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The Influence of Processing Conditions on the Properties and the Degradation of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

Renstad R., Karlsson S. and Albertsson* A.-C.

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

*To whom correspondence should be addressed

Abstract

The influence of melt-extrusion on the degradation behavior of poly(3-hydroxybutyrate-co-7% 3-hydroxyvalerate) in a small-scale compost and in salt media with *Aspergillus fumigatus* has been studied. The degradation has been monitored by Size Exclusion Chromatography (SEC), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and X-ray analysis. During the first 9 weeks of composting the degradation proceeds through surface erosion without any significant change in molecular weight or weight crystallinity. After 10 months the weight average molecular weight, Mw, has decreased by approximately 15-50%. It is suggested that degradation mechanism is converted from enzymatic to chemical hydrolysis as the porosity of the samples increases which facilitates water penetration. In addition, the acidic degradation products would accelerate the chemical hydrolysis inside the sample due to lowering of the pH. During degradation in media containing *A. fumigatus* the sample processed at low temperature exhibited extensive surface degradation and a 12% reduction of the Mw. In contrast the sample processed at high temperature showed an homogeneous surface degradation and no reduction in molecular weight. The differences in degradation are attributed to variations in the initial morphology of the samples caused by the processing conditions. Further investigations are, however, required to separate effects attributed to local differences in the compost environment and the structure of the samples.

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Introduction

A large number of studies have been conducted on the degradability of poly(3-hydroxybutyrate), P(3HB), and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate, P(3HB-co-3HV). The polymers have been shown to degrade in various natural environments, for example in compost, soil, and sewage sludge through the action of microorganisms (1, 2). In general the polymers degraded at the surface without major changes in the molecular weight.

In order to utilize the benefits of the polyhydroxyalkanoates as for example compostable packaging, the polymers have to be processed with commercial equipment. Unfortunately, it is well known that both P(3HB) and P(3HB-co-3HV) are sensitive to the high temperatures associated with melt-processing and rapidly lose molecular weight (3, 4). Studies involving injection molding have showed that an increasing amount of HV-units in the backbone causes smaller reductions in molecular weight because lower processing temperatures could be used (5, 6).

We have previously showed that melt-extrusion of P(3HB-co-7% 3HV) at different temperatures and screw speeds affects the molecular weight and the mechanical properties (7). A 30°C increase of the processing temperature from about 145° to 175°C caused a 20 to 45% decrease of the molecular weight. The decrease in Mw was more significant at lower screw speeds due to the increasing dwell times. The results are in the same magnitude as previous studies of P(3HB-co-5% HV) and P(3HB-co-12% 3HV) by melt pressing and injection molding (8, 9).

In addition the mechanical properties were strongly affected by the processing. The elongation at yield and break decreased with increasing processing temperature. A break point in the tensile stress was apparent at about 150 000 g/mol, below which the strength decreased rapidly. The degree of mass crystallinity was not affected by the processing (10). However, X-ray analysis and DSC measurements indicated that the atomic positioning and the lamellar morphology of the material was affected by the processing temperature.

Previous studies have shown that increasing crystallinity and lamellar perfection of P(3HB) and P(3HB-co-3HV) decreases the rate of enzymatic degradation (11, 12, 13, 14). In addition the degradation of P(3HB) is also strongly affected by the tacticity of the samples (15). During hydrolysis of P(3HB-co-20%HV) fabricated by different methods it was shown that the time to 10% weight loss increased for methods yielding higher crystallinity (5).

Thus it could be assumed that the differences in molecular weight and morphology of the P(3HB-co-3HV) samples induced by melt-processing could give different prerequisites for biodegradation. This paper will discuss how the processing conditions influence the degradation behaviour of melt-extruded P(3-hydroxybutyrate-co-3-hydroxyvalerate) with 7% HV in a small-scale compost and salt media containing the fungus *Aspergillus fumigatus*.

Experimental

P(3HB-co-3HV) was purchased from Zeneca Bio Products under the trade name Biopol D400G. The material has an added nucleant. The HV content was 7% according to the manufacturer. The average molecular weights of the granules were Mw: 262 000 (25 700) and Mn: 107 200 (22 600), the standard deviation being given inside the parentheses.

The extrusion was carried out with a Brabender Plasti-Corder PL2000 counter-rotating twin-screw extruder DSK 35/9D (diameter/length) equipped with a 25 x 0.5mm ribbon die. The processing parameters were recorded continuously during the processing. The samples were allowed to crystallize at room temperature for 24 hours after processing. Thereafter, they were stored at low temperature until conditioning and analysis in order to avoid secondary crystallization.

Two samples, AI and DI, processed at low (147°C) respective high processing temperature (177°C) at a screw speed of 5 rpm were subjected to degradation in salt media containing the fungus *Aspergillus fumigatus* for 46 days, for further details see Eldsäter *et al.*(16). Samples AI, AIV (148°C, 40 rpm), DI, DIV (176°C, 40 rpm), were subjected to degradation in a small-scale compost fed with garden waste. The composting was maintained for 10 months.

The melting behavior of P(3HB-co-3HV) was studied by using a Mettler Toledo DSC 820 calorimeter at a heating rate of 10°C/min under nitrogen atmosphere. The values of the heat of fusion originate from the first scan, and the melting temperatures from the second. The mass crystallinity was approximated by using the heat of fusion (Δh^0_f) of totally crystalline PHB: 146 J/g(17).

The SEC-measurements were performed on a chromatography system consisting of a 717 plus autosampler, a 6000A pump and a differential refractometer R401 all manufactured by Waters. The system was equipped with two PL gel 10μm mixed-B columns from Polymer Laboratories. The solvent during analysis was chloroform and the flow rate was 1.0 ml/min. The sample injection volume was 200μl. Polystyrene standards were used for calibration.

The surfaces of the samples were examined by a JEOL, JSM-5400, scanning electron microscope, using a acceleration voltage of 15kV. The surface of the samples were gold plated with a Denton Vacuum Desk II cold sputter etch unit for 2 * 30 seconds.

Results

Fig. 1 (a and b) shows micrographs of samples AI and DI after 9 weeks of composting. The sample processed at the higher temperature, DI, reveals a coarse surface with an apparently spherulitic structure. Sample AI exhibits a slightly finer surface structure but the surface has clearly been eroded which is obvious when comparing with the smooth surface of the undegraded sample AI (Fig. 1 c). In contrast, the undegraded sample DI (Fig. 1 d), exhibits a more uneven surface with small holes and ridges due to the higher processing temperature.

The results from the thermal analysis and X-ray analysis are showed in Tab. 1. The degree of crystallinity is largely unchanged during the composting as measured by DSC. In contrast the degree of crystallinity, as measured by X-ray diffraction, exhibits a slight increase. The melt temperature has decreased slightly and the melting endotherm of the first scan is slightly lowered after the composting. This is indicative of lamellar rearrangements due to thermal stimulation in the compost.

Sample	ΔH(J/g)	Wc(%)	Tm(°C)	Xcr(%)
AI	81	55	153.0	52
AIV	81	55	153.1	53
DI	83	57	151.2	52
DIV	79	54	152.4	48

Table 1. Results from thermal- and X-ray analysis of P(3HB-co-3HV) after 10 months of degradation in a small-scale compost.

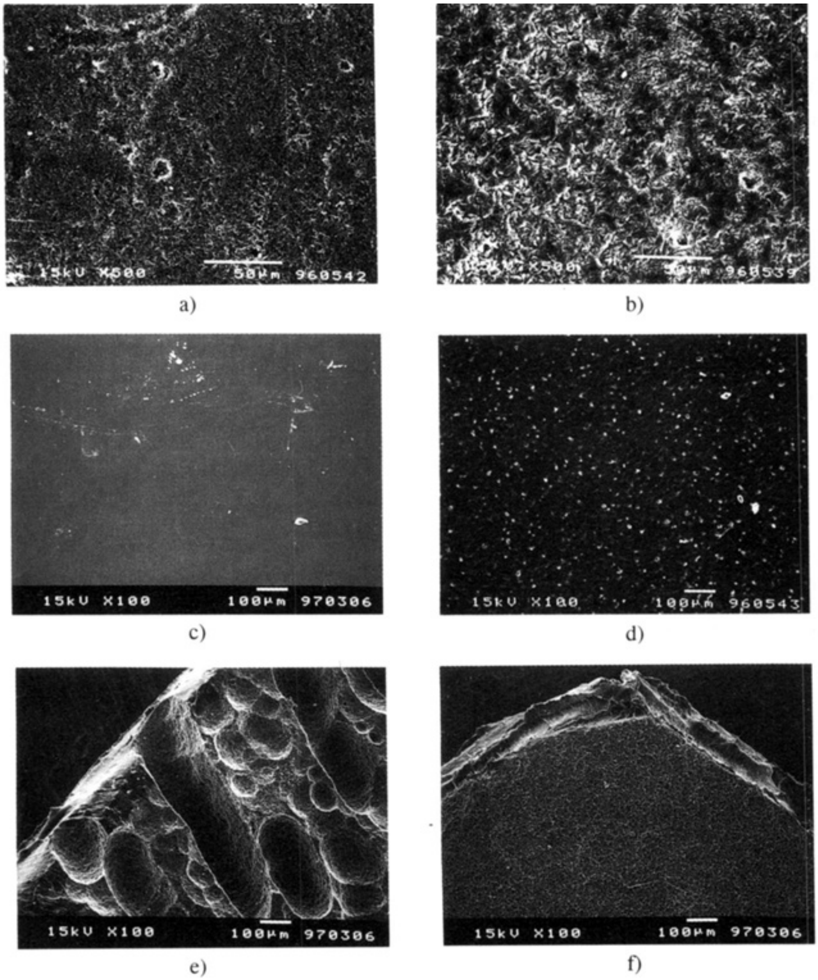

Figure 1. Scanning electron micrographs of the surface of melt-extruded P(3HB-co-3HV) after 9 weeks of composting (a and b), before degradation (c and d) and after 63 days of enzymatic degradation (e and f) for sample AI (a,c and e) and DI (b, d and f). Bar 50μm in a and b, 100μm in the other micrographs.

Fig. 2 shows the results from the SEC measurements of P(3HB-co-3HV) subjected to degradation in a small-scale compost for 10 months. The weight average molecular weight, Mw, has decreased considerably, about 45%, for samples AI and DIV. Samples AIV and DI exhibited approximately 15% decrease. After 9 weeks of composting the Mw was largely unchanged for all samples.

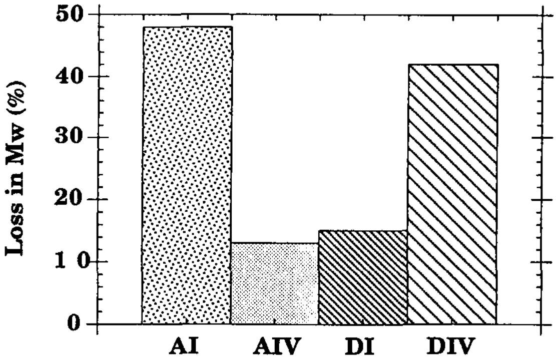

Figure 2. Percent decrease in weight average molecular weight, Mw, from SEC measurements of P(3HB-co-3HV) subjected to degradation in a small-scale compost for 10 months.

Samples AI and DI were subjected to microbial degradation in the presence of *Aspergillus fumigatus*. After 46 days of degradation sample AI exhibited extensive surface erosion in a dendritic or tree shaped pattern visible to the naked eye. The sample processed at higher temperature, DI, showed no such pattern. Fig. 1 (e) shows the heavily eroded surface of sample AI. In contrast, sample DI (Fig. 1 f) exhibited a more homogeneous erosion over the whole surface area. Table 2 gives the results from DSC and SEC measurements. The results are similar to the ones stated for the composted samples with minor changes in the degree of crystallinity and a slight decrease of Tm. The Mw of sample AI exhibits a 12% decrease, whilst sample DI was unchanged.

Sample	Mw (% change)	ΔH (J/g)	Wc (%)	Tm (°C)
AI	-12	81	55	153.1
DI	-1	82	56	152.4

Table 2. Results from thermal analysis and molecular weight measurements of P(3HB-co-3HV) subjected to degradation in the presence of *Aspergillus fumigatus* for 46 days.

Discussion

The P(3HB-co-3HV) samples exhibit degradation through surface erosion in both compost and in media containing *A. fumigatus*. After 9 weeks of composting the micrographs in Fig. 1 (a and b) show that the surface has eroded more rapidly at amorphous regions giving a spherulitic texture which has been described in the literature previously (13, 14). The degradation is preferentially occurring at the surface considering that bulk properties such as molecular weight and degree of crystallinity were unchanged.

The results after 10 months of composting indicate that the mode of degradation has changed during the composting, as the Mw of the samples has decreased significantly, now involving the whole matrix. A plausible explanation could be that chemical hydrolysis dominates during the later stages of the composting. This could be enhanced by the increasing porosity of the samples due to 10-30μm wide holes (see Fig 1 a and b) which appears in the composted samples and emerges far into the bulk which facilitates penetration of water molecules. Considering that the major degradation products of P(3HB-co-3HV) are 3-hydroxy butyric and 3-hydroxy valeric acid, the microenvironment inside the pores could autocatalyse the hydrolysis by lowering the pH (11, 16). The large difference in Mw between the individual samples in Fig. 2 indicate that the degradation was very local in the compost.

The samples subjected to *A. fumigatus* exhibit large variations in both molecular weight and surface erosion after 46 days of exposion. The surface erosion has evolved from small local craters to large crevices forming a macroscopic tree shaped structure in sample AI. In contrast, sample DI shows a more continuous erosion resembling that of the composted samples at shorter degradation times. Sample AI has twice the Mw of sample DI before the degradation; in spite of this the surface of sample AI exhibits a higher degree of surface erosion. In the small-scale compost the sample processed at low temperature, AI, also exhibited a greater reduction of the Mw compared with sample DI.

The sample produced at higher temperature DI show a larger amount of thinner crystalls and lower segmental mobility in addition to lower molecular weight (7). The results indicate that these morphologic factors reduce the rate of enzymatic degradation. In opposition to this theory is the fact that samples AIV and DI exhibit similar reductions of the Mw in the compost in spite of the differences in the factors described above. However, the local environment for the samples degraded in the small-scale compost can differ considerably due to variations in the density of microorganisms, temperature and moisture level which adds an uncertainity to the results. In order to investigate the degradability further a larger amount of samples and environments are presently being conducted.

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