Py-GC/MS an Effective Technique to Characterizing of Degradation Mechanism of Poly (L-lactide) in the Different Environment

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Received 30 December 1999; accepted 21 March 2000

ABSTRACT: The biotic and abiotic degradation of poly (L-lactide) (PLLA) has been studied with pyrolysis gas chromatography mass spectrometry (Py-GC-MS). A mixed culture of compost micro-organisms was used as the biotic medium. Size-exclusion chromatography (SEC), gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were utilized to monitor the degradation and degradation mechanism. Differences in pH, molecular weight, surface structure, and degradation mechanisms were noted between sample aged in biotic and abiotic medium. Using fractionated Py-GC-MS at 400 and 500°C, acetaldehyde, acrylic acid, lactoyl acrylic acid, two lactide isomers, and cyclic oligomers up to the pentamer were identified as thermal decomposition products of PLA as well as some other not completely identified products. The ratio of meso-lactide to L-lactide was lower in the sample aged in the biotic media than the abiotic media. This is a result of the preference of the micro-organisms for L-form of lactic acid and lactoyl lactic acid rather than the D-form that in turn influences the formation and the amounts of meso and D,L-lactide during the pyrolysis. Based on SEM micrographs, it was shown that degradation in the biotic medium proceeded mainly via a surface erosion mechanism, whereas bulk erosion was the predominant degradation mechanism in the abiotic medium. The SEC and Py-GC-MS data indicate that degradation was faster in the biotic than in the abiotic sample. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2369–2378, 2000

Key words: poly (L-lactide); meso-lactide; biodegradation; Py-GC-MS

INTRODUCTION

In recent years, much attention has been focused on biodegradable and biocompatible polymers, particularly from an ecological viewpoint. Polylactides (PLAs) are synthetic polymers that are known to be biocompatible and biodegradable. They are being used in biomedical applications such as absorbable sutures, controlled drug delivery, implants, and vascular prosthesis. It is also of interest to utilize PLA as packaging plastics that will biodegrade upon disposal.

PLA undergoes enzymatic or nonenzymatic hydrolysis when it is exposed to an aqueous environment. The hydrolysis of the ester groups is autocatalyzed by carboxylic acid end groups.[1,2]

Several factors affect the rate of hydrolysis of PLA, for example, temperature,[1] pH,[2] water permeability and solubility,[2] additives,[3] copolymerization,[4] initial molar mass,[5] specimen size,[6] residual monomer,[7] and degree of crystallinity.[8]

Nonenzymatic hydrolytic degradation of massive specimens of P(D,L)LA was studied by Grizzi et al.[6] They showed the effect of specimen size on the rate of degradation of P(D,L)LA. Compres-

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Contract grant sponsor: the Swedish Research Council for Engineering Sciences (TFR; contract grant number: 281-98-664.

Journal of Applied Polymer Science, Vol. 78, 2369–2378 (2000)

sion-molded plates, millimetric beads, microspheres, and cast films were made from the same batch of polymer and allowed to age in iso-osmolar phosphate buffer at pH 7.4 and 37°C. They showed that the plates and beads degrade more rapidly by bulk disintegration than the films and microspheres that degrade homogeneously by surface hydrolysis.[6] This is because the entrapment of degradation products in the center of the sample increases the concentration of carboxylic end groups.[6] Microstructure and degradation products also have a great effect on the diffusion of water into the polymer matrix. The diffusion coefficients of the soluble oligomers formed during the degradation process depend on factors such as molar mass and degree of matrix swelling.[9]

The hydrolytic degradation of PLA has been widely studied, although there have been only few studies of the biodegradation of PLA. Reeve et al.[10] studied various PLA stereocopolymers from mixtures of (D)- and (L)-lactide, which were exposed to proteinase K, and found that proteinase K degraded preferentially (L)-PLA relative than (D)-PLA.[10] It has been demonstrated that the easily assimilated lactic acid and lactoyl lactic acid formed during the degradation process promote the bio-degradation of PLA.[11] We have developed techniques to analyze and identify the hydrolysis products from aliphatic polyesters.[12,13]

Despite the extensive data reported in the literature, some aspects of PLLA biodegradation are, however, still not completely understood. Among these is the influence of environment on the polymer structure. There is, therefore, still some space for investigating it.

The objective is to show the use of Py-GC/MS in the characterization of PLLA. PLLA was degraded in biotic and abiotic media. A mixed culture of compost microorganisms was chosen as the biotic environment to include both fungi and bacteria. Size-exclusion chromatography (SEC), pyrolysis gas chromatography-mass spectrometry (Py-GC-MS), gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to monitor the degradation.

EXPERIMENTAL

Materials

The material was poly (L-lactide) made by Neste Ltd, Finland, and was used in the form of small granules. The ratio of L-lactide to D-lactide was 95 : 5.

Degradation Procedure

The degradation was performed in 2000-mL Fernbach culture flasks containing 800 mL of a salt medium and approximately 3 g of polymer sample in each flask. The salt medium contained the following per liter: 5.0 g $(NH4)_2C_4H_4O_6$, 1.0 g KH_2PO_4, 1.0 g $MgSO_4$. $7H_2O$, 0.8 mlLof a 1% solution of $FeCl_3 \cdot 6H_2O$, and 8 mL of a 1% solution of $ZnSO_4 \cdot 7H_2O$. The pH of the medium was adjusted to pH 5.5 by the addition of HCl. A mixed inoculum of micro-organisms from compost was added to the biotic samples. Five milliliters of 0.02% (w/w) NaN_3 was added to the abiotic medium in order to prevent the growth of microorganisms. NaN_3 was added after each sampling. The samples were kept at 30°C and 60 rpm.

Extraction Procedure

The low molecular weight products were extracted by diethyl ether from the surfaces of the granules of the biotic and abiotic samples after 11 weeks and from the original sample. About 70 mg of each sample was extracted by 0.2 mL diethyl ether for 1 h.

ANALYTICAL METHODS

Pyrolysis Gas Chromatography-Mass spectrometry (Py-GC-MS)

The pyrolysis was performed using a Pyrola® filament plus pyrolyzer (PyroLab AB, Sweden) with a Pt-filament. About 0.5 mg of each sample was dissolved in 0.2 mL chloroform. Two microliters of this solution was pyrolyzed. Fractionated pyrolysis was performed for 2 s at 400 and 500°C in a sequence to separate different thermo-labile fractions of the polymer.

Pyrolysis products were analyzed directly with a Perkin-Elmer 8500 model gas chromatography coupled to an ITD mass spectrometer (Electron Ionization (EI) or Chemical Ionization (CI) mode). Methane was used as CI reagent gas.

Chemical ionization (CI) is a soft ionization technique that minimizes the possibility of mixing the thermal oligomer fragments with fragment ions formed in the ionizing step.[14] The column used for the analysis was a DB-5 ms (30 m $\times$ 0.32 mm i.d.). The GC oven was programmed from 40 to 300°C at 10°C/min then held for 5 min

at 300°C. The injector temperature was 275°C. Helium was used as carrier gas.

Most products were identified by comparison with literature mass spectra or with pure standard substances.

Size-Exclusion Chromatography (SEC)

The changes in molar mass during the degradation process were determined with a chromatography system consisting of a Waters 6000A pump, a Waters 717 Plus Autosampler, and a PL-ELS 1000 light-scattering evaporative detector (Polymer Laboratories). The instrument was equipped with two PL gel 10 μm mixed-B column (300 $\times$ 7.5 mm) from Polymer Laboratories. Chloroform was used as mobile phase at room temperature. The flow rate was 1 mL/min. A polystyrene standard in the 1500-2 $\times$ 10^6 g/mol molecular weight range was used for calibration.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed on a Perkin-Elmer model Spectrum 2000 equipped with a Golden Gate ATR holder with a diamond FTIR crystal (P/N 10500 series from Graseby Spectra). Surfaces were analyzed in the attenuated total reflection mode (ATR). Each sample was analyzed three times.

Gas Chromatography-Mass Spectrometry (GC-MS)

Low molecular weight products were analyzed by a Finnigan GCQ gas chromatograph-mass spectrometer. The column was a CP-Sil 8 CB low bleed, ms (30 m $\times$ 0.25 mm i.d.). The column temperature was held for 5 min at 40°C, and then programmed to 250° at 10°C/min and held at 250°C for 10 min. The injector was in the splitless mode at 250°C. Helium was used as carrier gas.

pH Measuring

The pH values were measured at ambient temperature, with a digital pH-meter (PHTestr 3™ with ATC) with 0.01 pH resolution and $\pm$0.02 pH accuracy.

Scanning Electron Microscopy (SEM)

A JEOL scanning microscope model JSM-5400 using an acceleration voltage of 15 kV monitored the surface changes of the samples during degradation. Samples were mounted on metal stubs and sputter coated with gold-palladium (Denton Vacuum Desc II cold sputter etch unit) for 2 $\times$ 30 s.

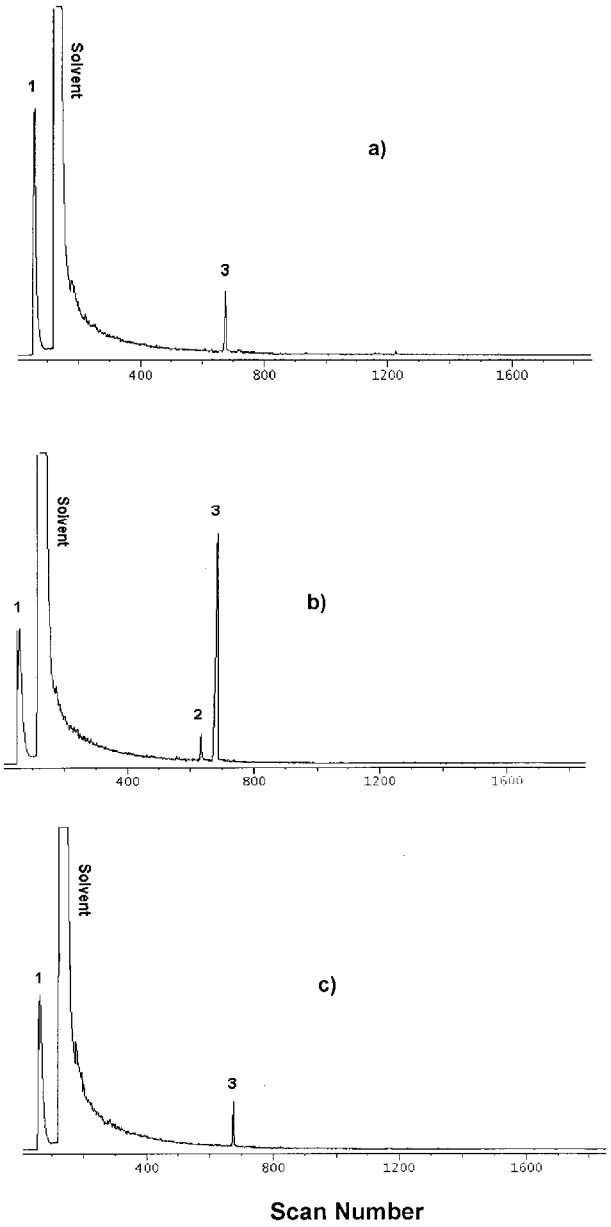

Figure 1 Fractionating Py-GC-MS at 400°C of: (a) unaged PLA, (b) PLA aged in biotic, and (c) PLA aged in abiotic media for 11 weeks. Peak assignment: 1 = acetaldehyde, 2 = meso-lactide, 3 = D,L-lactide.

RESULTS AND DISCUSSION

Pyrolysis-GC-MS

Figure 1(a)–(c) and Figure 2(a)–(c) show the results of fractionating Py-GC-MS at 400 and

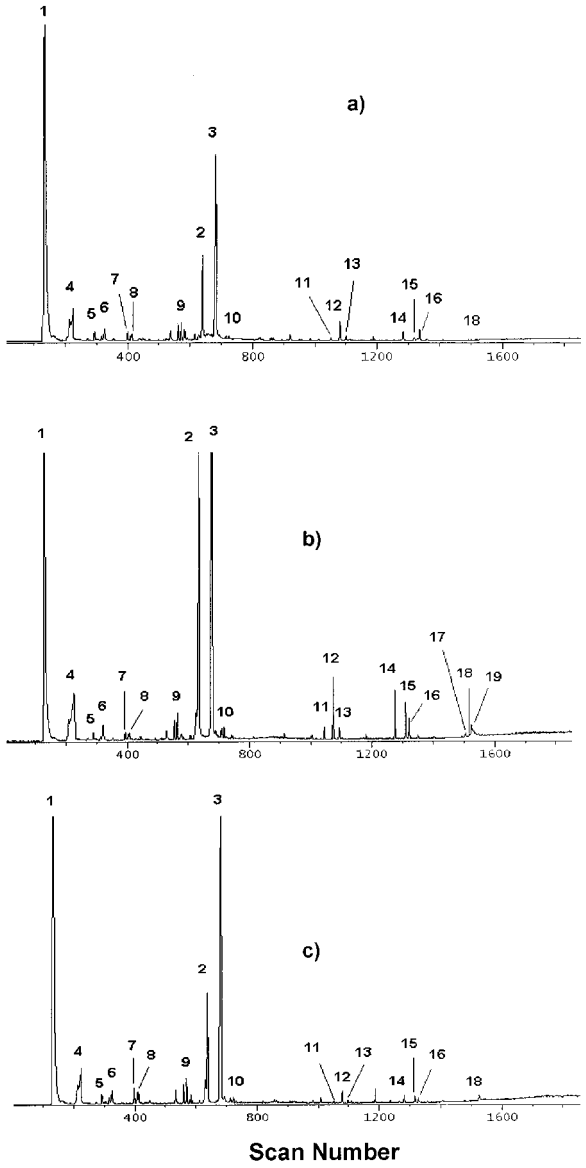

Figure 2 Fractionating Py-GC-MS at 500°C of: (a) unaged PLA, (b) PLA aged in biotic, and (c) PLA aged in abiotic media for 11 weeks, for peak assignment (see Table I).

500°C, respectively, of unaged PLA and PLA aged in the biotic and abiotic media. Table I shows the list of products formed during the pyrolysis of PLA samples at 400 and 500°C. Acetaldehyde, acrylic acid, 2,3-pentanedione, lactoyl acrylic acid, lactide, and cyclic oligomers up to pentamers were among the compounds that could be identified. A number of incompletely identified products were also detected. Among them were peak 6 in Figure 2(a)–(c) with *m/z* 27, 43,57, 101, 129, peak 7 with *m/z* 26, 42, 56, 126, peak 8 with *m/z* 26, 43, 57, 72, 85, 110, 128. Peak 10 with *m/z* 28, 43, 56, 128, and 157, is probably a compound with the structure $CH_3CH_2COCH(CH_3)COCOCH_3$ (4-methyl-heptane-2,3,5-trione) that can be formed by reaction between the dimer of methyl ketene and acetaldehyde. Figure 3 shows the mass spectrum of peak 10 (EI mode).

At pyrolysis temperature of 400°C, the amount of lactide increased with increasing degradation time. The amount of lactide was higher in the biotic sample than in the original and abiotic samples. This is due to the higher degradation rate in the biotic sample, and agrees with the SEC results that showed a lower M_n value in the biotic sample. This lower M_n value is evidence of the presence of a larger number of short chains in the biotic sample. During the pyrolysis, the formation of cyclic compounds such as lactide from the short chains polymer is probably energetically more favorable than their formation from the longer chains.

There was one lactide peak in the spectra for original and abiotic samples, but in the biotic sample there were two peaks with identical mass spectra corresponding to the lactide structure. The ratio of peak 2 to peak 3 in the biotic sample is 1 : 15. According to the literature,[15] the first peak represents the meso-lactide, while the second peak is the (L) or (D)-lactide.

At a pyrolysis temperature of 500°C, the amount of lactide in the biotic sample was also higher than the amounts in the original and abiotic samples. At 500°C there were, however, two peaks with identical mass spectra corresponding to the lactide in all the samples, although with different ratios [Fig. 2(a)–(c)]. Peak 2 corresponding to the meso-lactide shows a higher concentration in the biotic sample than in the abiotic sample and the ratio of peak 2 (corresponding to meso-lactide) to peak 3 (corresponding to L-lactide) was 1 : 4.7 for the abiotic sample and 1 : 2.4 for the biotic sample. An explanation for this could be that micro-organisms in the biotic medium prefer the L-form of lactic acid and lactoyl lactic acid rather than the D-form, which influences the formation and the amounts of meso- and (D) or (L)-lactide during the pyrolysis.

Kopinke et. al.[15,16] have studied the thermal decomposition of PLA by Py-GC-MS. In agreement with our results, they have found acrylic acid, cyclic oligomers, and acetaldehyde as thermal decomposition products. In addition, they observed carbon monoxide and carbon dioxide as decomposition products. We noticed the presence of carbon monoxide and carbon dioxide in the pyrogram at 400°C, but it was difficult to separate

Table I List of Products Formed During the Fractionating Py-GC-MS at 400°C and 500°C

Peak Number	Compounds	Ion[a] CI (m/z)	Ions[b] EI (m/z)	400°C	500°C
1	acetaldehyde[c]	45	43, **45**	+	+
2	meso-lactide[c]	145	27, 43, **56,** 73, 89, 145	+	+
3	D,L-lactide[c]	145	27, 43, **56,** 73, 89, 145	+	+
4	2-propenoic acid[c] (acrylic acid)	73	**26,** 45, 55, 73		+
5	2,3-pentanedione[c]	100	27, **43,** 57, 100		+
6	unknown	129	27, **43,** 57, 101, 129		+
7	unknown	126	**26,** 42, 56, 126		+
8	unknown	128	26, **43,** 57, 72, 85, 110, 128		+
9	lactoyl acrylic acid	117	27, **43,** 56, 72, 89, 117, 131, 144		+
10	4-methyl-heptane-2,3,5-trione	157	**28,** 43, 56, 128, 157		+
11	trimer	200	28, 45, **56,** 100, 128, 200		+
12	trimer	200	28, 45, **56,** 100, 128, 200		+
13	trimer	200	28, 45, **56,** 100, 128, 200		+
14	tetramer	272	28, 45, **56,** 100, 128, 200, 272		+
15	tetramer	272	28, 45, **56,** 100, 128, 200, 272		+
16	tetramer	272	28, 45, **56,** 100, 128, 200, 272		+
17	pentamer	272[d]	28, 45, **56,** 100, 128, 200, 272		+
18	pentamer	272[d]	28, 45, **56,** 100, 128, 200, 272		+
19	pentamer	272[d]	28, 45, **56,** 100, 128, 200, 272		+

[a] Molecular ion in chemical ionisation mode.
[b] Main ions (bold types denotes base peak) in electron ionisation mode.
[c] Identified by mass spectrometry through comparison with literature mass spectra and using pure substances.
[d] Molecular ion was missing probably due to the low concentration.
+ Presence.

them from each other and to distinguish them from the carbon dioxide peak present in the pyrolysis system.

All the cyclic oligomers appear with at least two peaks [Fig. 2(a)–(c)], with almost identical mass spectra. According to Kopinke and coworkers,[15] this indicates diastereomers derived from the asymmetric C atom in the lactic acid. *cis*-Elimination and *trans*-esterification are the two main pyrolysis mechanisms for PLA. These lead to the formation of lactide and cyclic oligomers (by *trans*-esterification) and acrylic acid and acyclic oligomers (by *cis*-elimination).[15–18] In addition, some radical and nonradical reactions can also occur above 300°C, and these lead to the formation of methyl ketene, acetaldehyde, and carbon dioxide or acetaldehyde and carbon monoxide.[15,18]

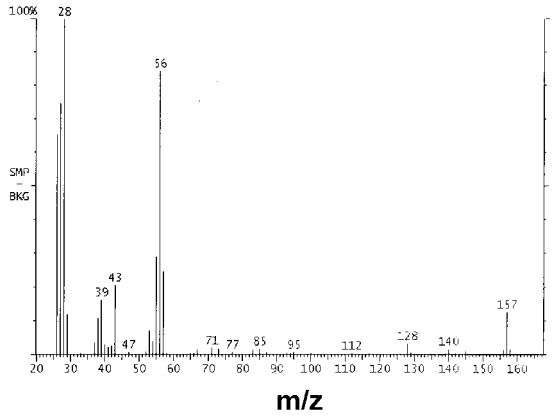

Figure 3 Electron impact (EI) mass spectrum of 4-methyl-heptane-2,3,5-trione ($CH_3CH_2COCH(CH_3)COCOCH_3$) (peak 10 in Fig. 2).

Changes in pH

Figure 4 shows the variation in the pH in the biotic and abiotic media. During the test period, the pH increased to around 9 in the biotic medium, whereas almost no pH change was detected in abiotic media.

The increase in pH together with turbidity in the biotic medium establishes the activity of microorganisms.[19] The increase in pH in the biotic medium is probably due to the assimilation of ammonium tartrate by the micro-organisms. Torres et al.[19] investigated the biodegradation of racemic PLA in the presence of micro-organisms. They have also reported the increase in pH up to 8 with time in biotic media, while no pH changes were detected in the abiotic medium.[19]

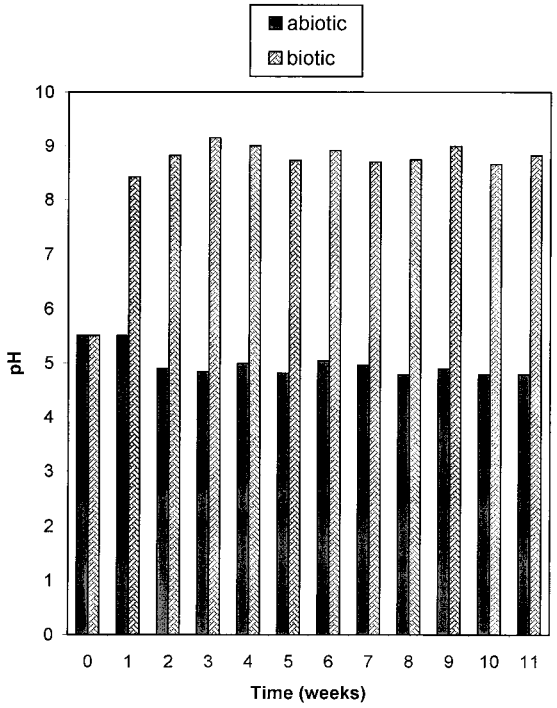

Figure 4 Changes in pH in biotic and abiotic media during 11 weeks.

Molecular Weight and Functional Group Changes

Figure 5(a)–(c) shows the changes in the weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity of PLA in the biotic and abiotic media. During the first week, both M_w and M_n decreased to almost the same extent in the biotic and abiotic samples. During the degradation M_n decreased faster than M_w in the biotic sample (92% compared to 78% of the initial value), whereas M_n and M_w decreased at almost the same rate in the abiotic sample (83% compared to 80% of the initial value). The faster decrease in M_n than in M_w in the biotic sample indicated a preferential degradation near the chain ends.[20] Furthermore, M_n decreased faster in the biotic sample than in the abiotic sample. During the first week, M_w also decreased faster in the biotic sample than in the abiotic sample, but it reached almost the same value after 11 weeks.

This confirms that the molecular weight decreases initially by chemical hydrolysis. When the molecular weight has decreased significantly, the micro-organisms assimilate the carboxylic end groups products and promote the biodegradation of PLA.

The polydispersity of the biotic sample increased from 1.92 to 3.86, whereas the polydisper-

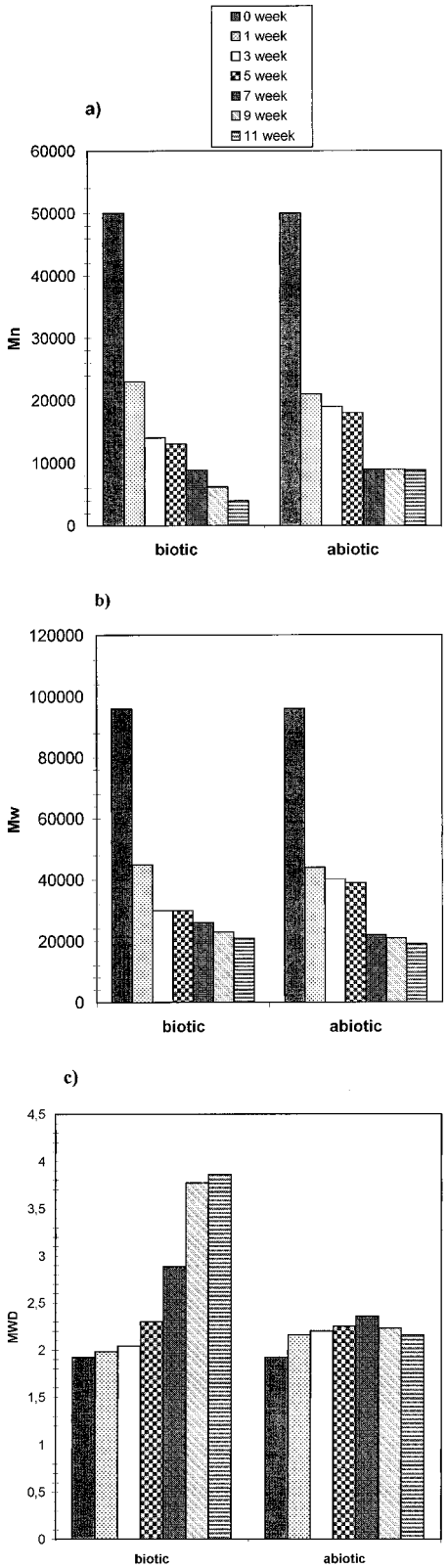

Figure 5 Changes in: (a) number-average molecular weight (M_n), (b) weight-average molecular weight (M_w), and (c) polydispersity (MWD) of samples aged in biotic and abiotic media.

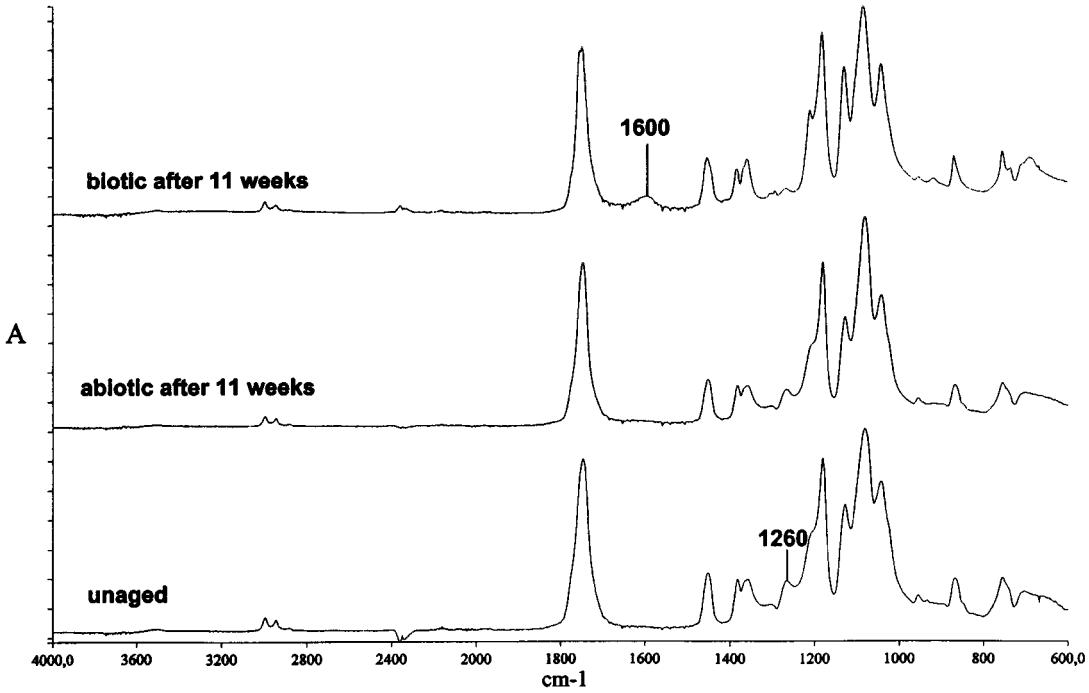

Figure 6 FTIR spectrum of unaged PLA and PLA aged for 11 weeks in biotic and abiotic media.

sity of the abiotic sample increased to 2.36 after 7 weeks, and subsequently dropped to 2.16 after 11 weeks.

Guaita et al.[20] reported that a completely random degradation process would take place if the polydispersity were close to 2. They calculated that if the polydispersity reaches a value lower than 2, then nonrandom degradation occurs and the cleavage near the center of polymer chain is favored. On the other hand, if the polydispersity reaches a value grater than 2, the cleavage near the chain ends is more possible. The apparent increase in polydispersity (to 3.86) for the biotic sample indicated that cleavage occurs mainly at the chain ends.[20,21] In the case of the abiotic samples, degradation occurred mainly randomly because the polydispersity remained closer to 2.

Figure 6 shows the FTIR spectrum of the unaged sample and of samples after 11 weeks in the biotic and abiotic media. The only apparent change is the appearance of a band at 1600 cm^{-1} corresponding to carboxylate ions in the biotic spectrum, while the band at 1260 cm^{-1} that corresponds to C—O stretch almost disappears in the spectrum of the biotic sample. The formation of carboxylate ions is due to micro-organisms, which consume lactic acid and its oligomers on the surface (one chain at a time) and leave carboxylate ions at the chain end.

Low Molecular Weight Products Extracted from the Granules

Figure 7(a)–(c) shows the GC-MS chromatograms of the low molecular weight products extracted in diethyl ether from the unaged samples and from the samples aged in biotic and abiotic media after 11 weeks. Lactic acid, 2-ethyl hexanoic acid, lactide and lactoyl lactic acid were the products that were identified in the biotic and abiotic samples and even in the original samples [Fig. 7(a)–(c)]. 2-Ethyl hexanoic acid is probably an additive that improves the adherence-lubricating layer.

The presence of lactic acid, lactide, and lactoyl lactic acid in the unaged samples can be explained by their formation during the processing. During the degradation studies the low molecular weight products can easily leak out from the sample matrix into the surrounding aqueous medium. The amounts of lactic acid and lactoyl lactic acid were lower in the biotic than in the abiotic sample. This was due to the assimilation of these products by micro-organisms.

Visual Examination and Scanning Electron Microscopy (SEM)

The PLA granules were initially transparent and slightly yellowish, but during the degradation they gradually turned whiter in both biotic and

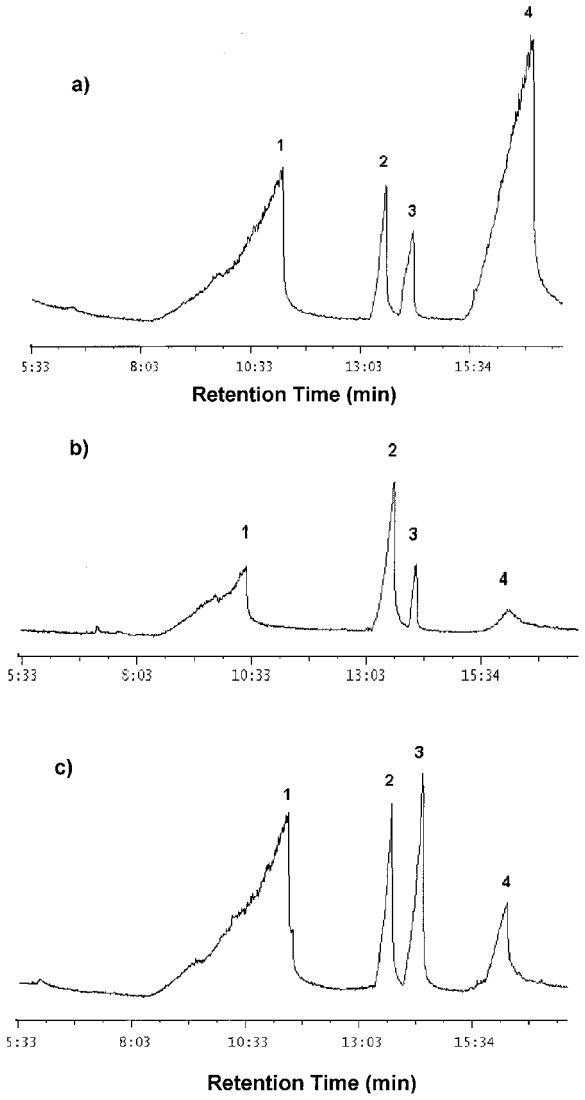

Figure 7 GC-MS chromatograms of the low molecular weight products extracted from: (a) unaged sample, (b) sample aged in biotic medium, and (c) sample aged in abiotic medium for 11 weeks. Peak assignment: 1 = lactic acid[d], 2 = 2-ethyl hexanoic acid[e], 3 = lactide[d], 4 = lactoyl lactic acid[e]. (d) Identified by mass spectrometry through comparison with literature mass spectra and using pure substances. (e) Identified by mass spectrometry through comparison with literature mass spectra.

abiotic media. The samples became brittle, and in the case of the abiotic sample, also porous. Cracks became visible at the surface of the samples. The crack formation was more apparent in the biotic sample than in the abiotic sample. During the degradation process, the samples from the biotic environment shrank diametrically, while the samples from the abiotic environment either became swollen or remained unchanged.

Figure 8(a)–(e) shows SEM micrographs of the unaged sample and of samples aged after 11 weeks in the biotic and abiotic media. The unaged sample was found to have a smooth surface. After 11 weeks in the biotic and abiotic media there were differences between the inner and outer parts of the samples. The biotic sample exhibited many cracks on the surface and the diameter of the samples became smaller as degradation proceeded, while the abiotic sample became swollen with small cracks in the surface. The swelling resulted from osmotic phenomena. The inner part of the abiotic sample was more degraded than the inner part of the biotic sample.

In abiotic media, water molecules are small enough to penetrate the polymer matrix and initiate an autocatalytic cleavage of the ester bonds, and this can lead to random cleavage of polymer chains. On the other hand, in biotic media, extracellular enzymes from micro-organisms attack the surface of the polymer and this results in surface erosion.[21–24] This can also partly prevent the water molecules from penetrating into the inner part of the sample, and the hydrolysis of the inner part of biotic samples thus occurs more slowly than the hydrolysis of the inner part of abiotic samples.

Biotic degradation is heterogeneous erosion, and results in the surface erosion and formation of lactic acid and its water-soluble oligomers that migrate easily into the aqueous media, whereas abiotic degradation is homogeneous erosion that occurs mainly randomly, and results in the formation of lactic acid and both short-chain and long-chain oligomers. These long-chain oligomers are mainly remained entrapped inside the abiotic samples and catalyze the degradation inside the samples.[25] Therefore, the inner parts of abiotic samples are more degraded than the inner parts of biotic samples.

CONCLUSION

Extensive investigation via Py-GC-MS, SEC, GC-MS, SEM has allowed to reach the following conclusions:

1. Acetaldehyde, acrylic acid, lactoyl acrylic acid, two lactide isomers, and cyclic oligomers up to pentamer were identified as thermal decomposition products of PLA by fractionated Py-GC-MS at 400 and 500°C.
2. Based on Py-GC-MS results, the decrease in the ratio of meso-lactide to L-lactide in the biotic medium shows the preference of the microorganisms for L-form of lactic

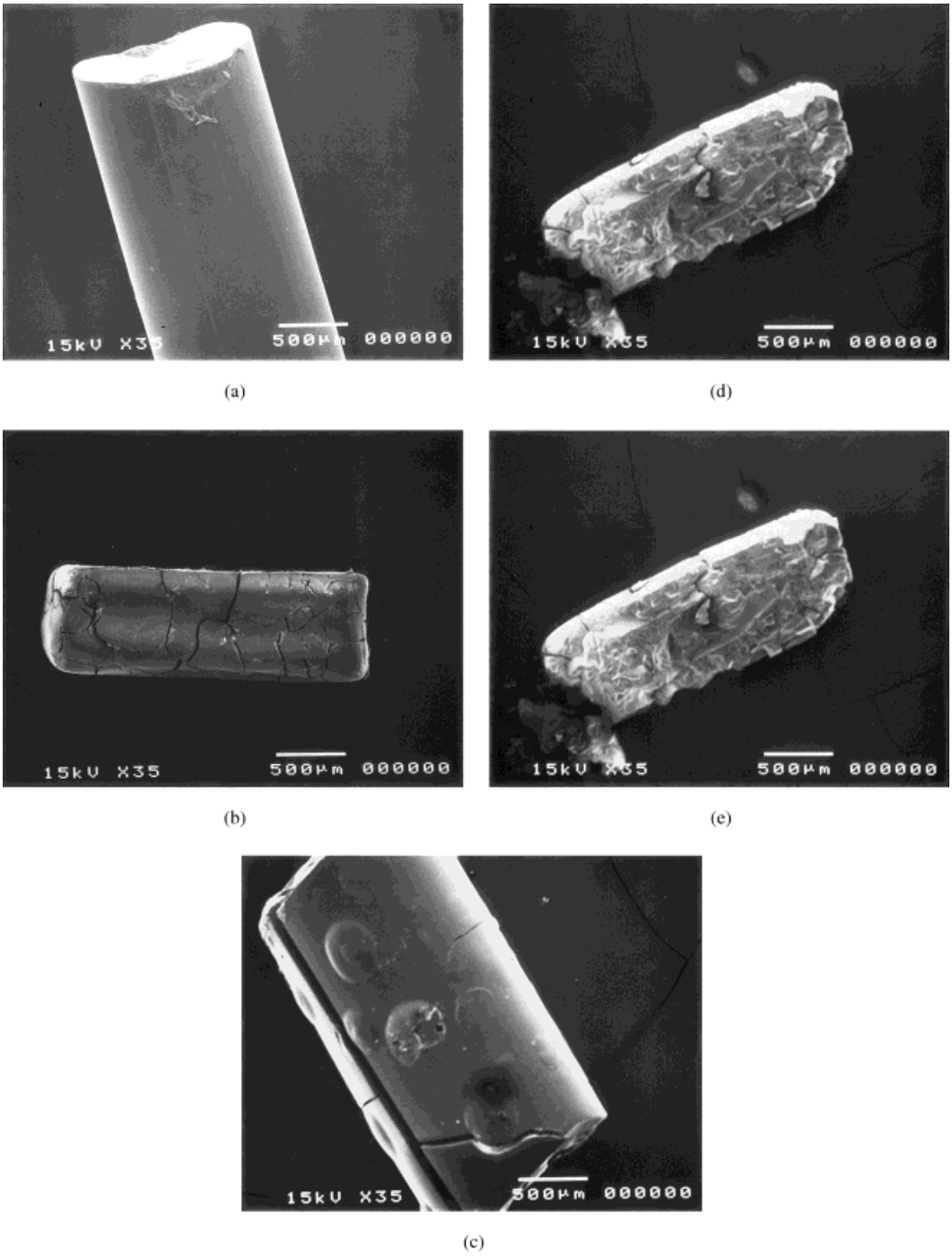

Figure 8 SEMs of the PLA samples: (a) the surface of the unaged sample, (b) the surface of the sample aged in biotic medium after 11 weeks, (c) the surface of the sample aged in abiotic medium after 11 weeks, (d) the cross-section of the sample aged in biotic medium after 11 weeks, and (e) the cross-section of the sample aged in abiotic medium after 11 weeks.

acid and lactoyl lactic acid rather than the D-form, which influences the formation and the amounts of meso- and (D) or (L)-lactide during the pyrolysis.

3. Different degradation mechanisms occur in the biotic and abiotic medium. Based on SEC results, the increase in polydispersity and more rapid decrease in M_n than in M_w

in the biotic sample explain the degradation near the chain end in the biotic sample. On the other hand, in the abiotic sample the polydispersity is closer to 2, and indicates mainly random degradation in this sample.

4. The SEM results show that in the biotic medium the degradation occurs mainly on the surface of the sample. These results also confirm that degradation in the abiotic medium is faster in the inner than the outer region.
5. Py-GC-MS and SEC data indicate that degradation was faster in the biotic than in the abiotic sample.

The Swedish Research Council for Engineering Sciences (TFR) is gratefully acknowledged for financial support of this work (281-98-664).

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