lactic acid, peak 2 is lactide, peak 3 is lactoyl lactic acid, and peak 4 is ethyl ester of lactoyl lactic acid.

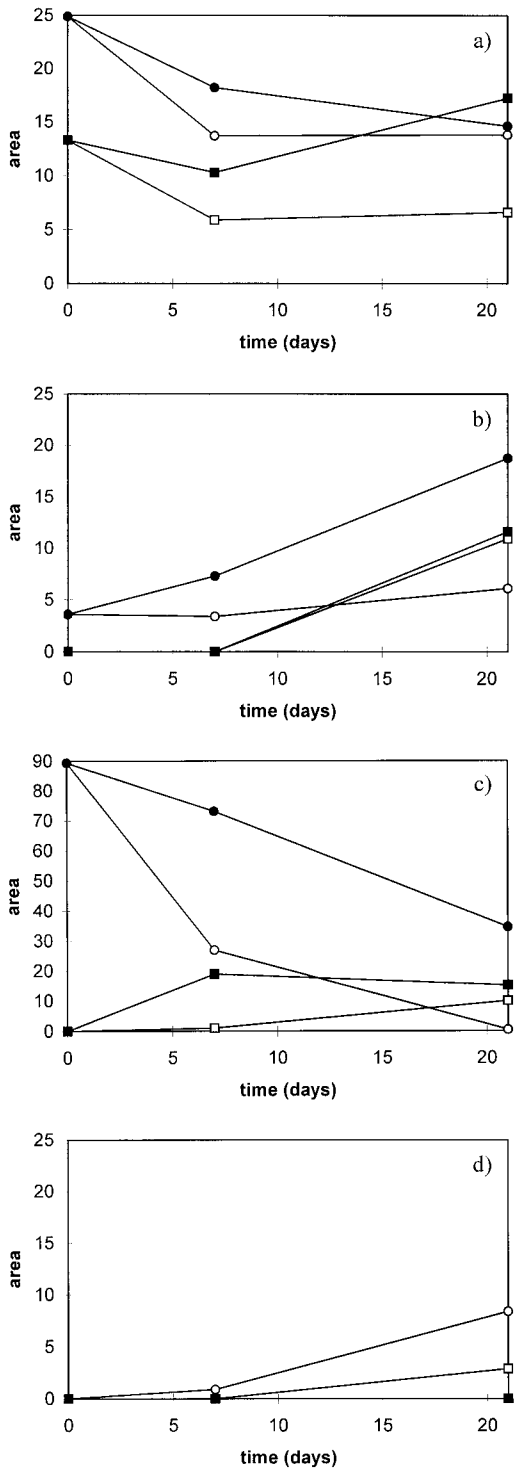

Figure 3 The relative areas of (a) lactide, (b) lactic acid, (c) lactoyl lactic acid, and (d) ethyl ester of lactoyl lactic acid as a function of degradation time for the 1 and 2 series. (○) b-1, (●) a-1, (□) b-2, and (■) a-2.

and mixed acid fermenters, for example. Acetic, butanoic, and pentanoic acid were detected earlier after aging of poly(3HB-*co*-3HV) in the presence of *Aspergillus fumigatus* at 25°C.[22,23] Other products detected in the biotic medium were C_4-C_4 dimer, C_4-C_5 dimer, C_5-C_4 dimer, and C_5-C_5 dimer. During the abiotic hydrolysis at 60°C crotonic acid, 2-pentenoic acid, 3-hydroxybutyric acid, 3-hydroxyvaleric acid, C_4-C_4 dimer, C_4-C_5 dimer, C_5-C_4 dimer, and C_5-C_5 dimer were formed.

Molecular Weight Changes

Figure 5 shows the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (H) for both series. The M_n and M_w of the b-1 films decreased about 25 and 45%, respectively, during 21 days. During the same time the molecular weight remained almost constant for the a-1 films. The polydispersity decreased for the b-1 and a-1 samples. Originally there was a small shoulder on the low molecular weight side of the molecular weight distribution curves. This shoulder was still seen in a-1 films after 21 days in the sterile mineral medium, but in the b-1 films the shoulder melted into the main curve and could no longer be detected after 14 days in the biotic medium. The molecular weight of the thermally treated samples used for the a-2 and b-2 series was originally lower and the polydispersity larger than for the a-1 and b-1 series. The thermal treatment decreased the degradability and almost no difference could be detected between the samples aged in abiotic and biotic media. This agrees with the analysis of the low molecular weight products.

Even though the M_n for the a-2 and b-2 films was originally only 60% of the M_n for the a-1 and b-1 films, after 14 days of inoculation with microorganisms the M_n for the b-1 films had decreased to the same level and after 21 days the M_n for the b-1 films was lower than the M_n for the b-2 films. The M_w showed similar behavior. In the abiotic hydrolysis the M_n and M_w of the a-2 films remained lower than the M_n and M_w for the a-1 films.

Thermal Analysis

Tables I and II show the changes in the degree of crystallinity and melting temperature for the 1 and 2 series, respectively. The original degree of crystallinity of the films used for the 2 series was about 2% higher because of the thermal treatment and removal of the low molecular weight products. During the aging the degree of crystal-

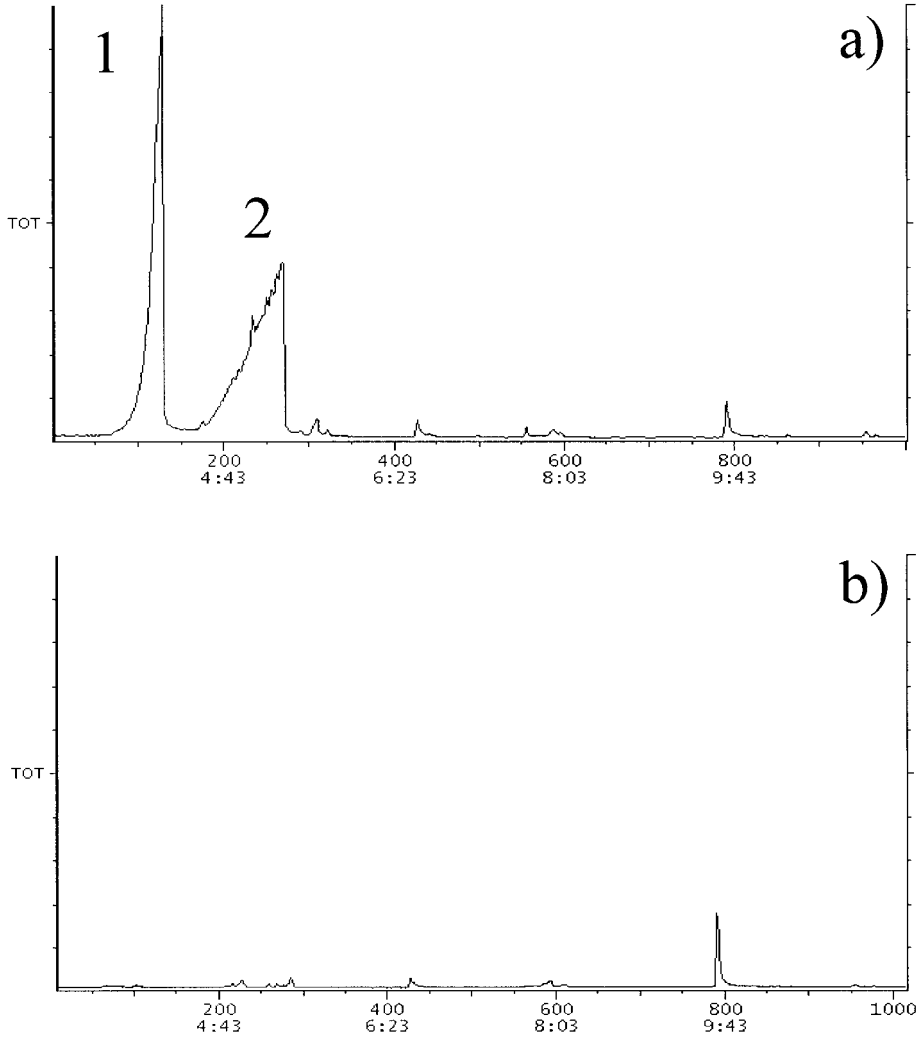

Figure 4 Low molecular weight products extracted from the mineral medium after 7 days for the (a) b-1 series and (b) a-1 series. Peak 1 is acetic acid and peak 2 is propanoic acid.

linity increased for the biotically and abiotically aged films. After 14 days the increase in the degree of crystallinity was higher for the b-1 and b-2 films than for the a-1 and a-2 films. During prolonged aging the degree of crystallinity decreased slightly in the biotic medium while it remained constant or increased further in the abiotic medium. It is well known that the degree of crystallinity increases during abiotic hydrolysis because of preferential hydrolysis of the amorphous regions. The initial increase in the degree of crystallinity in the biotic medium is explained by the preferential abiotic and biotic degradation of the amorphous regions. However, on prolonged aging the microorganisms may also attack the crystalline regions and the degree of crystallinity may decrease. The melting temperature decreased some degrees for the b-1 films aged in the biotic medium while it remained almost constant for a-1, a-2, and b-2 films.

Changes on Surface of Films

Figures 6 and 7 show scanning electron micrographs of the surfaces of the films from the 1 and 2 series, respectively. After 14 days in the biotic environment colonization of bacteria on the surface of the b-1 films was seen [Fig. 6(a)]. At 21 days of incubation the number of bacteria cells on the surface of the films had increased and the surface looked whitish [Fig. 6(b)]. The surface of the a-1 films remained smooth and no difference

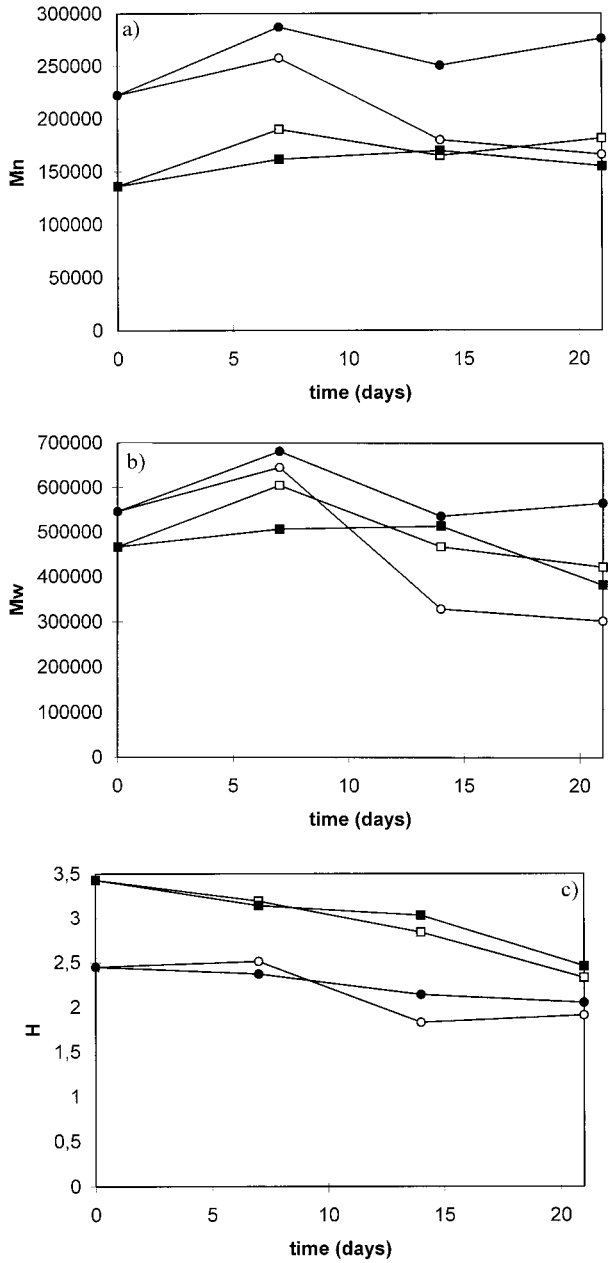

Figure 5 The changes in (a) number average molecular weight (M_n), (b) weight average molecular weight (M_w), and (c) polydispersity (H) as a function of degradation time in biotic and abiotic environments. (○) b-1, (●) a-1, (□) b-2, and (■) a-2.

could be observed compared to the unaged PLLA film. As seen in Figure 7, the bacteria also grew on the surface of the b-2 films, but the number was lower compared to the b-1 films and the bacteria seemed "looser" and did not penetrate the films. The colonization also increased between 14 and 21 days in b-2 films. Figure 8 shows fungi growing on the surface of the b-1 films after 21 days.

The analysis of the low molecular weight products implied that the absence of lactic and lactoyl lactic acid in the thermally aged films used for the 2 series made it more difficult for the microorganisms to attach to the surface of the films. This was confirmed by the SEM micrographs. The easily assimilated lactic acid and lactoyl lactic acid in the b-1 films enabled the initial attachment of the microorganisms on the b-1 films by affording nutrients to initiate multiplication of cells and a favorable pH. We believe that the difference in the degradation rate was mainly caused by the presence or absence of the low molecular weight products, because the slightly lower crystallinity (2%) of the b-1 films should not have such a large effect on the degradability and the higher molecular weight of the b-1 films should decrease and not increase the biodegradation rate.

In earlier studies we showed the positive effect of low molecular weight products and modification by surfactants on the biodegradation rate of polyethylene (PE).[24–27] When the hydrophilicity of the PE surface was increased by the surfactants, it facilitated the adherence of the microorganisms at the surface of the PE and increased the biodegradation rate.[26] In light microscopy a larger number of bacteria were observed on the surface of the low-density PE (LDPE) with Tween 80 incubated with *Pseudomonas aeruginosa* for 60 days than on the surface of pure LDPE.[27] The biodegradation rate decreased for high-density PE (HDPE) when the films were deprived of most of the low molecular weight compounds.[28] The low molecular weight oxidation products of PE were assimilated by microorganisms.[29,30]

Biotic and Abiotic Degradation Products of PLA

Different techniques including GC-MS,[6,31] HPLC,[32,33] capillary zone electrophoresis (CZE),[34] and enzymatic assays[11–13,35,36] were used to detect hydrolysis products of PLA and its copolymers. All of these techniques have advantages and limitations. GC-MS offers the best tools for identification of the products; however, it has to be combined with an effective extraction method and the analysis is limited to relatively volatile compounds. HPLC and CZE can detect even higher oligomers, but the identification of the products is difficult and can only be done by comparison to standard compounds. The enzymatic assays are limited to the detection of L-lactic acid and do not

Table I Melting Temperature (T_m), Heat of Fusion (ΔH), and Degree of Crystallinity (W_c) for Biotically and Abiotically Aged Samples of 1 Series as Measured by DSC

1 Series	ΔH_f^{1st} (J/g)	ΔH_f^{2nd} (J/g)	W_{Cr} (%)	T_m^{1st} (°C)	T_m^{2nd} (°C)
0 days	47.0	47.6	50.2	174.5	175.1
Biotic					
14 days	53.7	50.6	57.4	173.0	172.7
21 days	52.0	50.1	55.6	171.8	171.9
Abiotic					
14 days	50.8	50.3	54.3	173.8	174.0
21 days	50.7	50.5	54.2	174.6	174.6

give any information about other degradation products.

Lactic acid, lactoyl lactic acid, and higher oligomers were identified after hydrolysis of PLA and its copolymers. Oligomers up to nonamer were detected with CZE.[34] GC-MS analysis showed an increasing amount of lactic acid with increased hydrolysis time and finally total hydrolysis to lactic acid.[6] The weight loss started before the lactic acid formation due to release of soluble oligomers. The ester bond in the lactoyl lactic acid dimer was more stable than the ester bond in the higher oligomers, resulting in the preferential formation of the dimer.[34]

When PLA50 plates and films were aged in phosphate buffer at 37°C, the concentration of L-lactic acid in the aging medium was very low until around weeks 8–11.[11–13] In the hydrolysis of crystalline poly(L-lactic acid), lactic acid was not detected until week 31. The larger devices degraded faster and released more lactic acid. The release rate of lactic acid during hydrolysis of polydispersed poly(L-lactic acid) increased as the low molecular weight fractions increased.[35] During hydrolysis more lactic acid was released at pH 9.8 than at a lower pH.[36] In conclusion, lactic acid is the ultimate hydrolysis product of PLA and insoluble and soluble oligomers are intermediate degradation products.

Torres et al. subjected the intermediate and ultimate hydrolysis products of PLA to a filamentous fungus, *Fusarium moniliforme,* and a bacterium, *Pseudomonas putida.*[15] HPLC analysis showed that DL- and L-lactic acids and LL dimer were rapidly assimilated by both microorganisms, whereas the assimilation of the DD dimer proceeded slowly. Higher racemic oligomers were slowly assimilated, but higher LL oligomers were biostable that was probably due to the crystallinity. A synergistic effect was observed when both microorganisms were present in the same culture medium. In another study the microbial degradation of poly(L-lactic acid) oligomers of 260–2880 g/mol molecular weight was investigated.[37] Lactic acid was microbially metabolized in the biotic environment. Water soluble or dispersible oligomers (260–550 g/mol) were biodegraded at 25 and 58°C, while larger crystalline, hydrophobic oligomers biodegraded only at 58°C. The degree of biodegradation was measured by the aquatic aer-

Table II Melting Temperature (T_m), Heat of Fusion (ΔH), and Degree of Crystallinity (W_c) for Biotically and Abiotically Aged Samples of 2 Series as Measured by DSC

1 Series	ΔH_f^{1st} (J/g)	ΔH_f^{2nd} (J/g)	W_{Cr} (%)	T_m^{1st} (°C)	T_m^{2nd} (°C)
0 days	48.8	50.9	52.1	174.3	174.0
Biotic					
14 days	55.3	55.3	59.1	174.5	173.5
21 days	53.2	54.6	56.8	173.3	172.5
Abiotic					
14 days	52.3	53.1	55.9	174.7	174.1
21 days	54.9	54.7	58.7	174.9	173.5

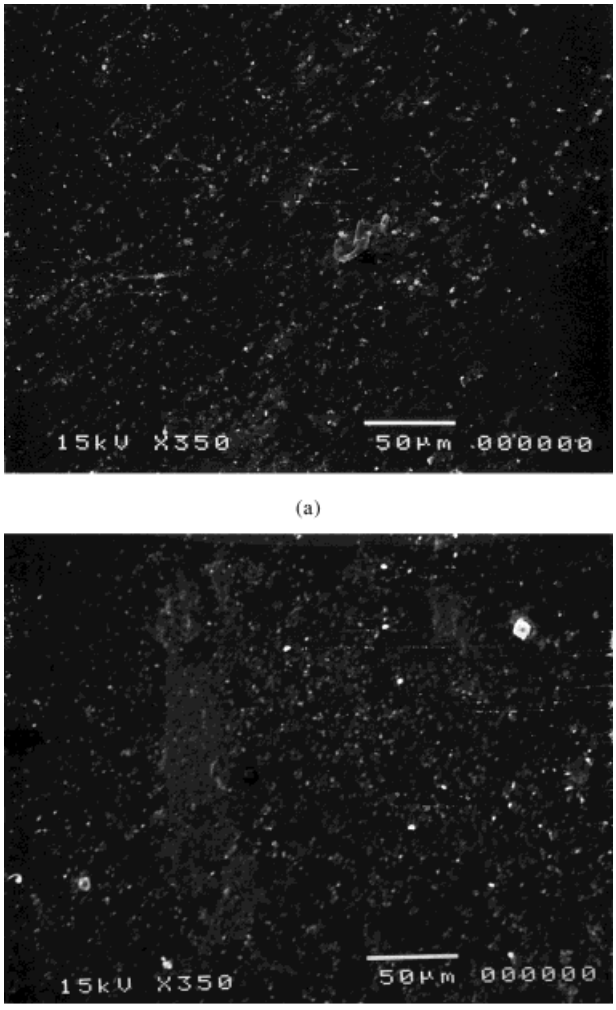

Figure 6 SEM micrographs of the surface of b-1 films after (a) 14 and (b) 21 days of aging.

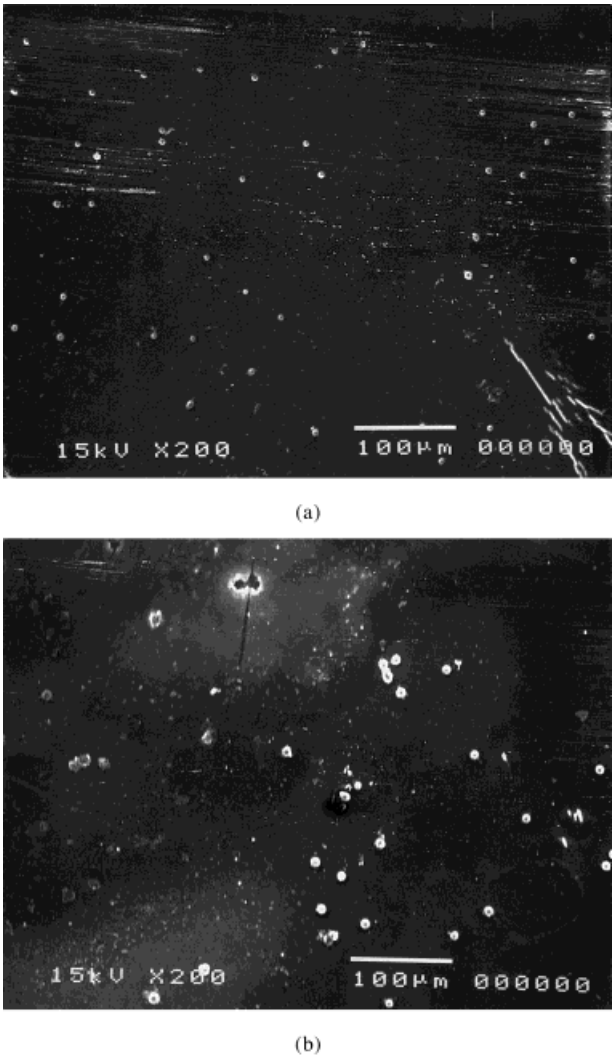

Figure 7 SEM micrographs of the surface of the b-2 films after (a) 14 and (b) 21 days of aging.

obic biodegradation test. However, this test is limited because it measures only the amount of CO_2 released, but it is not able to detect other biodegradation reactions taking place. In the present study acetic acid, propanoic acid, and ethyl ester of lactoyl lactic acid were identified as degradation products of PLA in a biotic medium. Lactic acid and lactoyl lactic acid were assimilated from the films aged in a biotic medium.

Thermal degradation of PLA results in the formation of cyclic oligomers through intramolecular transesterification reactions.[38–40] In addition to the homologous series of cyclic oligomers a second less abundant homologous series was identified either as linear oligomers or oligomers with acrylic end groups.[38,41] Acetaldehyde and carbon dioxide were formed by fragmentation reactions;

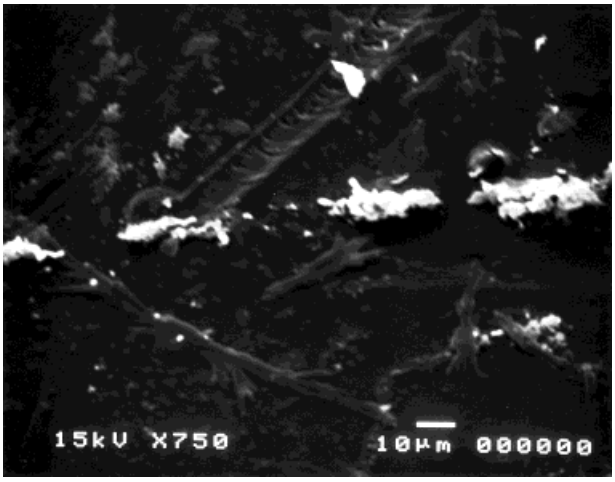

Figure 8 SEM micrographs showing the growth of fungi at the surface of b-1 films after 21 days of aging.

Table III Summary of Abiotic and Biotic Degradation Products of PLA

Hydrolysis[6,11,32,34]	(Bio)degradation	Pyrolysis[38–41]
Lactic acid	Acetic acid	Lactide
Lactoyl lactic acid	Propanoic acid	Cyclic oligomers
Lactic acid oligomers	Ethyl ester of lactoyl lactic acid	Carbon dioxide
		Acetaldehyde
		Acrylic acid
		Linear oligomers with acrylic end groups

acrylic acid and oligomers with acrylic end groups were formed by cis elimination.[40] Table III gives a summary of the PLA degradation products.

CONCLUSIONS

New degradation products (e.g., ethyl ester of lactoyl lactic acid, propanoic acid, and acetic acid) were formed during aging in a biotic medium. These products were not formed during the aging in the corresponding abiotic mineral medium. The presence of easily assimilated lactic acid and lactoyl lactic acid increased the degradation rate of PLA in the biotic media. The b-1 films, which initially contained some lactic acid and lactoyl lactic acid, decreased in molecular weight during 3 weeks in the biotic medium. The molecular weight of the b-2 films without these low molecular weight products was originally lower but remained almost constant during the experiment. Microorganisms rapidly colonized the surface and assimilated lactic acid and lactoyl lactic acid from the b-1 films. Less colonization was seen by SEM on the b-2 films without lactic and lactoyl lactic acid, confirming that the presence of the easily assimilated lactic acid and lactoyl lactic acid in the films was important in enabling the initial growth of microorganisms on the film surfaces.

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