ABIOTIC AND BIOTIC DEGRADATION OF ALIPHATIC POLYESTERS FROM "PETRO" VERSUS "GREEN" RESOURCES

Sigbritt Karlsson* and Ann-Christine Albertsson

Department of Polymer Technology, the Royal Insitute of Technology (KTH), S-100 44 STOCKHOLM, Sweden

Abstract: Aliphatic polyesters are degradable by abiotic and/or biotic hydrolysis. The accessibility of a polymer to degradative attack by living organisms is not dependent on its origin, but on its molecular composition and architecture. Synthetic polymers with intermittent ester linkage (*e.g.* polyesters, polyurethanes *etc.*) are accessible to biodegradative attack of esterase. On the other hand aliphatic polyesters are also quickly degraded by a pure abiotic hydrolysis. The results from abiotic and biotic hydrolyses of polycaprolactone (PCL) (from "petro" resource), poly(L-lactide) (PLLA) and polyhydroxyalkanoates (PHA) (from "green" resources) are presented and discussed with the respect to rate of degradation, molecular weight changes and degradation product pattern. For the environmental consequences, the type of formed degradation products are of importance and not the origin of the polymer.

INTRODUCTION

Considerable efforts have recently been made to develop polymers from renewable resources ("green" resources). The very smallest unit needed for the production of polymers is carbon [C] which is readily available from various sources. Tab. 1 compares some [C] resources with respect to time of regeneration (degree of renewability).

Tab. 1 Resources of [C] to prepare polymers.

Resources	Regeneration time	Comments
Oil	Billions of year	Exhaustion of possible oil well
Wood	70 years	Also material in itself
Plants	1 year (season)	Starch, PHA *etc.* ethanol
Microorganisms	8-24 hours	*e.g.* PHA

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It is already today possible to make polyethylene (PE) from growing plants via ethanol. A series of factors should be taken into account if alternative routes are used instead of starting with raw oil, not least important among them are the environmental aspects.

The degradation of polymers is not dependent on the resource, but is largely influenced on it molecular composition and the architecture. The true distinction between inert and degradable polymer is the rate of the degradation, even inert polymers degrade although very slowly. A degradable polymer should instead preferable degrade within months up to one year, or even faster. Biodegradable polymers degrade by the action of microorganisms and/or enzymes and this process should preferably proceed within a relativly short period of time (1). Several standard authorities have sought to produce definitions for biodegradable polymers and these were recently reviewed (2).

In the 60's poly(L-lactide), PLLA, was proposed as a biocompatible, biodegradable and bioresorbable material for biomedical applications (3). In recent years environmental concern has led to an escalated interest in PLLA, as well as other biodegradable polymers, as an alternative to traditional commodity plastics (4,5). PLLA has the advantage of being not only biodegradable but also renewable since the raw material, lactic acid, may be produced by microbial fermentation of biomass. The main drawbacks are, however, its brittleness, the moisture sensitivity and price. Homo- and copolymers of hydroxyalkanoates derived from the energy-storing polymer of many microorganisms are interesting materials from "green" resource. Intensive research in several parts of the biosynthesis of polyhydroxyalkanoates (PHA) has led also to the transfer of the genes coding for PHA-production in the microorganisms to plants which should facilitate the recovery of pure PHA.

Polycaprolactone (PCL) is another aliphatic polyester that has attained interest because of its biodegradability. During the 70's it was shown in several studies that PCL is easily degraded and utilized as carbon source by various microbal species (6-9). Even though it is a synthetic polymer, microorganisms capable of degrading PCL are widely distributed in nature (10). The reason is that enzymes hydrolysing naturally occurring hydrophobic (poly)esters such as cutin and lipids may also attack PCL (11,12). In most environments PCL have been found to biodegrade slower than other bidegradable polymers such as poly[hydroxybutyrate-co-valerate] (PHB/HV), regenerated cellulose, starch and chitosan. PCL is presently made from traditional "petro" resources, but may easily also be made from "green" resources.

This paper presents abiotic and biotic degradation of PCL, PLLA and PHB/HV and discusses molecular weight change, rate of degradation and degradation product patterns.

EXPERIMENTAL

Materials. Films of PCL (30 mm), PHB/HV with 6% HV (50 mm) and PLLA (120 mm) were blown using a Axxon double extruder (13).

Abiotic hydrolysis. Distilled water was used for neutral hydrolysis of film samples. Alkaline hydrolysis was performed in a pH 10.5 buffer solution consisting of 1.4 g/l KH_2PO_4 and 0.76 g/l KOH. NaN_3 was added to both solutions in order to prevent microbial growth. The samples where exposed to the solutions up to 30 weeks at either 23 °C or 50 °C (13). Biotic hydrolysis.Two different household-scale composting systems where used. One was a simulated compost formulated on 48% dehydrated cow manure, 16% saw dust, 35% water and 1% dried bacterial starter (Bio Composter™). At intervalls of 3 weeks vegetables where added to enhance microbial activity. The ambient temperature varied between 0 and 20 °C while the temperature within the compost varied from ambient to 35 °C. Other film samples where buried in a garden-waste compost. Aerobic conditions where obtained by occasionally rolling the compost. The ambient temperature varied between 8 and 20 °C during the test-period while the temperature within the compost varied from ambient to 40 °C (13).

Analyses. ^{1}H-NMR spectra where recorded with a Bruker AM 400 apparatus operating at 400 MHz. All samples where dissolved in $CDCl_3$ and data was collected during 96 scans. Molecular weight changes and degradation product patterns were obtained by analyses in size exclusion chromatography (SEC) and gas-chromatography-mass spectroscopy (GC-MS) (13, 14).

RESULTS AND DISCUSSION

The molecular weight change of PCL is slow at 23 °C but increases severely at the higher temperature (13). The alkaline buffer has little influence on the degradation where the hydrophobic nature of PCL prevents the buffer from penetrating the bulk of the material. The pH of the surrounding aqueous media has, however, an influence on the rate of degradation. A high pH favours extraction of oligomeric degradation products

by ionisation of end-groups. The type of acid/base causing the pH may also have a significant influence. It has been shown that organic acids and bases, capable of penetrating hydrophobic matrices in the unionized state, significantly increase the degradation rate of hydrophobic polyesters. The molecular weight changes of PLLA after exposure to the same media show instead a direct correlation with both temperature and pH (13).

The abiotic hydrolysis of poly(lactide)s (PLA) has earlier been reported to proceed in three stages (15). During the first stage the molecular weights decrease rapidly with little weight loss. In stage two, the decrease in molecular weight slows down and severe weight loss starts in parallel with which monomer formation is initiated. During the final third stage, when total weight loss is observed, about 50% of the polymer is converted to monomer. Typically a multimodal molecular weight distribution develops with prolonged degradation (15). The abiotic hydrolysis of PHB/HV is slower than for PLA, but the biotic hydrolysis is very rapid. The molecular weight is fairly constant in PHB/HV degraded by *Aspergillus fumigatus* for periods up to 21 days, when total collapse occurred (14). During that time the release of hydroxybutyrate as degradation product increased rapdily after around 7 days, reaching concentrations of 1.5 mg/ml just before the total collapse of polymer (14). Abiotic hydrolysis at elevated temperature had less effect during such short period as 21 days, a total collapse was instead observed after about one year incubation in sterile water at pH 7 and 60°C (14).

Tab. 2 presents the chemical shifts for the methine hydrogen of PLLA and related chemical structures. The methine hydrogen of PLLA gives a characteristic quartet due to coupling with the hydrogen atoms of the adjacent methyl group. This signal was found in three different regions of the spectra. By studying spectra of reference compounds (lactide, lactic acid, methyl lactate and highly purified PLLA) the signals could be matched with their corresponding chemical structures.

Tab. 2. Chemical shifts for the methine hydrogen of PLLA and related chemical structures.

5.1-5.2 ppm	Repeating unit of polymer
5.0-5.1 ppm	Lactide (cyclic dimer)
4.3-4.5 ppm	Methine group adjacent to a free hydroxyl group (lactic acid or hydroxy terminated end-group)

Tab. 3 gives the relative intensities (%) of the three different methine hydrogen signals of PLLA samples. The values show that lactide, often present in the raw material, is almost completely lost during processing. This is not surprising since lactide is quite volatile at the processing temperature. The increased intensity of the signal at 4.3-4.5 ppm indicates that chain scission occurs, during both processing and hydrolysis, but to a far greater extent than indicated by SEC-studies. This implies that hydrolysis of ester bonds is more likely to occur near chain ends wich leads to the formation of lactic acid and oligomers with molecular weights too low to be detected with conventional size exclusion chromatography. Tab. 3 also shows that extraction of such degradation products is favoured by high pH and high temperature. The effect on degradation rate of residual monomer and oligomers being present in PLA has been studied by Pennings and coworkers (16). It was shown that removal of such impurities by extraction with ethyl acetate yielded a material that was considerably more hydrolysis resistant at 37°C/pH 6.9 (16).

Tab. 3. Relative intensities [%] of the three different methine hydrogen signals of PLLA samples (n.d.=not detected).

Sample:	5.1-5.2 ppm	5.0-5.1 ppm	4.3-4.5 ppm
Raw material (pellets)	90.2	5.6	4.2
Virgin film	86.9	0.5	12.6
22 days, 23 °C/pH 7	75.4	n.d.	24.6
22 days, 23 °C/pH 10.5	84.4	n.d.	15.6
22 days, 50 °C/pH 7	97.7	0.5	1.8
22 days, 50 °C/pH 10.5	98.2	n.d.	1.8
7 weeks, simulated compost	87.9	n.d.	12.1

When PCL pellets, undegraded and hydrolysed PCL films and PCL films subject to composting were analysed by ^{1}H-NMR,peaks corresponding to free ε-caprolactone or chain ends were identified, but these were very small (maximum intensity of 0.1%).

PLLA was hydrolysed at a much faster rate than PCL even though the film was 4 times as thick. NMR studies showed that low molecular weight products were formed during thermoplastic processing and degradation of PLLA. Most of these products diffused out of the film during hydrolysis at 50 °C. The same phenomenon was not observed in the PCL films. It has earlier been shown that oligomers corresponding to about 50% of the PLA are present in abiotic hydrolyse-solutions and that these slowly degrades to lactic

acid (15). The major degradation product of PHB/HV are hydroxybutyrate and hydroxyvalerate. Once the polymer was consumed, acetic acid, butanoic acid and pentanoic acid were produced (14). C_4-C_4, C_4-C_5, C_5-C_4 and C_5-C_5 dimers were also identified. These were, however, rapidly further metabolized in the biotic environment either by remaining exoenzymes or by assimilation of *A. fumigatus* fungi itself (14).

The surface of aliphatic polymers subject to abiotic and biotic degradation change to various extent. Abiotic hydrolysis of PLLA resulted in many splits and holes and a constant increase in the formation of lactic acid. The same was seen also in biodegraded samples. The PHB/HV showed in general less effect on the surface, irrespective of the type of hydrolysis. For PCL films signs of erosion could be seen both in abiotic and biotic environments. The two different composts gave slightly different surface change. Composting in the simulated compost gave rise to ovale holes in the PCL-films, while no holes were observed in PCL samples degraded in the traditional garden waste compost. In 1977 we reported similar circular holes in biodegraded low density polyethylene (LDPE) (17). Recently Koyama and Doi proposed that such circular holes observed in enzymatically degraded P(3HB) corresponds to the centre of the spherulite and that this consists of less ordered lamellae which are more susceptible to enzymatic attack (18).

CONCLUSIONS

Aliphatic polyesters are in general very susceptible to hydrolysis. The degree of hydrolyse sensitivity depend on both the chemical composition and the morphology of the materials. PLA is in principle equally hydrolysable in both abiotic and biotic environments, with higher degradation rates at elevated pH and/or temperature. Monomer and oligomers are produced constantly and once a total collapse of the polymer has occurred the remaining oligomers are gradually transformed to lactic acid. The degradation rate of PCL is less influenced by pH and temperature in abiotic hydrolysis than similar samples of PLLA. Biotic hydrolysis in simulated compost gave rise to holes in the PCL films opposite to the case in the traditional garden waste composte. The PLLA showed no holes in either simulated or garden waste composte. PHB/HV is less susceptible to a pure abiotic hydrolysis, but show instead rapid hydrolysis in biotic environments. For the environmental consequences, the the type of formed degradation products are of importance and not the origin of the polymer.

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