The Influence of Thermal History on the Properties of Poly(3-hydroxybutyrate-co-12%-3-hydroxyvalerate)

HENK VERHOOGT, BRUCE A. RAMSAY,* BASIL D. FAVIS, and JULIANA A. RAMSAY

École Polytechnique de Montréal, Department of Chemical Engineering, C.P. 6079, succ. Centreville, Montréal, Québec, H3C 3A7 Canada

SYNOPSIS

The influence of thermal history on the properties of commercial P(3HB-co-12%-3HV) was studied. Thermogravimetric analysis and differential scanning calorimetry revealed that the plasticizer evaporated at 140°C or higher. The loss of plasticizer during thermal treatment at 170 and 180°C resulted in a slight increase of the melting temperature of the polymer. The processing time and temperature, as well as the cooling procedure influenced the thermal behaviour of the material. A decrease in molecular weight with time was found at the temperatures investigated and this significantly affected the mechanical properties of the polymer prepared at 180 and 200°C. The rate constant k_d of thermal degradation was slightly higher for samples during a shape-forming process in a Minimax apparatus than during a quiescent heating process (DSC) and its value increased with temperature. Limiting the processing at 170°C to 2 min gave a material with useful properties but increasing the residence time resulted in a decrease in strength, elongation at break, molecular weight and viscosity although it did not significantly influence the modulus of elasticity. Materials prepared at 180 or 200°C were more brittle and longer residence times resulted in a deterioration of the mechanical properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyhydroxyalkanoates (PHAs), produced by fermentation of a large variety of bacteria, are environmentally degradable thermoplastics that can be processed with conventional equipment.[1,2] Among the PHAs, poly(3-hydroxybutyrate) (PHB) is the most studied and the easiest to produce. It has thermal and mechanical properties similar to those of polypropylene (PP).[3] However, PHB has two major drawbacks which limit its use. These are its brittleness and a narrow processing window.[1–5]

Moulded PHB shows ductile behaviour, but progressive crystallization at ambient temperatures causes embrittlement due to constraining of the amorphous chains between the crystals. One method to lower the brittleness of PHB is to anneal it at a temperature of 100°C or higher which toughens the material.[6,7] Properties of the annealed material resemble those of PHB immediately after moulding and subsequent ageing is greatly decreased.

Another method of improving the mechanical properties is the incorporation of 3-hydroxyvalerate (3HV) units into the PHB backbone during the fermentation process. This produces poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB-co-3HV) copolymers which have improved flexibility and lower melting points than PHB.[2] The melting point decreases with increasing amounts of 3HV, with a minimum value around 75°C at approximately 40 mol % 3HV.[8] The lower melting point of the copolymers broadens the processing window since there is improved melt stability at lower processing temperatures.[5]

Poly(3-hydroxybutyrate) is thermally unstable.[9] Thermal degradation occurs by a non-radical, random chain scission mechanism involving a β-CH hydrogen transfer process.[5,9–11] The principal features, products and reaction mechanism of the thermal degradation of PHB have been described extensively.[11] In the temperature range of 170–200°C, chain scission results in a rapid decrease in molec-

Table I Melting Point and Molecular Weight Data of Undried and Dried
P(HB-co-12%-HV) as Determined with DSC and GPC

	Melting Point (°C)[A]		M_w (g/mol)[B]	M_n (g/mol)[B]	M_w/M_n
	1st Peak	2nd Peak			
Undried	134.4 ± 0.8	153.0 ± 0.5	410,200	120,900	3.39
Dried	150.8 ± 0.4	161.4 ± 0.2	393,500	115,600	3.41

[A] Determined from first heating scan from DSC.
[B] Determined from GPC.

ular weight. PHB is completely volatilized between 250 and 300°C with the main products being dimeric, trimeric and tetrameric oligomers together with crotonic acid. At even higher temperatures (340–500°C), these primary degradation products are degraded to acetaldehyde, ketene, propene and carbon dioxide. Performing the experiments under nitrogen, in static air or under vacuum does not significantly influence the thermal stability of PHB.[11] Addition of conventional stabilizers and antioxidants does not affect the polymer's thermal degradation.[5]

The lower melting point of P(3HB-co-3HV) copolymers make them more suitable for processing.[2,5] A melt flow index (MFI) doubling time of 2 min is reported for PHB at 170°C which was obtained by melting the polymer at 190°C and then cooling to 170°C. Addition of 3HV units to the PHB backbone increases the MFI doubling time to 10–15 min at temperatures 10–15°C above the melting point of the copolymer.[2,5] P(3HB-co-3HV) copolymers with a melting point below 160°C are unstable at temperatures above 170°C but have been found to be stable below 170°C, suggesting that they are applicable to conventional plastics processing at these lower temperatures.[12] However, injection moulding of copolymers, containing 5–22% 3HV,[13,14] at temperatures 10–15°C below their melting point has resulted in a severe decrease of up to 50% of the molecular weight. Injection moulding also caused a slight increase in the melting point of the material, which was attributed to partial orientation of the polymer.[14]

Quiescent thermal treatment of PHA copolymers above their melting temperature influences their properties due to a change in molecular weight.[15,16] Compression moulding and heat treatment at 180 and 190°C of P(3HB-co-5%-3HV) has resulted in a decrease in tensile strength and Young's modulus with time.[16] The change in mechanical properties has been explained by the decrease in molecular weight with time that alters the crystallization and

morphology, due to the shorter chain length of the polymer.

Thermal effects greatly influence the properties of PHA polymers. Knowledge of these effects is of great importance to processing these polymers. Unfortunately, no complete study of a single copolymer has been reported. In this work, we have studied the effects of thermal history on the properties of commercially available P(3HB-co-12%-3HV) to determine the time and temperature of exposure that will still allow the production of a material having useful mechanical properties. The effects of different processing temperatures and conditions on the molecular weight, complex viscosity, mechanical properties and melting behaviour are reported and discussed.

EXPERIMENTAL

The poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer studied is known by the trade name Biopol D610G (Zeneca Bio Products, Wilmington, Delaware, USA) and has an HV content of 12%. The resin contained a fully compounded nucleant and a plasticizer.[17] Experiments were performed with the as-received pellets and with pellets dried under vacuum at 100°C for 3 days. The melting transitions and molecular weight of these pellets, as determined with DSC and GPC, are presented in Table I.

Thermogravimetric Analysis

Weight loss studies as a function of time and temperature were carried out on dried and undried pellets with a DuPont TA 2950 thermogravimetric analyser (TGA) in a helium atmosphere. Dynamic measurements were performed from 25 to 350°C with a heating rate of 20°C/min. For isothermal measurements samples were heated at 20°C/min from 25°C to the desired temperature.

Tensile Properties

Tensile specimens were prepared in a Minimax CS130 MMV[18] by the following procedure. As-received, undried pellets were heated in the barrel for 2, 5, 10 or 20 min. The material was subjected to shear by rotation of the piston to obtain a homogeneous melt. The material was then injected into the desired mould to give a dumbbell-shaped specimen of 0.76 mm thickness. Samples were prepared at a barrel temperature of 170, 180 and 200°C and the temperature of the mould was set at 80°C. Fumes were observed during the preparation of the specimens at 180 and 200°C.

Tensile testing at room temperature was performed with an Instron 4201 one week after the preparation of the specimens. The clamp separation was 15 mm. The width of the sample was 4.8 mm and the crosshead speed was 5 mm/min. The reported values are the averages of five samples.

Differential Scanning Calorimetry

A DuPont 910 differential scanning calorimeter (DSC) was used to determine the melting behaviour of the dried and undried P(3HB-*co*-12%-3HV) pellets, of the tensile specimens and of the heat-treated samples. Samples were heated at 20°C/min in the 25–200°C range to record the melting point.

Isothermal heat treatment of P(3HB-*co*-12%-3HV) samples (5–10 mg) was performed in the same DSC apparatus. Samples were heated at 20°C/min to the desired temperature, held isothermally at this temperature for a specific time, then removed from the apparatus to cool to room temperature. Thereafter, a heating run (20°C/min) was performed to study changes in the thermal behaviour of the sample due to the heat treatment. Isothermal temperatures used were 170, 180, and 200°C and "treatment" times were 0, 5, 10, 15, 20 or 30 min.

Molar Mass Measurements

Gel permeation chromatography (GPC) was used to study variations in molecular weight as a function of thermal history. Samples analysed included the undried pellets, the materials treated in the DSC apparatus and the tensile specimens. The measurements were performed at 30°C in chloroform using a 10 μm PL Gel mixed bed column (Polymer Laboratories Inc., Amherst, MA) connected to a Spectra Physics 8430 RI detector and a 4290 integrator equipped with a GPC+ chip. Fifty μl of sample (0.5% w/v) dissolved in chloroform were analyzed. Chloroform was used as the mobile phase at a flow rate of 1.0 ml/min. A universal calibration was performed using monodisperse polystyrene (PS) standards. Only the Mark-Houwink constants for PS (K = 0.000049; a = 0.794)[19] were used since the precise values for P(3HB-*co*-12%-3HV) have not been reported.

Rheological Measurements

A Bohlin CSM 25 constant stress rheometer was used to study the rheological properties of P(3HB-*co*-12%-3HV) as a function of time at several temperatures. Time-sweep measurements in the plate-plate configuration, with a gap of approximately 1.2 mm, were performed at a frequency of 1 Hz and an applied stress of 25 Pa under a constant nitrogen flow at 160, 170, 180, and 200°C. Sample disks were prepared by compression moulding undried pellets for 10 min at 160°C under a load of 1000 psi. Fumes were observed during all tests and quite soon after the start of the test for those performed at 180 and 200°C.

RESULTS

Heating dried or undried P(3HB-*co*-12%-3HV) pellets up to 350°C resulted in complete weight loss due to thermal degradation between 225 and 250°C, as has been found for PHB.[11,20-22] Isothermal TGA measurements performed on dried pellets at 140, 160, and 170°C showed a weight loss of less than 1% during measurements that lasted up to 8 or 9 h. At 180°C, a weight loss of about 18% was observed after a residence time of almost 9 h while at 200°C an almost complete weight loss was obtained after about 200 min (Fig. 1). In contrast, for the undried pellets a total weight loss of approximately 10% was always found at 140, 160, and 170°C. This mainly occurred during heating from 25°C up to the desired temperature and during the first 10 min of isothermal heating. At 180°C, after an initial weight loss of about 10%, a more gradual decrease in weight was observed (Fig. 1). The process of thermal degradation was slow at 180°C and relatively fast at 200°C. At 200°C, the rate of degradation of the undried material, after an initial weight loss of approximately 10%, was almost the same as for the dried pellets (Fig. 1).

The values of the modulus of elasticity, E, (397.1 ± 9.0 MPa), and the strength at break, σ_b(18.9 ± 1.0 MPa), of the material processed for 2 min at 170°C (Fig. 2) compared well with those published by the
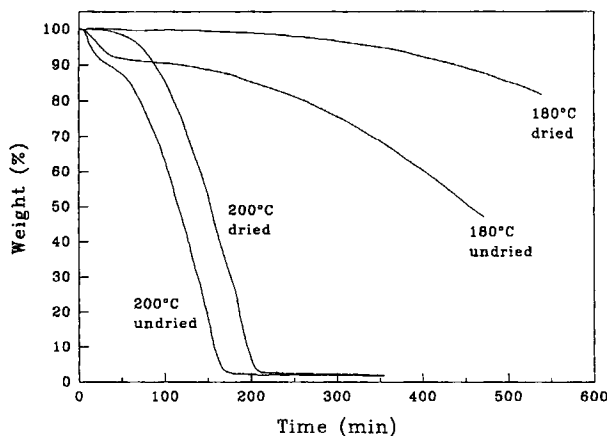
Figure 1 Weight loss as a function of time for dried and undried P(3HB-co-12%-3HV) at 180 and 200°C.

manufacturer (400 MPa and 20 MPa, respectively).[17] However, the values of the elongation at break, ϵ_b, differed significantly (18.8 ± 3.2% versus 42%).[17] This was probably due to differences in testing conditions, dimensions of the specimens and time-lapse between preparation and testing of the specimens.

The residence time in the Minimax at 170°C had little influence on the value of E but the modulus of elasticity increased as retention time increased at 180°C or higher (Fig. 2A). Processing at 170°C resulted in a slight reduction of σ_b with residence time while a more severe decrease of σ_b with increasing residence time was found at higher temperatures (Fig. 2B). The elongation at break, ϵ_b, was greatly influenced by the residence time and temperature (Fig. 2C), resulting in a two- or threefold decrease in ϵ_b with increasing time or temperature. Samples prepared at 200°C with a residence time of 10 min broke during clamping in the tensile tester due to their brittleness.

The melting points of dried and undried P(3HB-co-12%-3HV), as determined from the first heating DSC scan, are presented in Table I and the scans themselves are shown in Figure 3. The appearance of two (or more) melting transitions may be due to crystal thickening and/or recrystallization that occurred during the heating in the DSC.[14,15,23] Usually the lower-temperature peak is considered as the 'true' melting point since it represents the behavior of the original, unannealed crystals most closely. From this point of view, the value of the first peak of the undried material (134.4°C) compared well with the one given by the manufacturer, 136°C.[17] The DSC scans show that drying of the material influenced the shape of the curve but thickening or
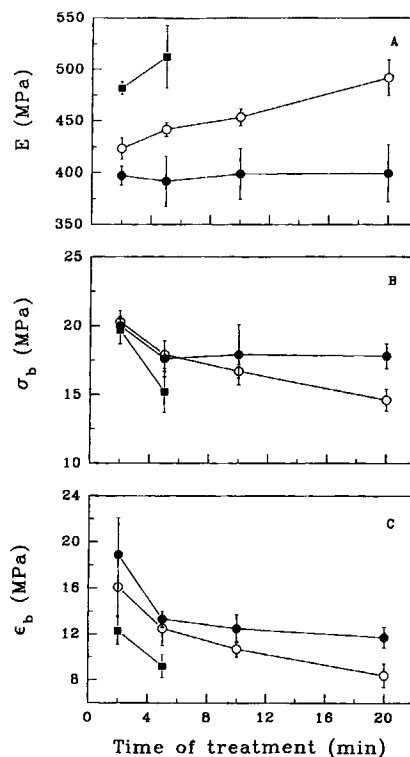

Figure 2 Modulus of elasticity, E (A), strength at break, σ_b (B) and elongation at break, ϵ_b (C) as a function of treatment time for P(3HB-co-12%-3HV) prepared at 170°C (●), 180°C (○) and 200°C (■).

recrystallization still occurred (Fig. 3). When compared to the undried material, a shoulder was found at the lower temperature transition and a new, higher temperature peak was found at 161°C after the drying procedure (Table I and Fig. 3).
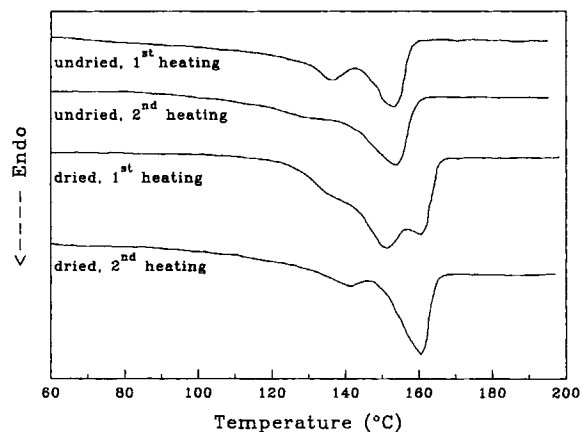

Figure 3 DSC-scans at 20°C/min of as-received, dried and undried P(3HB-co-12%-3HV) (1st heating) and of dried and undried samples after heating to 200°C and uncontrolled cooling to room temperature (2nd heating).

Table II   Melting Points of P(3HB-co-12%-3HV) Material Treated at 170, 180 and 200°C for Several Minutes

Treatment Temperature	Melting Point (°C) at Different Treatment Times (min)						
	0 min	2 min	5 min	10 min	15 min	20 min	30 min
Undried (DSC)							
170°C (sh)	131.2 ± 2.4		131.5 ± 0.3	131.4 ± 0.1	131.4 ± 0.1	132.4 ± 0.3	132.4 ± 1.7
(peak)	153.5 ± 0.8		154.0 ± 0.1	155.1 ± 0.1	155.4 ± 0.4	156.9 ± 0.1	157.0 ± 1.3
180°C (sh)	129.0 ± 0.3		129.7 ± 0.4	129.0 ± 1.6	130.9 ± 1.8	130.5 ± 0.5	129.5 ± 0.9
(peak)	152.6 ± 0.8		153.9 ± 0.1	155.1 ± 0.2	156.1 ± 1.3	156.2 ± 1.3	156.1 ± 0.5
200°C (sh)	128.8 ± 2.4		131.7 ± 1.3	127.3 ± 1.3	127.0 ± 4.8	121.7 ± 2.2	115.9 ± 4.7
(peak)	153.8 ± 0.7		156.6 ± 0.5	153.9 ± 0.1	152.1 ± 1.1	149.9 ± 1.0	145.6 ± 1.5
Dried (DSC)							
200°C (sh)	140.2 ± 0.1		139.0 ± 0.2	137.5 ± 0.4	135.4 ± 0.2	133.0 ± 0.5	127.4 ± 0.2
(peak)	160.2 ± 0.1		160.0 ± 0.2	158.6 ± 0.4	157.0 ± 0.5	154.8 ± 0.3	148.8 ± 0.4
Undried (Minimax)							
170°C (sh)		147.5 ± 0.1	147.6 ± 0.3	146.3 ± 0.2		145.6 ± 0.9	
(peak)		158.2 ± 0.1	159.0 ± 0.3	159.1 ± 0.2		158.9 ± 0.9	
180°C (sh)		144.6 ± 0.8	146.5 ± 0.8	144.7 ± 0.7		147.6 ± 2.0	
(peak)		158.6 ± 0.8	158.9 ± 0.8	159.0 ± 0.3		160.2 ± 1.1	
200°C (sh)		144.3 ± 0.1	145.7 ± 0.8	136.0 ± 4.3			
(peak)		158.3 ± 0.1	159.3 ± 0.4	155.9 ± 0.8			

sh = lower temperature transition; peak = higher temperature transition.

A second heating scan was performed on dried and undried material that were heated to 200°C and removed immediately from the DSC apparatus. For both materials a pronounced higher-temperature transition (peak) and a weak, lower-temperature transition (shoulder) were observed, indicating that a large proportion of both materials appeared to have undergone crystal thickening or recrystallization during the heating (Fig. 3). The value of the higher-temperature melting transition of the dried material is higher than that of the undried sample. The values of these melting transitions of P(3HB-co-12%-3HV) treated for several minutes at different temperatures in the DSC are presented in Table II. A slight increase in both transitions with treatment time was observed at 170 and 180°C for the undried material. A treatment time of 5 min at 200°C resulted in an increase of both melting transitions for the undried material while longer treatment times caused a decrease, due to degradation of the material. Treatment of the dried material at 200°C resulted in a gradual decrease of the melting transitions with increasing treatment time (Table II).

The melting behaviour of tensile test specimens prepared in the Minimax differed from that of the DSC-treated samples. All tensile specimens showed two melting peaks while only one peak was observed for the samples treated in the DSC [Figs. 4(A) and (B)]. The area under the higher-temperature peak increased with time and temperature for the tensile specimens. Longer residence times at 170 and 180°C resulted in a slight increase of the melting transition while at 200°C a decrease was found for residence times longer than 5 min (Table II).

For both undried samples heated in the DSC apparatus, and tensile test specimens prepared in the Minimax, a decrease of the molecular weight occurred with increasing treatment time (Fig. 5). The decrease was more pronounced at higher temperatures and was slightly more severe for material prepared in the Minimax apparatus due to the mixing. Increasing the time of treatment resulted in complete breakdown of the polymer to low molar mass fragments, as indicated by the plateau for the material heated at 200°C in the DSC.

Rheological measurements, performed on melt-pressed P(3HB-co-12%-3HV) disks, were started after different pre-heat times. The results obtained were corrected for the pre-heat time used in each experiment and thereafter were similar for several tests performed at a specific temperature. The correction was carried out to study the influence of time on the rheological properties from the moment that the sample touched one of the plates of the rheometer. Using this correction, it is possible to simulate the thermal history of pellets that will be processed on conventional melt processing equipment.
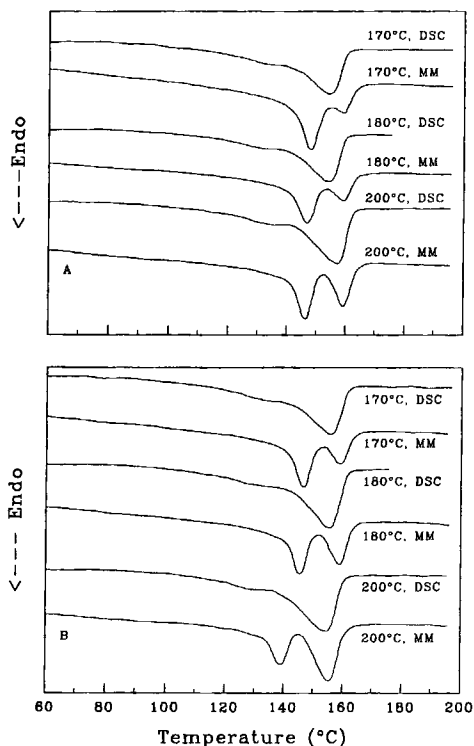
Figure 4   DSC-scans at 20°C/min of P(3HB-co-12%-3HV), quiescently heated (DSC) or "processed" (MM) for 5 min (A) and 10 min (B) at several temperatures.

Figure 6   Complex viscosity, corrected for time delays, as a function of time and temperature of melt-pressed P(3HB-co-12%-3HV).

The complex viscosity of samples measured at a frequency of 1 Hz under an applied stress of 25 Pa decreased with time at a specified temperature (Fig. 6). The decrease in viscosity was more rapid (indicating a more severe degradation) at higher temperatures. A reasonable limit for viscous stability was assumed to be a decrease of 10% within the first
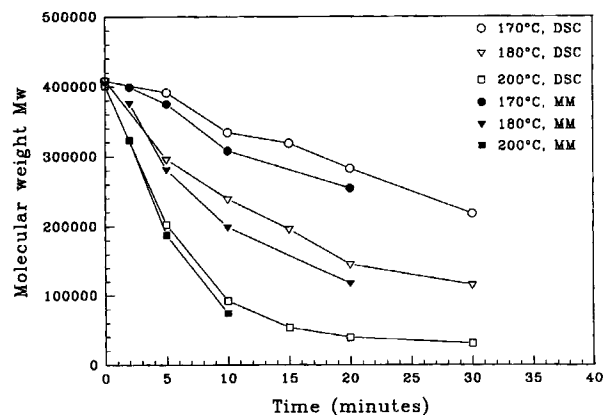
5 min. When the initial portion of the viscosity curves are observed in more detail (Fig. 7) it is clear that the polymer exhibited viscous stability only at 160°C. At 170°C, a 10% reduction in the complex viscosity was already obtained after 200 s while a residence time of only 2 min resulted in a decrease in viscosity of almost 10% at 180°C and of more than 20% at 200°C.

DISCUSSION

Two distinct effects influencing the properties of commercially available P(3HB-co-12%-3HV) copolymer have been revealed by the experiments reported above. First, there was the loss of plasticizer which mainly influenced the thermal properties.

Figure 5   Weight average molecular weight, M_w, as a function of treatment time and temperature for quiescently heated (DSC) and "processed" (MM) P(3HB-co-12%-3HV).
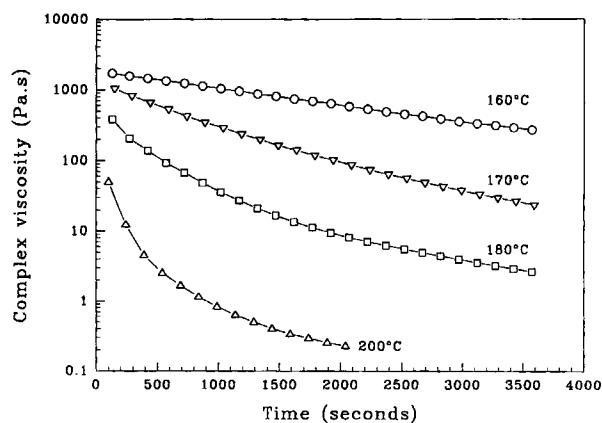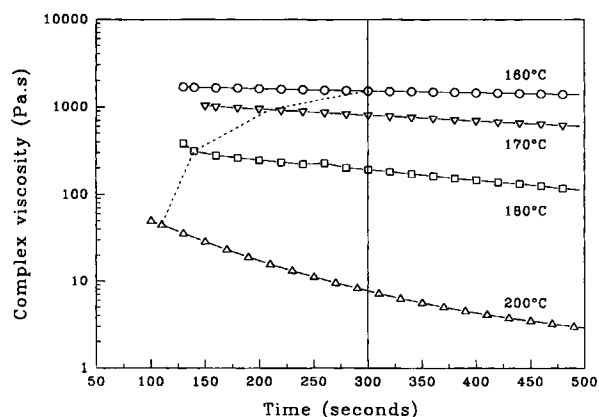

Figure 7   Influence of time on the complex viscosity of P(3HB-co-12%-3HV) during the first 500 s of testing at several temperatures; ---- = tie line representing 10% decrease in viscosity.

Secondly, there was a decrease in molecular weight due to thermal degradation which strongly influenced the polymer properties. These issues will be discussed separately.

Effect of Plasticizer

P(3HB-co-12%-3HV) should be thermally stable below $160°C$[12] and the formation of volatile degradation products is unlikely to happen below or at this temperature.[11] The minor weight loss found for dried samples measured at $160°$ or lower shows that volatile products were not present or formed which confirms the stability of the polymer under these conditions. Drying of the polymer at $100°C$ for 3 days resulted in the evaporation of moisture. However, a moisture content of 10% is probably too high for this polymer. The weight loss observed for the undried samples at $170°C$ or lower therefore has to be attributed to both the evaporation of moisture and of the plasticizer. The results with the dried samples indicate that the plasticizer was lost during drying. The time for complete evaporation of the plasticizer decreases with increasing temperature, but even at 180 and $200°C$, this time is much longer than typical residence times in conventional processing equipment.

Plasticizers influence the thermal behaviour of thermoplastic polymers by decreasing their glass transition temperature T_g and/or their melting temperature T_m and by suppressing the formation of perfect crystals.[24,25] The plasticizer added to P(3HB-co-12%-3HV) will probably influence the crystal thickening or reorganization that should occur when the polymer is heated.[14,15,23,26] Drying of P(3HB-co-12%-3HV) was performed below its melting point. Therefore, melting and recrystallization, in the absence of a plasticizer, could only have occurred during heating in the DSC. Higher melting, unplasticized crystals were formed in the dried sample but lower melting, plasticized crystals, as found in undried samples, were also present as seen by the peak at approximately $150°C$ (Fig. 3). The heating rate was probably too high to ensure a complete reorganization of all material. Reheating of such a sample resulted in a single, higher-temperature melting peak for the dried material, indicating only the presence of unplasticized crystals. A large proportion of both dried and undried material underwent crystal thickening and/or recrystallization during the reheating, due to the presence of only a small number of original crystals formed during the uncontrolled cooling (small shoulder in Fig. 3). The 7–8°C difference between the melting tran-

sitions (both shoulder (sh) and peak) of dried and undried samples (Table II) is comparable to the difference between unplasticized and plasticized commercial samples.[17] This further confirms that the dried samples must have lost the plasticizer during the drying process.

Evaporation of the plasticizer from undried P(3HB-co-12%-3HV) occurred relatively slowly at 170 and $180°C$ (Fig. 1). Therefore, only part of the plasticizer evaporated during quiescent thermal treatment in the DSC apparatus at these temperatures resulting in a slight increase in the thermal transitions with time for material treated this way (Table II). Undried samples treated for 5 min at $200°C$ showed higher melting transitions while longer heating times resulted in a decrease in melting transitions, indicating that thermal degradation of the polymer was more pronounced (Table II). Reheating the dried polymer, quiescently treated at $200°C$ for 10 min or longer, confirms that a severe thermal degradation occurred at $200°C$ (Table II). A similar influence of time was found for the thermal transitions of tensile specimens prepared in the Minimax at 170, 180, and $200°C$ (Table II). The thermal transitions were found at slightly higher temperatures, due to a more severe loss of the plasticizer during mixing.

The presence of two melting peaks for all tensile specimens may be the result of the preparation method. Crystallization probably occurred in the mould at $80°C$. The first peak represents the melting of original crystals formed at $80°C$ while the second one represents the melting of crystals formed by thickening or recrystallization during the heating process. The uncontrolled cooling of the DSC-treated samples resulted in a crystallization at a lower temperature than $80°C$, which makes the determination of the melting of original crystals difficult due to the thickening effects that occur during the heating.[23,27]

Effect of Thermal Degradation

GPC measurements clearly showed that thermal treatment of P(3HB-co-12%-3HV) results in a breakdown of the polymer chains, most likely via a random chain scission mechanism comparable to that of PHB and P(3HB-co-3HV) copolymers.[5,10–12,22] Provided that the chain scission is completely random and that no volatilization occurs during the thermal degradation, the number-average degree of polymerization $P_{n,t}$ at time t is given by[28]

$$\frac{1}{P_{n,t}} - \frac{1}{P_{n,0}} = k_d t \qquad (1)$$

where $P_{n,0}$ is the initial number-average degree of polymerization and k_d is the rate constant of degradation. The k_d values of P(3HB-co-12%-3HV) in the temperature range of 170–200°C, as determined from the slopes of the plots of eq. (1), (data in Table III) and compare well with those reported for other PHA polyesters.[12,16] The k_d values of the Minimax processed tensile specimens were higher than those of quiescently heat treated material which indicates that the shearing forces and the more efficient heat transfer in the Minimax resulted in a more severe breakdown of the polymer chains.

The weight loss of P(3HB-co-12%-3HV) at 180 and 200°C, after the initial loss of the plasticizer, was undoubtedly due to the evaporation of volatile degradation products. At 200°C, this weight loss started about 15 min after the desired temperature was achieved (Fig. 1) and a severe decrease in molecular weight was obtained for samples treated for 15 min at 200°C (Fig. 5). The fumes, observed during the preparation of tensile specimens and during rheological measurements at 200°C, most likely consisted of the plasticizer and degradation products. Although a significant decrease in molecular weight with time occurred the formation of volatile products was much slower at 180°C (Fig. 1). It is likely that the fumes observed during preparation of tensile specimens at this temperature were due to evaporation of the plasticizer. However, volatile degradation products were part of the fumes that

evaporated during longer lasting rheological measurements at 180°C.

Short-chain polymers possess lower values of strength and elongation at break and higher values of the modulus than long-chain polymers.[29] The mechanical properties of P(3HB-co-12%-3HV) prepared at 180 and 200°C indicate that short-chain polymers were present in these samples and was confirmed by the low molecular weights measured (Figs. 2 and 5). For the material prepared at 170°C, a decrease in molecular weight with residence time resulted in a more brittle material with a lower strength and elongation at break. The value of the modulus of elasticity remained almost unchanged, probably due to the crystal structure of the samples. The short residence times used to prepare the samples allowed only very small amounts of the plasticizer to evaporate suggesting that enough plasticizer was present in the material to contribute to the formation of similar crystals in all samples prepared at 170°C.[30]

The decreasing of the tensile strength with residence time of P(3HB-co-12%-3HV) at 180°C or higher is comparable to that found for PHB and P(3HB-co-5%-3HV).[16] All three polymers showed a decrease in molecular weight with treatment time at these temperatures resulting in the formation of brittle material. However, for P(3HB-co-5%-3HV) a decreasing modulus of elasticity with time was reported and this is contradictive to the explanation on embrittlement due to the formation of spherulites with a large diameter, as given by the authors.[16]

The breakdown of the polymer chains greatly influenced the rheological behavior of P(3HB-co-12%-

Table III   Molecular Weight of P(3HB-co-12%-3HV) Treated for Different Times at 170, 180, and 200°C Gave K_d Value in the DSC of 1.3 × 10⁻⁵, 3.2 × 10⁻⁵, and 1.5 × 10⁻⁴ Min⁻¹ and in the Minimax Apparatus of 3.7 × 10⁻⁵, 6.4 × 10⁻⁵, and 1.8 × 10⁻⁴ Respectively

Temperature	170°C			180°C			200°C		
	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
Treated in DSC									
0 min	408,100	167,300	2.44	409,000	161,700	2.53	401,100	163,700	2.45
5 min	391,200	131,100	2.98	295,900	123,300	2.40	202,500	102,300	1.98
10 min	334,100	131,500	2.54	239,000	107,200	2.23	92,100	41,500	2.22
15 min	318,800	120,800	2.64	196,000	90,300	2.17	53,300	30,100	1.77
20 min	282,800	115,400	2.45	145,700	73,600	1.98	39,300	22,300	1.76
30 min	218,000	96,000	2.27	115,200	57,900	1.99	30,600	19,300	1.59
Treated in Minimax									
2 min	399,100	130,200	3.07	375,600	110,800	3.39	322,900	109,100	2.96
5 min	375,000	125,100	3.00	281,000	96,900	2.90	187,400	74,300	2.52
10 min	307,800	121,700	2.53	198,700	70,400	2.82	74,000	34,900	2.12
20 min	254,300	64,900	3.92	117,700	49,700	2.37	—	—	—

3HV) (Figs. 6 and 7). When the limit for viscous stability is assumed to be a viscosity reduction of 10% within the first 5 min, then this polymer exhibits viscous stability at temperatures lower than 170°C only. At 170°C, extreme care is required to keep the residence time in the processing equipment as low as possible. Retention times as short as 3 min resulted in a 10% reduction in viscosity (Fig. 7), due to a decrease in molecular weight (Fig. 5). The rheological results compare well with MFI-data of P(3HB-*co*-3HV) copolymers at temperatures of 170°C and higher.[5] The results show that processing of P(3HB-*co*-12%-3HV) copolymer should be performed at 160°C or lower as with other PHA copolymers.[12]

CONCLUSIONS

The effects of thermal history on several of the most important properties of a single PHA copolymer, P(3HB-*co*-12%-3HV), were studied. Thermal treatment of P(3HB-*co*-12%-3HV) at a temperature of 170°C or higher resulted in a loss of its plasticizer. This mainly affected the thermal behaviour of the polymer by increasing its melting transitions with time of heat treatment. The loss of the plasticizer did not significantly influence the mechanical and rheological properties of the polymer. The time for complete evaporation of the plasticizer decreased with increasing temperature but was always much longer than usual residence times in processing equipment.

P(3HB-*co*-12%-3HV) was thermally unstable at temperatures higher than 170°C. The breakdown of the molecules, probably by a random chain scission process, resulted in short polymer chains leading to a deterioration of the mechanical properties and a rapid decrease of the complex viscosity. A processing temperature of 170°C allowed the production of materials with useful properties but residence times of less than 5 min were required. Although the change of the modulus of elasticity with time was relatively marginal, there was a decrease in the molecular weight and in viscosity after 5 min at 170°C. Increasing the time of exposure at 170°C resulted in a decrease of the strength and elongation at break, indicating that a more brittle material was formed. This decrease was caused by the decrease of the molecular weight which influenced these parameters more than the modulus of elasticity. The lack of change in the modulus of elasticity was probably due to the presence of a relatively large amount of plasticizer. Materials prepared at 180 and 200°C

were more brittle and longer residence times resulted in a further deterioration of the mechanical properties. The rate constant, k_d, of thermal degradation was slightly higher for P(3HB-*co*-12%-3HV) samples prepared in the Minimax apparatus than for quiescently treated material and its value increased with temperature.

The loss of the plasticizer, but especially the breakdown of the polymer at elevated temperatures, shows that extreme care is required for the processing of P(3HB-*co*-12%-3HV). Materials with useful properties can only be obtained at temperatures at or below 170°C. A decrease in molecular weight and complex viscosity was still observed when the polymer was heat treated for only 2 min at 170°C. This process of thermal breakdown is supposed to continue when the polymer is processed several times under the same conditions and might limit its use for recycling although it has been reported that four processing cycles had little deleterious effect on the mechanical properties of P(3HB-*co*-11%-3HV).[31]

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