Materials Research. 2013; 16(2): 327-332 DOI: 10.1590/S1516-14392012005000180

# The Influence of the Industrial Processing on the Degradation of Poly(hidroxybutyrate) – PHB

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Received: May 28, 2012; Revised: October 6, 2012

PHB was characterized after different industrial processes by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Melt Flow Index (MFI), Complex Dielectric Relaxation (CDR) and Size Exclusion Chromatography (SEC). Some properties of PHB were investigated before and after processing, in order to understand how temperature and other extrusion or injection conditions affect the polymer degradation. All the processed samples showed an increasing in the melt flow index, a decreasing of the dynamic crystallization temperature, and a reduction in the molar mass, suggesting some degradation. The molar mass reduction after processing, predicted when only thermal degradation is considered, was calculated in function of the kinetic parameters, such as constant thermal degradation and residence time during the industrial processing. It was found that the real molar mass reduction was higher than the theoretical value, indicating an important contribution of the shearing of polymeric chains during processing in the PHB degradation.

**Keywords:** poly(hydroxybutyrate), PHB, biodegradable polymer, degradation

### 1. Introduction

Poly(hydroxybutyrate) – PHB – is a biodegradable polymer that can be synthesized by bacterial fermentation using renewable raw materials such as sugarcane<sup>1</sup>. PHB has high crystallinity, hydrophobicity, is a 100% biodegradable<sup>2</sup> and, like most thermoplastics, can be processed by extrusion, injection, and melt press molding<sup>3</sup>. However, PHB has a limited stability at high temperatures required for melting processes<sup>4,5</sup> and undergoes thermal degradation, which affects its physical and mechanical properties, impairing industrial application<sup>6</sup>.

It has been shown that the thermal degradation of PHB is caused almost exclusively by a random scission on the ester bond at high temperatures (above 200 °C). This degradation is stereoselective, by a non-radical cis-elimination mechanism and shearing of the polymeric chain, leading to the reduction of the molar mass of the polymer and the formation of crotonic acid, with an activation energy of 235 kJ<sup>7,8</sup>. It was found that, after processing, the viscosity of PHB decreases due to degradation by random leakage of polymer chains. In extrusion, the molecular weight is proportional to the residence time, although no relation was found between the polidispersivity and the same parameter<sup>9</sup>. Further studies about mechanical properties of extruded PHB showed that the average number of molecular weight decreases with the increasing of temperature and screw speed, along with a significantly drop observed for the elongation and stress at break values, while elasticity modulus was not affected<sup>10</sup>.

On the other hand, the biodegradation rate of PHB increases when the polymer is processed at higher temperatures, which is explained by the decreasing of the polymer crystallinity, which facilitates the capability of the extra-cellular enzymes responsible for PBH degradation to attack its chains<sup>11</sup>.

More recently, some efforts to overcome the poor processing window of PHB are directed to the preparation of copolymers with, for example, poly-(3-hydroxyvalerate (HV)<sup>12</sup> or poly-(3-hydroxyhexanoate) (HH)<sup>13</sup>. Thermal, rheological and mechanical properties of these copolymers were investigated, showing the improvement on thermal stability for some compositions, although they are still unstable at temperatures higher than 160 °C. The use of polymeric additives such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN) and biocompatible polyvinylpyrrolidone (PVP) were also studied, in order to achieve thermal stability and controlled crystallization of PBH<sup>14</sup>. The results indicate that crystallization rate, crystallinity, and crystal size were significantly affected, because the additives affected the degraded reaction, highlighting the correlation between crystallization and the PHB thermal degradation.

Most studies about PHB degradation are concerned only about thermal degradation, and were carried out

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using samples prepared in laboratory conditions, such as casting, compression using molding sheets, or even the PHB powder without any processing methodology. To be suitable for common industrial applications, however, PHB should be processed in large scale, mostly by melt processing techniques such as extrusion and/or injection. In this case, the polymeric chains are submitted not only to high temperatures (above 170 °C for PHB), but also to the shearing tension. When this tension is excessive, it may lead to a scission on the polymeric chain, causing reduction in the molar mass and characterizing a further degradation.

Based on these findings, the present work aims to characterize the degradation caused by heating and/or shearing resulting from the melt processing of PHB. Techniques such as Differential Scanning Calorimetry, Melt Flow Index, Complex Dielectric Relaxation, Infrared Spectroscopy and Size Exclusion Chromatography were used to study changes of molar mass and chemical structure in samples of PHB after common industrial processing, such as extrusion, or extrusion followed by injection.

# 2. Experimental

The poly(hydroxybutyrate) – PHB – ( $\overline{M_w}$  of 534,000 g.mol<sup>-1</sup>) was manufactured at PHB Industrial S/A by the FE 145 fermentation process. Table 1 lists extrusion and injection parameters which represent an optimized situation of processing with minimum thermal degradation. PHB is a white powder that was processed in an Imacom modular twin-screw co-rotational extruder L/D = 30, in order to produce PHB pellets. For studies about degradation after extrusion and injection, these pellets were then processed in an Arburg 270V-300-120 Allrounder injection machine, with a mold for injecting tensile (ASTM 638) and impact (ASTM 256) test specimen. Residence time of PHB during extrusion and injection was measured as 30 seconds for each processing step.

Thermal studies were made by Melt Flow Index (MFI) and Differential Scanning Calorimetry (DSC). MFI measurements were taken according to the condition foreseen for polyethylene under the ASTM 1238 standard, using a DSM MI-1 plastometer at 190 °C, under a load of 2,160 g and cut-off time of 10 seconds. A TA Instruments DSC Q100 calorimeter was used for the DSC characterization in the range of –25 to 200 °C at a heating rate of 20 °C/min and a cooling rate of 80 °C/min under N,

atmosphere. The crystallinity ( $X_c$ ) was calculated from the melting peak in conventional DSC curves as follows:

$$X_c = \frac{\Delta H_{\text{exp}}}{\Delta H_{100\%}} \tag{1}$$

Where  $\Delta H_{exp}$  is the area of the melting peak obtained by the experimental curves, and  $\Delta H_{100\%}$  is the enthalpy for 100% crystalline PHB ( $\Delta H_{100\%}$  = 146 J.g<sup>-1</sup>) taken from literature<sup>15</sup>.

Changes on polymers structure after processing were investigated by Fourrier-Transformed Infrared Spectroscopy (FT-IR), Size Exclusion Chromatography (SEC), and Complex Dielectric Relaxation (CDR). IR spectra were recorded by a Perkin Elmer Spectrum 1000 FTIR spectrometer, in the region 4000-400 cm<sup>-1</sup>. A Tosoh chromatograph with a refraction index detector system was used to characterize the molar mass of PHB before and after processing by SEC. The solvent in the mobile phase was chloroform and the analytical column (300 mm  $\times$  7.8 mm) used was Water Styragel HR (7.8 × 300 mm). Dielectric relaxation experiments (CDR) were performed using a Novocontrol GmbH Concept 12 System coupled to a Solartron SI 1260 Impedance analyzer and a measuring cell. PHB films of ≈30 µm in thickness were prepared by dissolution in chloroform and subsequent casting at room temperature. Circular Au electrodes (3 cm in diameter) were deposited onto the film surfaces by sputtering. Measurements on the frequency domain of the real and imaginary parts of the dielectric function were taken from  $10^{-1}$  to  $10^{7}$  Hz, from -150 to 170 °C.

#### 3. Results and Discussion

Initial investigations with the Fourier Transform Infrared Spectroscopy (FT-IR) and Complex Dielectric Relaxation (CDR) techniques were concerned on the chemical structure of PHB before and after extrusion, in order to evaluate if this process could yield degradation products that would influence its properties, such as crystallinity and mobility of the polymeric chain. In order to characterize PHB degradation due to procedure, injected samples were also studied, in which were analyzed, by Size Exclusion Chromatography (SEC), Differential Scanning Calorimetry (DSC) and Melt Flow Index (MFI) along with all the processing cycle, modifications of molecular weights and thermal properties.

**Table 1.** Processing parameters used for PHB extrusion and injection.

		PHB	Extrusion						
C C	Floor (loo/le)	Temperature (°C)							
Screw Speed (RPM)	Flow (kg/h)	<b>Z</b> 1	<b>Z</b> 2	<b>Z</b> 3	<b>Z4</b>	<b>Z</b> 5	Die	Melted	
200	1.5	100	150	165	165	170	170	175	
		PHB	Injection						
Pressure (l	Temperature (°C)								
Final	Holding	<b>Z</b> 1	<b>Z</b> 2	<b>Z</b> 3	<b>Z4</b>	Z	.5	Mold	
560	330	158	162	174	174	17	72	30	

# 3.1. Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 1 shows the IR spectra of PHB before and after processing by extrusion. The characteristic absorption bands of PHB can be seen at 2928 cm<sup>-1</sup> corresponding to the methylene C-H vibration, the symmetric -C-O-C- stretching vibration in the range of 800-975 cm<sup>-1</sup> and the C=O stretching at 1722 cm-1[16]. There are many studies regarding the use of FT-IR technique to determine the crystallization degree of PHB by monitoring the C=O stretching vibrational region (1780-1700 cm<sup>-1</sup>)[17,18]. It is known that the most evident spectral changes during PHB crystallization are in the carbonyl band at 1740-1720 cm<sup>-1</sup>, where the amorphous phase presents a broad band near 1738 cm<sup>-1</sup>, while the crystalline phase band shifts to lower wavenumbers near 1722 cm<sup>-1[13]</sup>. Also, the asymmetric -C-O-C- stretching vibration in the range of 1180-1150 cm<sup>-1</sup> may shift, when the degree of crystallization is reduced after the processing<sup>14</sup>. According to these findings and since no significant differences between samples before and after processings were observed in all spectra of Figure 1, it can be concluded that the extrusion conditions showed at Table 1 causes no effect in the reduction of the degree of crystallization or cause drastic chemical changes on the PHB chain.

## 3.2. Complex Dielectric Relaxation (CDR)

CDR analysis was used in order to determine glass transition temperature (T<sub>o</sub>) and possible changes on the polymer chains mobility caused by their reduction size in PHB samples. Figure 2 shows plots of the dielectric loss,  $\varepsilon$ ", as a function of temperature at different frequencies for PHB before (Figure 2a) and after (Figure 2b) extrusion. Two main relaxation processes, which appear as a maximum in  $\varepsilon$ " ( $\alpha$  and  $\beta$ , in order of decreasing temperature), were detected in the investigated temperature range. The graphs of dielectric relaxation at constant frequency (isochronal graphs) show a  $\beta$ -relaxation starting at -50 °C, and an α-relaxation starting at 0 °C. It is known that PHB presents these primary  $\alpha$  and  $\beta$  relaxations<sup>19,20</sup>, where  $\beta$ -relaxation was attributed to local shifts of ester groups attached to the polymeric chains, while the α-relaxation was ascribed to shifts in the polymer chains in the amorphous phase in the range of the glass transition temperature. These relaxations also shift to higher frequencies as the temperature rises, due to the higher mobility resulting from heating. The temperature dependence of the  $\beta$ -process follows an Ahrrenius behavior, while the  $\alpha$ -process displays a curvature at the higher measured frequencies characteristic of a Vogel-Fulcher-Tamman dependence, as already observed in previous works19,20.

For semi crystalline polymers, like PHB, at temperatures higher than  $T_g$ , the amorphous polymer chains are confined to move between the crystalline regions. This restriction leads to an  $\alpha$ -relaxation behavior, well established in literature by the CDR technique. When some degradation occurs, it can result in a polymer crystallinity variation, leading to a modification in the dynamics of the  $\alpha$ -relaxation. If the polymer degradation improves crystallinity, its  $\alpha$ -relaxation will change in three aspects: a) a decrease in the intensity;

b) an increase in relaxation time; and c) a concurrent change in its shape, where amorphous systems are asymmetric and the presence of crystals produce a broadening and a symmetrization of the relaxation. A comparative analysis

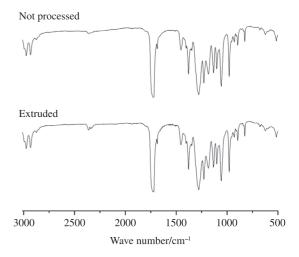
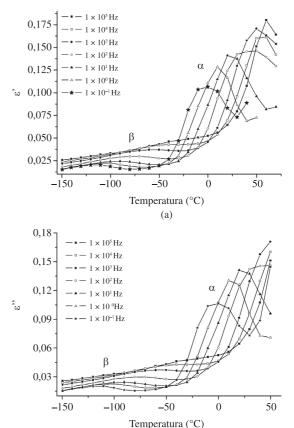


Figure 1. FT-IR spectra of PHB before and after processing by extrusion.



**Figure 2.** Isochronal dielectric loss,  $\varepsilon$ ", as a function of temperature for PHB before and after processing by extrusion from  $10^{-1}$  to  $10^{5}$  Hz.

(b)

<b>Table 2.</b> Thermal transitions of PHB before and after processing measured by DS	Table 2, T	Thermal	transitions o	f PHB	before	and after	processing	measured by	DSC
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РНВ	$T_g$ (°C)	$T_{cc}$ (°C)	$\Delta H_{cc} \left( \mathbf{J.g^{-1}} \right)$	$T_m({}^{\circ}\mathbf{C})$	$\Delta H_{_{m}}\left(\mathbf{J}.\mathbf{g}^{-1}\right)$	Crystallinity $X_c^*(\%)$
Before processing						
1st Cycle	-	-	-	139 168	11.6 79.7	7.95 54.6
2 <sup>nd</sup> Cycle	0.25	61.5	-69.5	168	82.7	56.6
Extruded						
1st Cycle	-	-	-	166	85.9	58.8
2 <sup>nd</sup> Cycle	1.05	50.3	-39.6	169	89.0	61.0
Extruded and injected						
1st Cycle	-	-	-	171	82.0	56.1
2 <sup>nd</sup> Cycle	1.30	49.8	-38.0	170	89.0	61.0

<sup>\*</sup>Xc = degree of crystallinity estimated from the DSC thermograms as described in Equation 1. The standard deviations (σ) are smaller than 2 °C.

of the isochronal graphs in Figure 2, however, indicates a similar behavior for PHB before and after extrusion, presenting a  $T_{\rm g}$  of 1.0 °C for both samples. These results show that processing did not affect the polymeric relaxation for PHB, but a further thermal analysis is needed in order to investigate crystallization processes after extrusion and injection.

# 3.3. Differential Scanning Calorimetry (DSC) and Melt Flow Index (MFI)

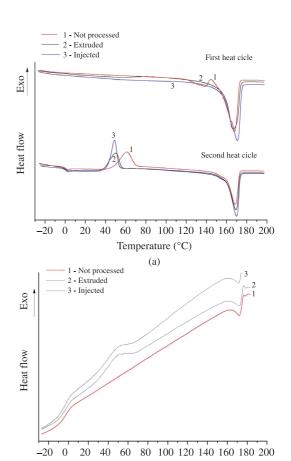
Figure 3 shows DSC thermograms of PHB samples in the first and second heating runs and in the cooling scan. First heating cycle shows an endothermic peak assigned as the polymer melting. The curve of no processed PHB indicates the presence of spherulites with melting temperature slight inferior than the whole material. This behavior is not seen by the processed samples since they had already suffered a heating cycle during extrusion and injection, promoting the previous melting of these small crystals and completely mixture into the polymer.

In the second heating cycle, it is possible to estimate the glass transition temperature  $(T_a)$  as the shift near 1.0 °C in the thermograms of all studied samples (as already verified by CDR results), while the endothermic peaks indicate the melt temperature  $(T_m)$  near 170 °C. Table 2 shows the specific values of temperature and enthalpy for all transitions for the three samples. No significant variation was observed in the glass transition and melt temperatures for PHB before and after processing. However, in the second cycle, the exothermic peak, frequently attributed to crystallization, indicates that cold crystallization temperature  $(T_{cc})$  decreased in value when PHB is processed. The crystallization enthalpy of processed PHB is also reduced due to the partial crystallization occurred in the cooling scan between the first and second heating runs. This behavior suggests that the polymer crystallization is facilitated after processing and a higher crystallization enthalpy is observed when PHB is extruded and injected.

On the other hand, the melt flow index, Table 3, increases after every processing step. The effect of rising MFI (greater fluidity) is related to the higher mobility of the polymer chains, which occurs by the chain shearing due to degradation after extrusion and injection. The reduction

**Table 3.** Melt Flow Index of the three PHB samples.

РНВ	Melt Flow Index (g/10 minutes)		
Before processing	19 ± 2		
Extruded	$21 \pm 2$		
Extruded and injected	$26 \pm 2$		



**Figure 3.** DSC curves showing: a) first and second heating runs, and b) cooling scan of PHB before processing, after extrusion and after extrusion followed by injection.

Temperature (°C)

(b)

**Table 4.** Molar mass values measured by SEC, and calculated considering only the thermal degradation effect for PHB samples before and after extrusion and injection processing.

РНВ	$\overline{M_n}$ (10 <sup>3</sup> g.mol <sup>-1</sup> )	$\overline{M_{\scriptscriptstyle W}}~(10^3~{\rm g.mol^{-1}})$	Polydispersity $\left(\frac{\overline{M_{_{W}}}}{\overline{M_{n}}}\right)$	$\overline{M_n}$ * (theoretical)
Before processing	246	535	2.17	-
Extruded	175	383	2.19	245
Injected	104	208	1.99	244

<sup>\*</sup>Molar mass values calculated according to Kuniok et al.4, using  $k_d = 2.2.10^{-8} \,\mathrm{min^{-1}}$  at 175 °C.

observed in  $T_{cc}$  may be related to the increasing mobility of the polymeric chains, caused by the reduction in molar mass, when shearing and thermal degradation occur due to process. This interpretation is also congruent with the degradation mechanism of PHB, which is based on cis-elimination reactions and scission of the polymeric chain, lowering its molar mass<sup>4,5</sup>.

# 3.4. Size Exclusion Chromatography (SEC)

In order to corroborate the interpretation of the results showed by DSC and MFI analysis, the variation in the PHB molecular weight after each processing step was investigated by SEC. Table 4 shows the molar mass values obtained from PHB before process, and samples obtained after extrusion and injection. These results show a huge drop of PHB molar mass after each processing step, and it also observes a reduction in the polydispersity, proportional to the reduction of the molar mass, which indicates a systematic and preferential rupture of the high length chains. According to Kunioka et al.<sup>4</sup>, this chain rupture occurs by a random scission of an ester group of the structure, generating low molar mass products and forming carboxylic and crotonate vinyl groups in a rate calculated by Equation 2:

$$\frac{1}{P_{N,1}} - \frac{1}{P_{N,0}} = k_d.t \tag{2}$$

where  $P_{N,0}$  is initial average molar mass,  $P_{N,I}$  is the molar mass after a specific time t, and  $k_d$  is the thermal degradation rate, given by the Arrhenius relation, with an activation energy of 212 kJ.mol<sup>-1</sup>.

Using the residence time of PHB at extrusion and injection (0.5 minutes for each step) and the average molar mass of the polymer before processing (245,790 g.mol<sup>-1</sup>) as  $P_{N,0}$ , the average molar mass of the polymer after each processing step can be estimated, considering that there are losses only due to the thermal degradation at 175 °C ( $k_d = 2.2.10^{-8} \, \mathrm{min^{-1}})^{[4]}$ . Results calculated by using Equation 1 are also showed in Table 4. If only thermal degradation could occur during 0.5 minutes of extrusion at 175 °C, average molar mass loss of PHB should be only 0.3% of its original value, while experimental results showed a reduction of 29%. Similar conclusions can be taken when

results from injected PHB are analyzed. It suggests that the processing of PHB causes not only thermal degradation of the polymer, but the mechanical forces involved at extrusion and injection also promote the reduction of its molar mass by the shearing of the polymeric chains.

#### 4. Conclusions

The aim of this work is to understand the degradation occurred in PHB when this biodegradable polymer is processed in large scale by melt processing techniques such as extrusion and injection. Although thermal degradation of this polymer is largely studied, poor attention is paid to the effect of the mechanical forces that are also involved in the industrial processing techniques. Chemical changes in PHB after processing could not be detected by FT-IR and CDR, although evidences of some degradation were observed by the decreasing on the  $T_{\rm cc}$  and the increasing of MFI values after extrusion and injection. These effects are justified by the reduction of the molar mass when PHB is processed, causing the high mobility of its polymeric chains, as already predicted when thermal degradation occurs.

Molar mass data obtained by SEC for PHB before processing were used to estimate the reduction of molar mass, due to thermal degradation of the processed polymer and compared with the experimental values obtained from PHB after extrusion and after extrusion followed by injection. Results showed that the reduction of the polymeric chain after industrial processing was higher than expected, suggesting that thermal degradation was not the main cause to promote this decrease of the PHB molar mass. In the conditions studied in this work, the shearing of the polymeric chain existing in extrusion and/or injection processes acts as an important factor to considerate when dealing with large scale/industrial applications of PHB.

### Acknowledgements

Authors gratefully acknowledge Dr. Tiberio A. Ezquerra, Instituto de Esctrutura de la Materia, IEM-CISIC, for CDR analysis, and to PHB Industrial S/A for PHB supply. W. M. Pachekoski acknowledges CAPES and FAPESB/CNPq for financial support.

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