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DEGRADATION PRODUCTS IN DEGRADABLE POLYMERS

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ABSTRACT

Diffusion and migration of small molecules in polymers affect the long-term properties of the materials and also the surrounding environments. The interaction of such small molecules (i.e., low molecular weight compounds) with the environment are one of the main factors governing in-vitro and in-vivo behavior of degradable polymers. The type and amount of formed degradation products are the crucial points deciding the applicability of degradable polymers. The number of low molecular weight compounds obtained during long-term use of degradable polymers depends on the polymeric chain. Hydrolyzable polymers like the polyesters give few degradation products (mainly the monomer) where it is possible to relate the amount of products formed with the weight loss and the molecular weight changes. On the other hand, nonhydrolyzable polymers like polyethylene form hundreds of products in different amounts, thus complicating this comparison. Degradation products of hydrolyzable polyesters (PHB, PLLA, PDLLA/PGA, and PAA) as obtained by (head-space)-GC-MS are presented. The concept of fingerprinting based on the abiotic and biotic degradation products formed in degradable LDPE (LDPE + starch + prooxidant) is described and can be related to our proposed biodegradation mechanism of polyethylene.

INTRODUCTION

Increased interest in the use of degradable polymers has led to the need for accurate and precise test methods. Parallel with the demand for controllable and quick degradation is the demand for the development of nonharmful low molecular weight compounds which can be part of natural cycles. In this context the questions to be addressed are the type and amount of single products and the total amount of low molecular weight compounds present in degradable polymers.

The interaction of low molecular weight compounds from degradable polymers is one of the major factors governing the in-vitro and in-vivo behavior of materials. There are several types of small molecules in polymers. Some are present from the beginning, i.e., synthesis related (trace monomers, catalysts, solvents, and additives). Other products can be related to the type of processing and the processing conditions. Yet others are formed during use; they are usually referred to as degradation products. These degradation products are complex mixtures of compounds formed during biodegradation, thermooxidation, hydrolysis, etc. Degradation products of additives are also generally identified. Different polymers form different numbers of degradation products, ranging from the monomer and oligomer of the monomer (e.g., polyesters) up to hundreds of products (e.g., polyethylene).

Diffusion, migration, and leakage of additives and/or degradation products increase the degradation rate and also leave the polymeric matrix more brittle, thus making the material more prone to further degradation. The monitoring of small molecules in recycling is important as these will affect the new products and their performance. Continuous loss of additives demands addition of new additives in order to fulfill the material properties.

In this paper some results are presented concerning the detection and identification of degradation products in degradable polymers. Examples will be given from polyesters [polyhydroxyalkanoates (PHA), poly(lactic acid) (PLA), PLA copolymerized with poly(glycolic acid) (PGA) and poly(adipic anhydride) (PAA)]. The concept of fingerprinting is discussed for the first time in connection with synthetic degradable polymers to describe abiotic and biotic degradation products of LDPE + starch + prooxidant (i.e., LDPE + 20% MB) and related to our proposed biodegradation mechanism of polyethylene.

EXPERIMENTAL

Samples and Degradations

Commercial Biopol MBL granules of PHB and PHB-*co*-PHV (7% PHV) were dissolved in chloroform at 20 g/L by refluxing. To this solution was added nine times its volume of methanol, and the precipitated polymer was filtered and washed with methanol. The purified granules were thermooxidized. PHB (200 mg) was aged in sealed head-space vials at 100°C for up to 500 hours.

PLLA (100 mg) and PDLLA/PGA (75/25) were immersed in phosphate buffer (described elsewhere [1]) of pH 7.4, incubated at three different temperatures (37, 60, and 90°C), and aged for periods up to 60 days. The PAA samples were polymerized from oxepan-2,7-dione in our laboratory and immersed in 10 mg

of phosphate buffer as described above. Samples were withdrawn at regular intervals for periods up to 35 hours.

LDPE films (80 μm) were made by a conventional blown film process using a Betol extruder with a 25-mm screw of L:D 20:1, a blow-up ratio of about 2.5:1, and a die temperature of 185°C [2]. The pro-degradant additives were incorporated into the LDPE matrix in the form of a masterbatch in the amount of 20%, mostly consisting of corn starch (7.7%), styrene-butadiene copolymer (SBS), maganese stearate, and LLDPE. The degradation took place according to the following procedure. The films were preoxidized by heating in air at 100°C for 6 days in order to surpass the induction period and ensure that oxidation of the LDPE matrix had commenced. Thereafter the films were subjected to either sterile aqueous media [2] or to the bacteria *Arthrobacter paraffineus* (biotic media). Incubation took place at ambient temperature for periods up to 15 months.

Extractions

Acidified buffer solutions of PLLA, PDLLA/PGA, and PAA were extracted three times with diethylether (p.a.). The extracts were combined and evaporated by a stream of nitrogen. The same type of extraction was performed with the LDPE–20% MB samples [2].

Derivatization

PLLA, PDLLA/PGA, and PAA extracts needed to be derivatized before GC-MS analysis, and this was done as follows. 20 μL MTBSTFA (*N-tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide, 98%) was added to the dry residue of the extracts, and the solutions were diluted with 0.1 mL isooctane. The reaction was complete after 30 minutes at 60°C. The derivatized samples were injected into the GC-MS.

Analysis

The head-space (Hs)-GC-MS analysis was carried out using a Perkin-Elmer 8500 GC to which a head-space unit HS 101 and an ion trap detector (MS) were connected. The column was a Chromopack wall-coated open tubular fused silica, 25 m × 0.32 mm (CP-SIL-19 CB), and a temperature program from 40 to 180°C at 5°C/minute were used. The HS unit was thermostated for a period of 50 minutes at 100°C. The ITD operating conditions were: mass range, 20–600 u; scan time, 1.000 second; peak threshold, 1 count; mass defects, 0.03 mmu/100 amu; multiplier voltage, 1600 V; and a transfer line temperature of 250°C. The temperature program for PLLA, PDLLA/PGA, and PAA was an oven temperature 40°C (1 minute), programmed to 200°C at 10°C/min, and then isothermic temperature of 200°C (8 minutes). The derivatized samples were separated on a CP-SIL-43 CB column.

The LDPE–20% MB extracts were injected into a Varian 3400 GC equipped with a J&W 30 m × 0.32 mm DB-5 column, film thickness 0.25 μm, and a flame ionization detector (FID). Oven temperature was held at 50°C at 1 minute, raised at a rate of 5°C/min to 310°C, and then held for 10 minutes. Nitrogen was used as

the carrier gas. Identification was made by comparison with retention indices from standard compounds.

The SEC analysis was performed using a Waters Associates M-6000A size-exclusion chromatograph equipped with a set of Styragel columns, thermostated with a 1 mL/min flow, with chloroform as the mobile phase. The molecular masses [number average (M_n) and mass average (M_w)] were calculated using a calibration curve for polystyrene.

RESULTS AND DISCUSSION

The polyhydroxyalkanoates (PHA) represent a large group of polyesters produced from renewable resources. This fact, together with their degradability, makes them interesting materials for packages, etc. The degradation products from poly(β-hydroxybutyrate) (PHB) are fairly simple, and the monomer and oligomers of the polymer can be identified [3]. The conversion of β-hydroxybutyrate to crotonic acid is so fast that often only crotonic acid can be identified [3]. The hydrolysis of PHA can be done in different media and at different temperature, and the amount of products formed is dependent on the pH, the temperature, and the duration of degradation [3]. The increased degradation rate at higher pH depends partly on the increasing solubility of the polymeric degradation products at higher pH in addition to the overall increased hydrolysis rate.

Figure 1 shows the production of crotonic acid as a function of thermooxidation time at 100°C as obtained by head-space GC-MS. The same figure also shows the changes in molecular weights (M_n) during degradation. The lowest value of M_n is noted for those samples where a large amount of crotonic acid was formed. In addition 2-ethoxyethyl acetate and acetaldehyde were identified in thermooxidized native polyesters. The thermal decomposition of PHB and its copolymers is the result of random chain scission occurring by a six-membered ring ester decomposition process to form carboxylic ends in the polymer.

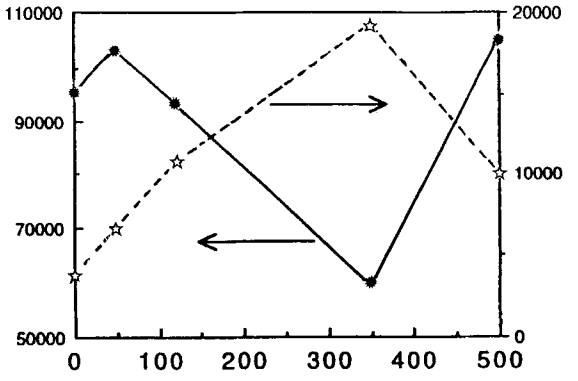

FIG. 1. M_n (✹, solid line) and amount of crotonic acid (☆, broken line) produced as a function of aging time of PHB at 100°C. y-axes in surface units (to the right) and g/mol (to the left).

Figure 2 shows the formation of lactic acid (LA) in aged PLLA (phosphate buffer) at three different temperatures. In the 37 and 60°C aged samples, a steady state in the formation of LA is quickly reached; the 90°C aged samples releases LA in a continuously increasing way. The weight loss of PLLA materials follows a similar pattern; 5 days of aging at 90°C corresponds to a 40% weight loss. A 75/25 copolymer of PDLLA and poly(glycolic acid) (PGC) releases about twice as much lactic acid during the same hydrolysis time as the PLLA homopolymer. This parallels the observations of the molecular weight reductions. It was observed by SEC that the molecular weight changes are largest during the first 10 days and that copolymers with glycolic acid give a material with increased susceptibility to hydrolysis at different temperatures. The onset of a rapid evolution of lactic acid is simultaneous with a drastic decrease in molecular weight.

Figure 3 presents the volatile degradation product of poly(adipic anhydride) (PAA) obtained by head-space GC-MS. Contrary to the polyesters presented in Figs. 1 and 2, this polymer degrades very quickly and has therefore found application in slow release formulations. Only one degradation product (adipic acid) was identified in amounts increasing with hydrolysis time. The formation of AA from hydrolyzing PAA is parallel with the detection of released pharmaceutical. The increase in the amount of evolved AA per milligram of PAA is quick; a steady-state level is reached after 10 hours.

In microbiology and bacteriology it is customary to identify the type of microorganism responsible for a certain disease by detecting its degradation products [4, 5]. Different microorganisms have different metabolisms (or degradation mechanisms), and this is reflected by their degradation products. This is referred to as

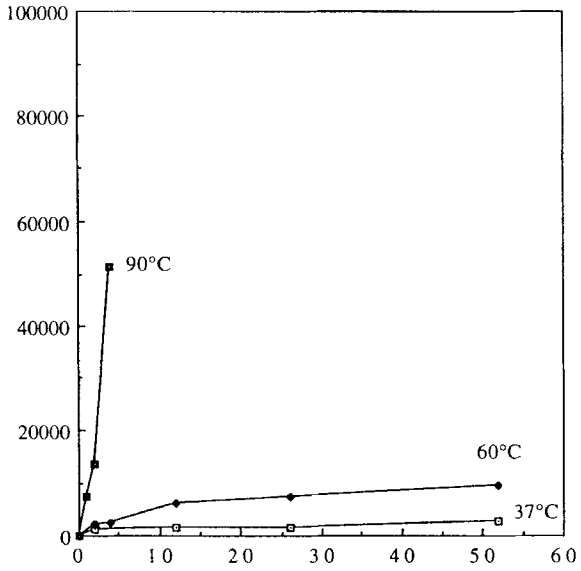

FIG. 2. Hydrolysis of poly(lactic acid) in phosphate buffer (pH 7.4). The amount of lactic acid detected after different hydrolysis times and at different temperatures. Analysis performed by ion-trap GC-MS instrument. x-axis = hydrolysis time (days); y-axis = absorption units (lactic acid).

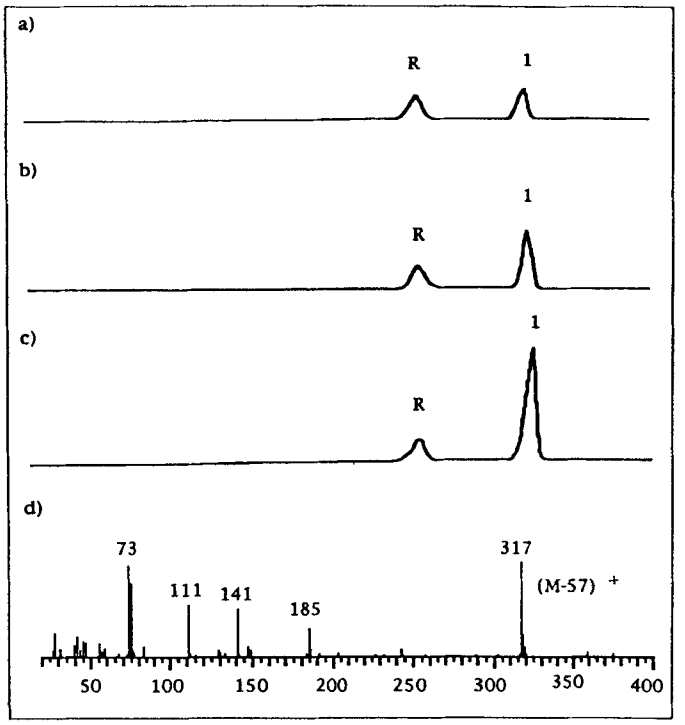

FIG. 3. Head-space GC-MS chromatograms of hydrolyzed PAA. All samples were derivatized with MTBSTFA before analysis. Chromatograms of released adipic acid after a) 0.5 hour, b) 2 hours, and c) 6 hours in phosphate buffer at 37°C (pH 7.4). d) Mass spectra of TBDMS ester derivative of AA, Peak 1. R = Reagents.

"fingerprinting" and can also be applied to the degradation of synthetic polymers in different environments. Figure 4 displays chromatograms of the degradation products of LDPE + 20% MB aged for 10 weeks in aqueous biological and sterile environments. Figure 4(a) represents the fingerprint of a biologically degraded sample. The absence of a substantial amount of carboxylic acid should be noted; instead, different late esters are found. The sterile sample contains several peaks identified as carboxylic acid (Fig. 4b). Both chromatograms agree well with the LDPE biodegradation mechanism proposed by us in 1987 [6].

In parallel with the use of a new, specialized chromatography, we have developed a sophisticated prepreparation process to avoid the loss of different classes of compounds. It is based on solid phase extraction which is superior to ordinary liquid extraction. We have succeeded in identifying over 50 different degradation products in aged LDPE + MB samples [2]. Our research has also demonstrated that comparison with molecular weight changes, weight losses, and/or FT-IR is fruitful in properly describing the degradation mechanisms. The present results also show that the product pattern can be used as fingerprints, e.g., look for the presence or absence of special groups of homologous series (volatile acids, hydrocarbons, etc.). Thus, the fingerprints correlate with the degradation mechanisms.

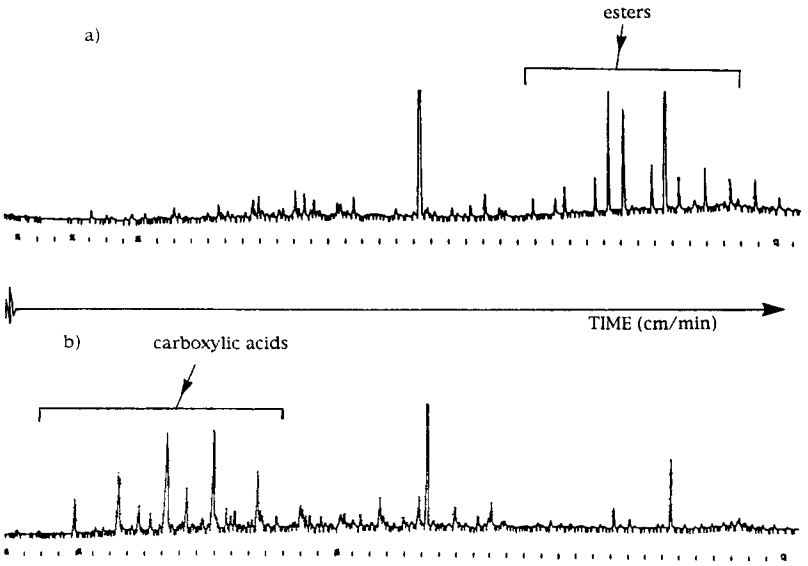

FIG. 4. GC chromatograms of degradation products evolved in aqueous biotic environments and aqueous abiotic environment from LDPE + 20% masterbatch (starch + prooxidant). a) biotic environment and b) abiotic environment. The *x*-axis is the time scale.

CONCLUSIONS

Specialized chromatography (head-space GC-MS, LC, etc.) has been developed allowing the detection and identification of low molecular weight compounds in degradable polymers. We have demonstrated that the product pattern can be used as fingerprints and that the product pattern is related to the degradation mechanism and the kinetics. In addition it was also shown that the type of compounds formed is highly dependent on the environment.

The interaction of polymers with the environment governing the in vitro and in vivo behavior of degradable polymers is partly due to the evolution of low molecular weight compounds. The crucial point when using degradable polymers is, thus, the determination of the interaction of degradable polymers with the environment as manifested by the evolution of degradation products.

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