Antioxidant Efficiency of Irganox® 1010 on Processing and Properties of Plasticized Poly(3-Hydroxybutyrate) Films

Mayte M. Quispe[1], Olivia V. López[1] and Marcelo A. Villar[1,2,*]

[1]*Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Camino La Carrindanga Km 7, 8000, Bahía Blanca, Argentina*

[2]*Departamento de Ingeniería Química, Universidad Nacional del Sur, Alem 1253, 8000, Bahía Blanca, Buenos Aires, Argentina*

Abstract: Polyhydroxybutyrate (PHB) is one of the few biopolymers that can be processed at industrial scale. Nevertheless, PHB applications in film form are limited, mainly due to the high biopolymer crystallinity and its narrow thermal processing window. In this work, it was studied the effect of glycerol tributyrate (GTB) incorporation as plasticizer, in addition to Irganox® 1010 (I) as phenolic antioxidant on the processability and final properties of PHB-based films. PHB was melt processed in the presence of GTB (5-30 %w/w, PHB basis) and Irganox® (0.3 %w/w, PHB basis) and films were obtained by thermo-compression. PHB films without the plasticizer and the antioxidant were used as control sample. Thermal properties of films demonstrated that PHB thermal processing window was increased due to a synergistic effect of both additives. Improvement can be attributed to changes in the crystalline structure corroborated by X-ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC). Oxygen Transmission Rate (OTR) of PHB films increased in the presence of GTB and Irganox due to the crystalline changes induced by both additives.

Keywords: Poly(3-hydroxybutyrate) films, Phenolic antioxidant, Glycerol-based plasticizer, Thermal processing, Crystalline structure.

1. INTRODUCTION

Polymers can be oxidized during their processing or final use, which results in the loss of chemical, optical, and mechanical properties, among others. Because of the combination of high temperature, often high shear stress and the presence of oxygen, polymers usually suffer degradation reactions by radical chain mechanisms, which lead to a change of the molecular structure by chain scission or crosslinking [1]. Thermal oxidation results in the formation of free radicals, which react with oxygen-producing oxy- and peroxy-radicals. Besides, these radicals can participate in many reactions between them or remove hydrogen from polymer chains [2]. Generally, several approaches are used to prevent early degradation of polymers, particularly during thermal processing. Therefore, a variety of additives have been used for these purposes with different success, including processing aids (plasticizers and lubricants), thermal and UV stabilizers, mineral and vegetable fillers, nano-fillers, as well as curing and grafting agents [3]. In the research field of biopolymers, one of the fundamental objectives of adding additives is to improve final mechanical properties.

Particularly, PHB has a pronounced brittleness, very low deformability, high susceptibility to rapid thermal degradation, challenging its processing by conventional technologies for thermoplastics polymers. These characteristics, along with a high price compared to commodity plastics, are considered the major obstacles for a broad application of this biopolymer [3]. The mechanism of PHB degradation is based on an elimination reaction with the formation of oligomers and crotonic acid [4]. A detailed study of PHB thermolysis found that thermal degradation is a statistical process based on a random chain scission but some kinetically favored scission occurs near the ends of the macromolecules [5]. Predominant polymorphism in PHB crystal structure is the α-form, which takes place under typical conditions of melting, cold, and crystallization. However, β-form can also be obtained in uniaxially stretched films, resulting in a metastable phase that can be re-annealed to the α-form at 130 °C with an increase in crystallinity [6]. According to some authors, β crystals are responsible for the high traction resistance of PHB films, mainly because these crystals are formed from the molecular chains stretching in the restricted amorphous region between small crystal nuclei, which act as cross-linking points [7, 8]. These authors stressed that the formation of these small crystals is generated by random chain scission during polymer thermal degradation. These shorter chains have greater mobility and can be packaged during crystallization [3]. Some alternatives to avoid polymer degradation could be a reduction of processing

---

*Address correspondence to this author at the Planta Piloto de Ingeniería Química - PLAPIQUI (UNS-CONICET), Bahía Blanca, Argentina;
Tel: +5492915732826; E-mail: mvillar@plapiqui.edu.ar

E-ISSN: 2311-8717/21

temperature and the addition of plasticizers in order to improve processing conditions [9]. Another option to overcome this drawback is the use of antioxidants during polymers processing to inhibit the beginning of the thermal oxidation and to retard the resulting degradative processes [10].

Phenolic antioxidants scavenge alkoxy and peroxy radicals by donating hydrogen radicals that neutralize these kinds of species formed through the harsh processing conditions in presence of oxygen or by the cleavage of hydroperoxides. Therefore, these additives protect polymers during processing, as well as in the final application, as long-term thermal stabilizer [11, 12]. Ghaffari and Ahmadian studied the performance of different phenolic antioxidants for the thermal oxidation stability of low-density polyethylene (LDPE) and reported that Irganox® 1010 is the most effective [13]. Irganox® 1010 is a primary antioxidant since its mechanism mainly resides in the ability of removing radicals from the polymer main chain, decomposing the hydroperoxides to non-radical products [14].

On the other hand, several studies have been published in the last years analyzing different plasticizers for PHB, being glycerol tributyrate (GTB) one of the most employed [15-18]. Plasticizers provide ductility that is suitable for injection molding and thermo-compression, favoring films applications [2]. However, there are few studies where evaluate the feasibility of incorporating antioxidants. Marinho *et al*. [19] processed PHB in the presence of Bruggolen® H10, a mix of Joncryl® and Irganox® 1010, and reported that mechanical properties have not appreciably changed [19]. Bruggolen® H10 is a sodium phosphonate processing stabilizer and synergist, which protects against polymer degradation during processing, but also prolongs lifetime of polymers.

This work aimed to evaluate the combined effect of a phenolic antioxidant (Irganox® 1010) and different concentrations of glycerol tributyrate (GTB) on thermal, mechanical, and barrier oxygen properties of poly(3-hydroxybutyrate) (PHB) films. Besides, changes on PHB microstructure and crystallinity induced by the presence of the antioxidant were also evaluated by several analytical techniques.

2. EXPERIMENTAL

2.1. Materials and Methods

2.1.1. Materials and Processing

Poly(3-hydroxybutyrate) powder (PHB) was purchased from Biomer (Germany). Additives used were glycerol tributyrate (GTB, 98.5 % purity, Sigma Aldrich, Switzerland) as plasticizer and pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (Irganox® 1010, 98 % purity, Sigma Aldrich, Switzerland) as phenolic antioxidant. PHB powder and additives were manually mixed in order to well-impregnate the polymer. Studied formulations are described in Table **1**. Mixtures were melt-processed in a Brabender Plastograph (Germany) at 180 °C and 60 rpm, for 15 min. Films were obtained from processed samples by thermo-compression using a hydraulic press at 5 kg cm^{-2} and 195 °C, for 15 min. Thickness was measured using an electronic digital caliber MAX-CAL (Fowler & NSK, Japan). At least 10 measurements were taken for each specimen and values correspond to the average thickness were employed in the calculation of mechanical properties and oxygen transmission rate.

Table 1: Formulations Based on Poly(3-Hydroxybutyrate) (PHB), Glycerol Tributyrate (GTB), and IRGANOX® 1010 (I)

Sample	GTB (% w/w, PHB basis)	I (% w/w, PHB basis)
PHB	-	-
PHB-5GTB	5	-
PHB-10GTB	10	-
PHB-20GTB	20	-
PHB-30GTB	30	-
PHB-I	-	0.3
PHB-5GTB-I	5	0.3
PHB-10GTB-I	10	0.3
PHB-20GTB-I	20	0.3
PHB-30GTB-I	30	0.3

2.2. Films Characterization

2.2.1. Thermal Properties

Thermal analyses were performed by Differential Scanning Calorimetry (DSC) using a calorimeter Instrument Discovery Series (USA), under nitrogen atmosphere. Samples (~10 mg) were first heated from -90 to 195 °C at a heating rate of 10 °C/min. After being kept at 195 °C for 2 min, samples were cooled to -90 °C at 10°C/min and kept at this temperature for 2 min. They were again heated at 10 °C/min to 195 °C. Onset and peak melting temperature ($T_{m\ onset}$ and $T_{m\ peak}$) and melting enthalpy (ΔH_m) were obtained from both first and second heating cycle. Degree of crystallinity ($X_{C\text{-}DSC}$) was determined using Equation (1), according to the procedure described by Wellen *et al*. [20].

$$X_{C-DSC} = 100 \times \frac{\Delta H_m}{\Delta H^0_{m\,PHB} \times w} \tag{1}$$

where $\Delta H_{m\ PHB}$ is the melting enthalpy of the sample, $\Delta H^0_{m\ PHB}$ = 146 J/g is the melting enthalpy of a 100 % crystalline PHB [21] and w is the weight fraction of PHB in the sample.

Thermal degradation was evaluated by Thermogravimetric Analysis (TGA) using a thermogravimetric balance TA Instrument Discovery Series (USA). Samples (~10 mg) were heated from 25 °C to 350 °C at 10 °C/min, under nitrogen atmosphere (20 mL/min). Curves of mass percentage as a function of temperature were recorded, and the onset and maximum decomposition temperature was obtained from the first derivative as it was reported by Seoane *et al*. [18].

2.2.2. Diffraction X-Ray (XRD)

Diffractograms were obtained in an X-ray diffractometer Philips PW1710 (Philips, Holland), provided with a tube, a copper anode, and a detector operating at 45 kV and 30 mA within 2θ from 5 to 60°. Degree of crystallinity ($X_{C\text{-}XRD}$) was calculated following Equation (2), according to the procedure reported by Cyras *et al*, [22].

$$X_{C-XRD}(\%) = \frac{A_{crystalline\ peaks}}{A_{total}} \times 100 \tag{2}$$

where $X_{C\text{-}XRD}$ (%) corresponds to the ratio between crystalline peaks area ($A_{\text{crystalline peaks}}$) and the total diffractogram area (A_{total}), expressed as percentage.

Similarly, the degree of crystallinity ($X_{C\text{-}XRD\ \beta}$) attributed to β-form crystals was calculated considering the peak at 2θ = 20°, following Equation (3).

$$X_{C-XRD\ \beta}(\%) = \frac{A_{\beta\ crystalline\ peak}}{A_{total}} \times 100 \tag{3}$$

where $X_{C\text{-}XRD\ \beta}$ (%) corresponds to the ratio between the area of the crystalline peak at 2θ = 20° ($A_{\beta\ \text{crystalline peak}}$) and the total diffractogram area (A_{total}), expressed as percentage.

In order to calculate the area of all crystalline peaks ($A_{\text{crystalline peak}}$) and the area of the crystalline peak at 2θ = 20° ($A_{\beta\ \text{crystalline peak}}$), a peaks deconvolution using Lorentzian functions was carried out.

2.2.3. Tensile Tests

Tensile tests were carried out in an Instron Tensile Testing Equipment model 3369 (UK), using a cross-head speed of 5 mm/min and a load cell of 1 kN. At least ten probes of 13 x 100 mm of each film formulation were assayed and stress-strain curves were obtained from load displacement data. Maximum tensile strength (σ_m), Young's modulus (E), and elongation at break (ε_B) were calculated, according to ASTM D882-91 standard method.

2.2.4. Oxygen Transmission Rate (OTR)

Oxygen mass transfer rates (OTR) and oxygen permeability were determined at 25 °C using a Mocon OX-Tran2/20 (Mocon Inc., USA) based on the ASTM 3985 standards method. Test cell was composed of two chambers separated by the sample (5 cm^2). On one side of the film, 100 % oxygen gas was flowing and, on the other side, there was a flow of nitrogen gas (100 % N_2).

3. RESULTS AND DISCUSSION

3.1. Thermal Properties

The combined effect of GTB and I was first evaluated based on thermal properties derived from DSC and TGA analysis. Melting temperature and degree of crystallinity of thermo-compressed films corresponding to the first heating of DSC analysis are shown in Table **2**. It is important to highlight that thermal behavior of samples subjected to the first heating would be associated to thermal properties of films after being melt-mixed and thermo-compressed. No evident tendency was observed on PHB films by GTB addition on onset and melting temperatures, as well as on melting enthalpy. Otherwise, the addition of antioxidant allowed an increment on these thermal parameters. The combined effect of both additives led to a notable decrease in melting properties of PHB based films. Degree of crystallinity, calculated from enthalpy values, are shown in Figure **1**. GTB addition at 5 % w/w allowed a significant increase in the degree of crystallinity of plasticized PHB films, probably due to a nucleating effect, as it was reported by Seoane *et al*. [18] and Quispe *et al*. [23]. Accordingly, Janojivá *et al*. suggested that a partial polymer degradation could contribute to an increase in the degree of crystallinity [4]. As it can be observed, this increment was not so noticeable in samples containing 10, 20, and 30 % w/w GTB. In the case of the antioxidant incorporation an increase in the degree of crystallinity was evidenced. On the other hand, the combined effect of both additives led to a slight decrease in this parameter. The absence of a clear trend in the influence of separate and combined additives on thermal properties and

Table 2: Thermal Properties of PHB Films with GTB and Irganox® 1010 Obtained by DSC, from the First Heating

Sample	$T_{m\ onset}$ (°C)	$T_{m\ peak}$ (°C)	ΔH_m (J/g)	$X_{C\text{-}DSC}$ (%)
PHB	160.7	168.3	51.3	35.1
PHB-5GTB	175.2	182.9	69.9	50.5
PHB-10GTB	159.7	170.4	60.1	45.7
PHB-20GTB	164.6	169.4	56.0	47.9
PHB-30GTB	150.4	164.5	60.9	59.6
PHB-I	165.9	181.2	64.4	44.2
PHB-5GTB-I	161.8	171.0	48.0	34.7
PHB-10GTB-I	160.1	174.7	65.0	49.6
PHB-20GTB-I	149.5	162.4	56.1	48.2
PHB-30GTB-I	144.0	157.4	56.1	55.1

$T_{m\ onset}$: onset melting temperature, $T_{m\ peak}$: peak melting temperature, ΔH_m: melting enthalpy, and $X_{C\text{-}DSC}$: degree of crystallinity

degree of crystallinity could be attributed to samples heterogeneity. Therefore, to evaluate the influence of the plasticizer in conjunction with the antioxidant, it is necessary to erase the sample thermal history and analyze the results derived from the second heating.

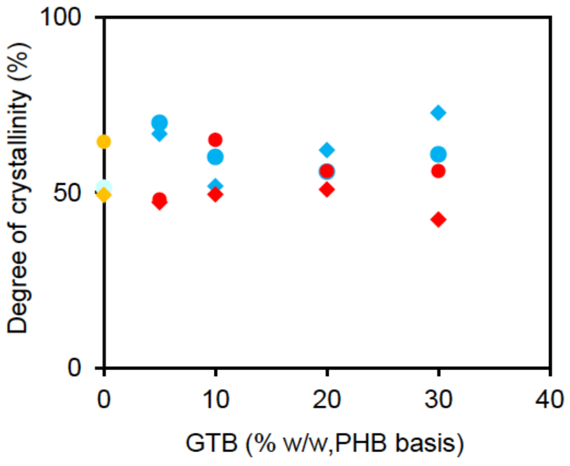

Figure 1: Degree of crystallinity of PHB films calculated from the DSC first heating. Symbols: (○) PHB, (●) PHB-I, (●) PHB-GTB, and (●) PHB-GTB-I. Degree of crystallinity calculated from DSC second heating. Symbols: (◇) PHB, (◆) PHB-I, (◆) PHB-GTB, and (◆) PHB-GTB-I.

Melting temperature and degree of crystallinity of thermo-compressed films corresponding to the second heating, after erasing the sample thermal history, are presented in Table **3**. Two endothermic peaks were detected in almost all analyzed films: the first melting peak ($T_{m\ peak1}$) can be attributed to the melting of more imperfect crystals and the second melting peak ($T_{m\ peak2}$) to the most ordered and perfect crystals. In accordance with Ziaee and Supaphol [24] and Liu *et al*. [25], the melting peak at lower temperature corresponds to primary crystals formed during cooling, and the second peak at higher temperature is due to crystals melted and recrystallized in subsequent heating. PHB films containing only GTB presented lower melting temperatures attributed to a higher chain mobility by plasticizer addition [4]. This tendency is common in polymers and can be attributed to differences in the crystals morphology (width of the sheets and size of the spherulites) [26]. The addition of 0.3 % w/w Irganox® decreased the melting temperature of PHB-GTB films. Degree of crystallinity calculated from DSC are included in Table **2** and **3** and Figure **1**. As a general trend, it can be observed that plasticizer addition led to an increase in the degree of crystallinity. On the other hand, antioxidant presence decreased the degree of crystallinity of plasticized films, mainly those containing 20 and 30 % w/w GTB. This tendency could be probably due to Irganox® preventing the formation of short polymer fragments generated by degradation that can be more easily packed into a crystalline structure [4]. As a consequence, the nucleating effect of GTB would be avoided, favoring the increase of the amorphous phase. Thus, the presence of Irganox® 1010 improved GTB plasticizing effect on PHB and might avoid the formation of short molecular chains. Table **3** also shows the glass transition temperature (T_g) of all studied samples. As it was expected, plasticizer addition reduced T_g values and the antioxidant presence markedly increased this reduction. For example, in the case of PHB-30GTB this temperature was reduced from -24.6°C to -39.3°C by adding 0.3 % w/w Irganox® 1010. Thermal properties of plasticized PHB films are in good agreement with an

Table 3: Thermal Properties of PHB Films with GTB and Irganox® 1010 Obtained by DSC, from the Second Heating

Sample	T_g (°C)	$T_{m\ peak1}$ (°C)	$T_{m\ peak2}$ (°C)	ΔH_m (J/g)	$X_{C\text{-}DSC}$ (%)
PHB	-2.3	---	176.2	75.1	51.4
PHB-5GTB	-4.4	166.1	172.3	92.5	66.7
PHB-10GTB	-14.4	165.9	166.1	68.1	51.8
PHB-20GTB	-23.6	158.7	166.8	72.5	41.0
PHB-30GTB	-24.6	158.4	167.0	74.3	72.7
PHB-I	-3.9	---	169.8	72.0	44.1
PHB-5GTB-I	-4.9	163.4	171.6	65.4	47.3
PHB-10GTB-I	-19.2		165.6	65.1	49.7
PHB-20GTB-I	-27.7	153.4	165.6	59.5	51.1
PHB-30GTB-I	-39.3	152.6	162.0	43.2	42.5

T_g: glass transition temperature, $T_{m\ peak1}$: first peak melting temperature, $T_{m\ peak\ 2}$: second peak melting temperature, ΔH_m: melting enthalpy, and $X_{C\text{-}DSC}$: degree of crystallinity.

increase in the amorphous phase as reported for other authors for plasticized PHAs [27, 28].

Thermal degradation was evaluated by TGA and obtained onset and maximum degradation temperatures were included in Table **4**. PHB films plasticized with GTB showed a slight decrease in both temperatures. These results are in accordance with Seoane *et al.* [18] and Quispe *et al*. [23] who reported that the incorporation of this additive produce a decrease on the degradation temperature. On the other hand, Irganox® 1010 allowed a significant increase on degradation temperature because this additive acts as stabilizer of the polymer matrix [29], reacting and neutralizing the formation of free radicals responsible for the degradation of polymeric chains when increasing the temperature.

Table 4: Onset and Maximum Degradation Temperature of PHB Films with GTB and Irganox® 1010 Obtained by TGA

Sample	$T_{d\ onset}$ (°C)	$T_{d\ max}$ (°C)
PHB	270.5	280.6
PHB-5GTB	242.4	264.8
PHB-10GTB	232.4	255.9
PHB-20GTB	244.6	273.3
PHB-30GTB	234.0	272.5
PHB-I	271.5	290.0
PHB-5GTB-I	276.8	289.2
PHB-10GTB-I	273.7	287.5
PHB-20GTB-I	275.1	286.9
PHB-30GTB-I	276.5	288.1

$T_{d\ onset}$: onset degradation temperature, $T_{d\ max.}$: maximum degradation temperature.

Thermal processing of polymers is a key point in the feasibility of large-scale processing. PHB thermal stability during melting processing and its narrow thermal processing window hinder to broad its applications, particularly in film form, and the feasibility to be an ecological alternative to replace commercial non-biodegradable polymers [30]. Therefore, the use of additives, such as antioxidants and plasticizers, could widen the PHB processing window facilitating the application of this biopolymer. The processing window of thermoplastic polymers is given by a certain range of temperature, pressure, and time. The range of processing parameters is limited both by the processing equipment (*e.g.*, maximum mold temperature or clamping force) and the material properties. Independent of the process and the equipment used, the processing window is limited by the degradation and viscosity of the polymer melt [31]. Onset melting temperature ($T_{m\ onset}$) and onset degradation temperature ($T_{d\ onset}$) allow calculating the thermal processing window of PHB and the effect of GTB and I addition. Obtained results for PHB plasticized films are shown in Figure **2**. Regarding neat PHB, the addition of antioxidant did not significantly modify the thermal processing window. On the other hand, when only the plasticizer was incorporated, this temperature range decreased drastically, negatively affecting the biopolymer thermal processing. However, the addition of both additives allowed increasing the PHB processing window, achieving an increment of 21.5 % for PHB-30GTB-I respect to neat PHB. This favorable increment can be mainly attributed to two factors: a decrease in PHB melting temperature caused by the GTB plasticizing effect and the increase in PHB degradation temperature.

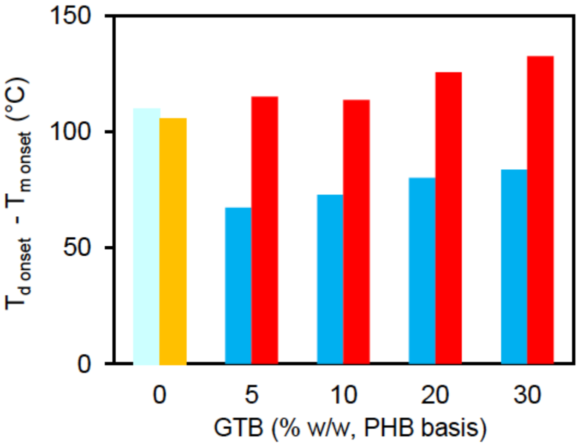

Figure 2: Processing windows of PHB films calculated from the difference between onset degradation temperature ($T_{d\ onset}$) and onset melting temperature ($T_{m\ onset}$). Symbols: (⬜) PHB, (🟧) PHB-I, (🟦) PHB-GTB, and (🟥) PHB-GTB-I.

3.2. X-Ray Diffraction (XRD)

Diffractograms of PHB films are shown in Figure **3A** (PHB-GTB) and Figure **3B** (PHB-GTB-I). X-Ray studies of PHB highly oriented films and fibers indicated the existence of two types of molecular conformations: the 2/1 helix conformation (α-form) [32] and the planar zig-zag conformation (β-form) [33]. Besides, PHB generally crystallizes in an orthorhombic unit cell [34]. All studied PHB films presented two strong scattering intensity peaks at around 2θ = 13° and 17° assigned to (020) and (110) of the orthorhombic unit cell, respectively [35, 36]. Besides, weaker reflections located at around 2θ = 21.5° and 22.5° corresponding to (101) and (111) reflections of α-form PHB crystals were also detected [37]. Others peaks detected at around 2θ = 26° and 27° were reported in literature as (130) and (040) reflections, respectively [38]. At around 2θ = 20° it can be observed a diffraction peak attributed to the β-form crystals [39]. It can be seen that when GTB concentration increased, the intensity of the peak corresponding to the fraction of phase β decreased, especially in the case of PHB films containing only the plasticizer (Figure **3A**).

On the other hand, the addition of Irganox® 1010 induced an increase in the intensity of the peak corresponding to the β phase, particularly at the higher studied GTB concentrations (20 and 30 % w/w) (Figure **3B**).

As mentioned before, β-phase is formed in the polymer amorphous phase [40]. In this sense, Wang *et al*. [39] reported that β-form crystals are indicative of a high level of molecular stretching only in the amorphous region. For PHB-20GTB and PHB-30GTB films, the lower intensity of the peak associated to β-phase in comparison with films containing the antioxidant could indicate a better organization of the crystalline phase [38]. In this way, the incorporation of Irganox® can explain the crystallinity reduction generated by the nucleating effect of the plasticizer. This nucleating effect is likely to be aided by the presence of short polymer chain segments produced during thermal processing in the absence of the antioxidant.

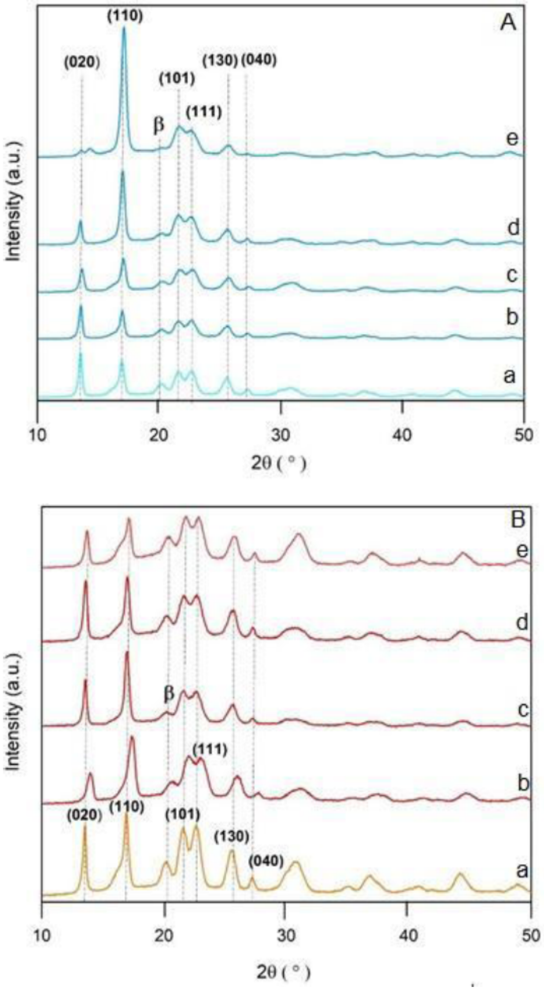

Figure 3: Wide Angle X-ray diffractograms of PHB films. References: **A**): a) PHB, b) PHB-5GTB, c) PHB-10GTB, d) PHB-20GTB, and e) PHB-30GTB and **B**): a) PHB-I, b) PHB-5GTB-I, c) PHB-10GTB-I, d) PHB-20GTB-I, and e) PHB-30GTB-I.

The degree of crystallinity, calculated from XRD, of PHB films and those containing GTB and I are shown in Figure **4**. In general, the presence of both additives did not change significantly the degree of crystallinity of PHB films. However, the degree of crystallinity attributed to the β-form showed appreciable differences in PHB films plasticized with 20 and 30 % w/w GTB. The increase in the β-phase crystals in PHB-20GTB-I and PHB-30GTB-I could be due to the compression molding, as it has been reported [37]. β-form is introduced by the orientation of free chains in amorphous regions between α-form lamellar crystals, as it was reported for P(3HB) films and fibers [38, 39]. Since β-phase is directly related to the amorphous phase, other authors have reported that antioxidant has a stabilizing effect and prevents the formation of nucleation sites in polymers [38]. In particular, the antioxidant reduces the formation of short chains that crystallize together with a nucleating plasticizer, thus increasing the amorphous phase. This is particularly reflected in the degree of crystallinity obtained by DSC (second heating), when comparing PHB-30GTB with PHB-30GTB-I.

Unlike the diffractogram of films containing only GTB, a slight increase in the peak at $2\theta = 20°$ is observed in PHB plasticized in the presence of the antioxidant (Figure **3B**). The β-form increases when the amorphous phase increases. In addition, when performing the calculations to estimate the β-form of the total crystalline phase, this fraction increased in films containing Irganox® 1010 (Figure **4**).

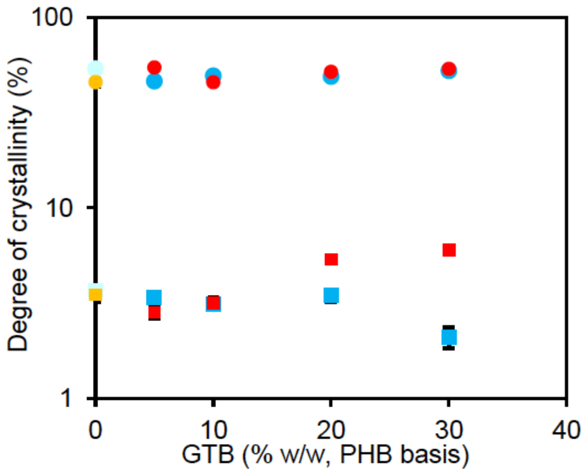

Figure 4: Degree of crystallinity of PHB films (logarithmic scale), calculated from XRD. Symbols: (●) PHB, (●) PHB-I, (●) PHB-GTB, and (●) PHB-GTB-I; and degree of crystallinity attributed to β-form crystals. Symbols: (■) PHB, (■) PHB-I, (■) PHB-GTB, and (■) PHB-GTB-I.

3.3. Tensile Properties

The influence of GTB and Irganox® 1010 on mechanical properties of PHB films was evaluated through tensile tests and the corresponding results are presented in Figure **5**. The use of GTB as plasticizing led to a reduction in σ_m and E values; meanwhile ε_B increased. As an example, by adding 30 % w/w GTB it was achieved a reduction of 74 % and 39 % in E and σ_m, respectively; and an increment of around 300 % in ε_B. These results demonstrated the plasticizing effect of GTB due to the high compatibility with the PHB [8,23]. According to Răpă *et al*. [16], plasticization allows the material to soften, increasing its ductility.

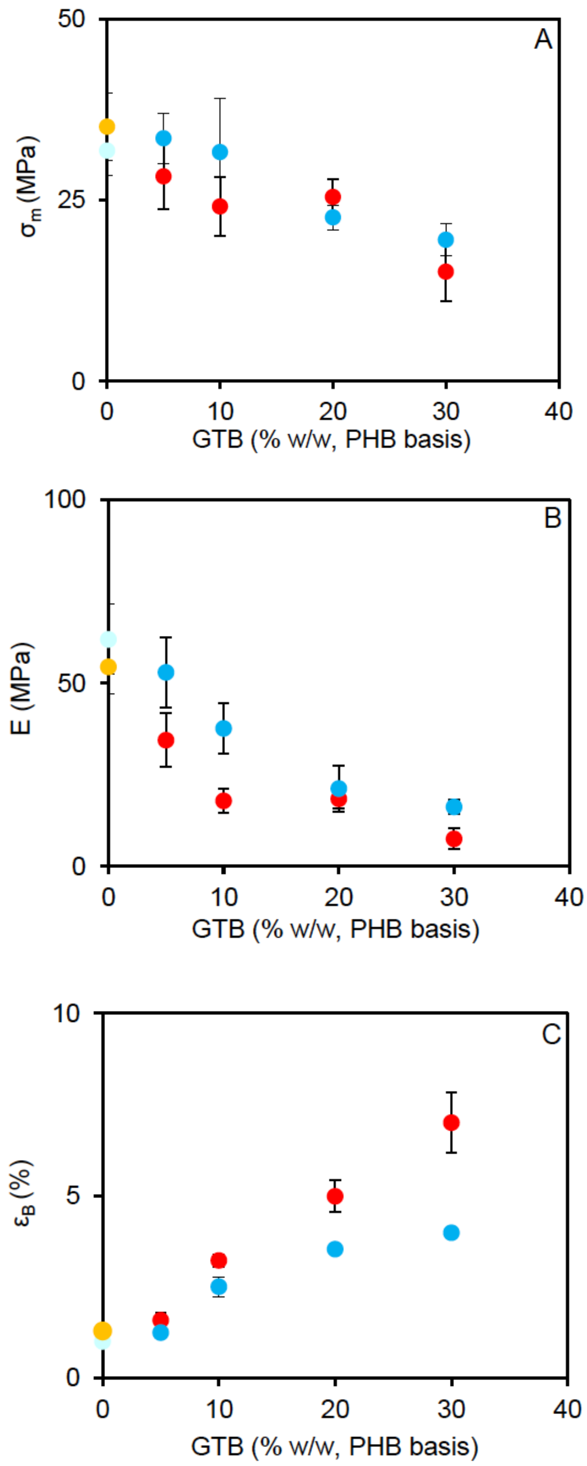

Figure 5: Mechanical properties of PHB films. **A**) Tensile strength (σ_m), **B**) Young´s modulus (**E**), and **C**) Elongation of break (ε_B). Symbols: (●) PHB, (●) PHB-I, (●) PHB-GTB, and (●) PHB-GTB-I.

Furthermore, mechanical behavior of PHB and PHB-GTB films was improved when PHB was processed in the presence of Irganox® 1010. Regarding the elongation at break, the presence of this antioxidant during the melt-mixing of PHB and PHB-GTB generated a remarkable increment in ductility. It is important to highlight that the effect of Irganox® 1010 on films elongation at break was more marked for samples with the highest studied GTB concentration. These results could be related with the structural changes evidenced by XRD analysis in which it was demonstrated that the presence of antioxidant induced changes in the fraction of β-form crystalline as well as in the degree of crystallinity. Besides, PHB films ductility increased since the addition of Irganox® reduced the polymer degradation during thermal processing.

3.4. Oxygen Transmission Rate

Figure **6** shows the effect of Irganox® 1010 on the oxygen transmission rate (OTR) of PHB and PHB-GTB films. Values of samples with only GTB are within the range of typical PHAs films [41]. Adding Irganox® 1010 during samples processing favored GTB plasticizing effect and increased the free volume of amorphous phase, probably due to the reduction of the molecular constriction, which increased the OTR [4, 42]. As it was observed by DSC and reported by other authors, Irganox® 1010 presence decreases PHB crystallinity, weakening the macromolecular bonding (in amorphous phase) and facilitating conformational changes that favors the diffusion of O_2 molecules [39, 43].

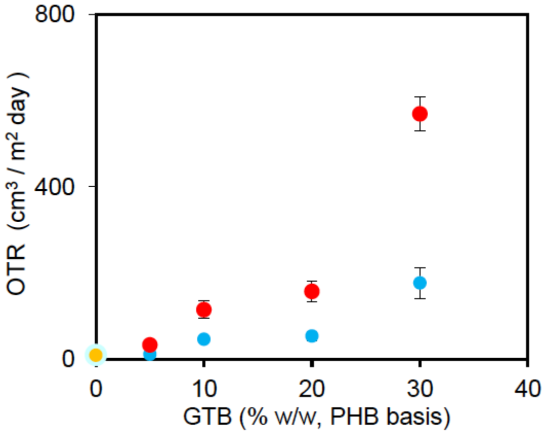

Figure 6: Oxygen transmission rate (OTR) of PHB films. Symbols: (●) PHB, (●) PHB-I, (●) PHB-GTB, and (●) PHB-GTB-I.

4. CONCLUSIONS

The addition of Irganox® 1010 improves final properties of PHB plasticized films, mainly by preventing the degradation during thermo-processing. Oxidation reactions during processing lead to the formation of shorter and more mobile chains, which can act as nucleating agents. This increases the crystallinity of the material in the absence of Irganox® and generates a detriment in final properties of GTB plasticized PHB films. On the other hand, parallel to the increase of the amorphous content, an increase of β-form crystals in that region gives a lower decrease of total degree of crystallinity, which contributes to the improvement of final properties of plasticized PHB films.

5. ACKNOWLEDGEMENTS

We express our gratitude to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PIP 11220150100127), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, PICT-2014-2410), and Universidad Nacional del Sur (UNS, PGI 24/M154) for their financial support.

REFERENCES

[1] Voigt W, and Todesco R, New approaches to the melt stabilization of polyolefins, Polymer Degradation and Stability 2002; 77(3): 397-402. https://doi.org/10.1016/S0141-3910(02)00089-7

[2] Špitalský Z, Lacík I, Lathová E, Janigová I, and I Chodák, Controlled degradation of polyhydroxybutyrate via alcoholysis with ethylene glycol or glycerol, Polymer Degradation and Stability 2006; 91(4): 856-861. https://doi.org/10.1016/j.polymdegradstab.2005.06.019

[3] Balakrishnan P, and Sreekala MS, Common Additives used in Recycling of Polymers, Recycling of Polymers: Methods, Characterization and Applications, First., R. Francis, Ed. Wiley-VCH Verlag GmbH & Co, 2017, pp. 11-30.

[4] Taylor R, Chemistry of Functional Groups, Applied Science Publishers, S. Patai, Ed. London, 1979.

[5] Lehrle R, Williams R, French C, and Hammond T, Thermolysis and Methanolysis of Poly(3-hydroxybutyrate): Random Scission Assessed by Statistical Analysis of Molecular Weight Distributions, 1995. https://doi.org/10.1021/ma00117a008

[6] Laycock B, Halley P, Pratt S, Werker A, and Lant P, The chemomechanical properties of microbial polyhydroxyalkanoates, Progress in Polymer Science 2013; 38(3): 536-583. https://doi.org/10.1016/j.progpolymsci.2012.06.003

[7] Tanaka T, Yabe T, Teramachi S, and Iwata T, Mechanical properties and enzymatic degradation of poly[(R)-3-hydroxybutyrate] fibers stretched after isothermal crystallization near Tg, Polymer Degradation and Stability 2007; 92(6): 1016-1024. https://doi.org/10.1016/j.polymdegradstab.2007.02.017

[8] Yamane H, Terao K, Hiki S, & Kimura Y. Mechanical properties and higher order structure of bacterial homo poly(3-hydroxybutyrate) melt spun fibers, Polymer 2001; 42(7): 3241-3248. https://doi.org/10.1016/S0032-3861(00)00598-X

[9] Billingham NC, Henman TJ, and Holmes PA. Degradation and stabilisation of polyesters of biological and synthetic origin. Developments in Polymer Degradation-7. Springer,

Dordrecht, 1987; 81-121. https://doi.org/10.1007/978-94-009-3425-2_3

[10] Hahladakis JN, Velis CA, Weber R, Iacovidou E, and Purnell P, An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling, Journal of Hazardous Materials, 2018; 344: 179-199. https://doi.org/10.1016/j.jhazmat.2017.10.014

[11] Zweifel, Hans. Stabilization of polymeric materials. Springer Science & Business Media, 2012.

[12] Voigt W and Kenny J, Liquid antioxidants: a new choice for increased cleanliness and productivity in the production of cross-linked cable insulation, Wire Journal International 2002; 34(5): 196-201.

[13] Ghaffari M and Ahmadian V, Investigation of antioxidant and electron beam radiation effects on the thermal oxidation stability of low-density polyethylene, Radiation Physics and Chemistry 2007; 76(11-12): 1666-1670. https://doi.org/10.1016/j.radphyschem.2007.02.101

[14] Al-Malaika S, Mechanisms of antioxidant action and stabilisation technology-The Aston experience, Polymer Degradation and Stability, 1991; 34(1-3): 1-36, https://doi.org/10.1016/0141-3910(91)90109-5

[15] Erceg M, Kovačić T, & Klarić I. Thermal degradation of poly (3-hydroxybutyrate) plasticized with acetyl tributyl citrate. Polymer degradation and stability, 2005; 90(2): 313-318. https://doi.org/10.1016/j.polymdegradstab.2005.04.048

[16] Râpă M, Darie-Niţă RN, Grosu E, Tănase EE, Trifoi AR, Papa T, & Vasile C. Effect of plasticizers on melt processability and properties of PHB. J. Optoelectron. Adv. Mater, 2015; 17(11-12): 1778-1784. https: //joam.inoe.ro/articles/effect-of-plasticizers-on-melt-processability-and-properties-of-phb/

[17] Requena R, Jiménez A, Vargas M, and Chiralt A, Effect of plasticizers on thermal and physical properties of compression-moulded poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] films. Polymer Testing 2016; 56: 45-53. https://doi.org/10.1016/j.polymertesting.2016.09.022

[18] Seoane IT, Manfredi LB, and Cyras VP, Effect of two different plasticizers on the properties of poly(3-hydroxybutyrate) binary and ternary blends, Journal of Applied Polymer Science, 2018; 135(12): 1-12. https://doi.org/10.1002/app.46016

[19] Marinho VAD, Almeida TG, Carvalho LH, & Canedo EL. Aditivação e Biodegradação de Compósitos PHB/Babaçu. Revista Eletrônica de Materiais e Processos, 2018; 13(1): 37-41. http: //www2.ufcg.edu.br/revista-remap/index.php/REMAP/article/viewArticle/647.

[20] Wellen RMR, Rabello MS, Araujo IC, Fechine GJM, and Canedo EL, Melting and crystallization of poly(3-hydroxybutyrate): Effect of heating/cooling rates on phase transformation, Polímeros, 2015; 25(3): 296-304. https://doi.org/10.1590/0104-1428.1961

[21] Parra DF, Fusaro J, Gaboardi F, and Rosa DS, Influence of poly (ethylene glycol) on the thermal, mechanical, morphological, physical-chemical and biodegradation properties of poly (3-hydroxybutyrate), Polymer Degradation and Stability, 2006; 91(9): 1954-1959. https://doi.org/10.1016/j.polymdegradstab.2006.02.008

[22] Cyras VP, Fernández NG, and Vázquez A. Biodegradable films from PHB-8HV copolymers and polyalcohols blends: crystallinity, dynamic mechanical analysis and tensile properties. Polymer international, 1999; 48(8): 705-712. https://doi.org/10.1002/(SICI)1097-0126(199908)48:8<705::AID-PI205>3.0.CO;2-P

[23] Quispe MM, Lopez OV, Boina DA, Stumbé J-F, and Villar MA, Glycerol-based additives of poly(3-hydroxybutyrate) films, Polymer Testing, 2021; 93: 107005. https://doi.org/10.1016/j.polymertesting.2020.107005

[24] Ziaee Z and Supaphol P, Non-isothermal melt- and cold-crystallization kinetics of poly(3-hydroxybutyrate), Polymer Testing, 2006; 25(6): 807-818. https://doi.org/10.1016/j.polymertesting.2006.04.009

[25] Liu WJ, Yang HL, Wang Z, Dong LS, and Liu JJ, Effect of nucleating agents on the crystallization of poly(3-hydroxybutyrate-co-3-hydroxyvalerate), Journal of Applied Polymer Science, 2002; 86(9): 2145-2152. https://doi.org/10.1002/app.11023

[26] Pilla S and Kramschuster A, Microcellular injection-molding of polylactide with chain extender, Materials Science & Engineering, 2009; 29: 1258-1265. https://doi.org/10.1016/j.msec.2008.10.027

[27] El-Hadi A, Schnabel R, Straube E, Müller G, and Henning S, Correlation between degree of crystallinity, morphology, glass temperature, mechanical properties and biodegradation of poly (3-hydroxyalkanoate) PHAs and their blends, Polymer Testing, 2002; 21(6): 665-674. https://doi.org/10.1016/S0142-9418(01)00142-8

[28] de Koning GJM and Lemstra PJ, Crystallization phenomena in bacterial poly[(R)-3-hydroxybutyrate]: 2. Embrittlement and rejuvenation, Polymer, 1993; 34(19): 4089-4094. https://doi.org/10.1016/0032-3861(93)90671-V

[29] Groenewoud, Wim M., ed. Characterisation of polymers by thermal analysis. Elsevier, 2001; 69. https://doi.org/10.1016/B978-044450604-7/50010-8

[30] Arrieta MP, Samper MD, López J, and Jiménez A, Combined Effect of Poly(hydroxybutyrate) and Plasticizers on Polylactic acid Properties for Film Intended for Food Packaging, Journal of Polymers and the Environment, 2014; 22(4): 460-470. https://doi.org/10.1007/s10924-014-0654-y

[31] [31]. Lee SN., Lee MY, and Park WH, Thermal stabilization of poly(3-hydroxybutyrate) by poly(glycidyl methacrylate),Journal of Applied Polymer Science, 2002; 83 (13): 2945-2952. https://doi.org/10.1002/app.10318

[32] Mills N, Jenkins M, Kukureka S, Chapter 6 - Effects of melt processing. Plastics (Fourth Edition), Butterworth-Heinemann, 2020; 6: 95-109, ISBN 9780081024997. https://doi.org/10.1016/B978-0-08-102499-7.00006-0

[33] Yokouchi M, Chatani Y, Tadokoro H, Teranishi K & Tani H. Structural studies of polyesters: Molecular and crystal structures of optically active and racemic poly (β-hydroxybutyrate). Polymer 1973; 14(5): 267. https://doi.org/10.1016/0032-3861(73)90087-6

[34] Aoyagi Y, Doi Y, & Iwata T. Mechanical properties and highly ordered structure of ultra-high-molecular-weight poly[(R)-3-hydroxybutyrate] films: Effects of annealing and two-step drawing. Polymer Degradation and Stability 2003; 79: 209-216. https://doi.org/10.1016/S0141-3910(02)00273-2

[35] Nishiyama Y, Tanaka T, Yamazaki T & Iwata T. 2D NMR observation of strain-induced β-form in poly[(R)-3-hydroxybutyrate]. Macromolecules 2006; 39: 4086-4092. https://doi.org/10.1021/ma060291h

[36] Zhijiang C, Chengwei H, & Guang Y. Crystallization behavior, thermal property and biodegradation of poly(3-hydroxybutyrate)/poly(ethylene glycol) grafting copolymer. Polymer Degradation and Stability 96, 1602-1609 (2011). https://doi.org/10.1016/j.polymdegradstab.2011.06.001

[37] Sun X, Guo L, Sato H, Ozaki Y, Yan S, Takahashi I. A study on the crystallization behavior of poly(β-hydroxybutyrate) thin films on Si wafers. Polymer 2011; 52: 3865-3870. https://doi.org/10.1016/j.polymer.2011.06.024

[38] Pospıšil J, Horák Z, Pilař J, Billingham, NC, Zweifel H, & Nešpůrek S. Influence of testing conditions on the performance and durability of polymer stabilisers in thermal oxidation. Polymer Degradation and Stability, 2003; 82(2); 145-162. https://doi.org/10.1016/S0141-3910(03)00210-6

[39] Wang C, Hsu CH, and Hwang IH, Scaling laws and internal structure for characterizing electrospun poly[(R)-3-hydroxybutyrate] fibers, Polymer 2008; 49(19): 4188-4195. https://doi.org/10.1016/j.polymer.2008.07.033

[40] Orts WJ, Marchessault RH, Bluhm TL, and Hamer GK, Observation of strain-induced β form in poly(β-hydroxyalkanoates), Macromolecules, 1990; 23(26): 5368-5370. https://doi.org/10.1021/ma00228a014

[41] Mekonnen T, Mussone P, Khalil H, Bressler D. Progress in bio-based plastics and plasticizing modifications. Journal of Materials Chemistry 2013; A(1): 13379-13398. https://doi.org/10.1039/c3ta12555f

[42] Sun X, Guo L, Sato H, Ozaki Y, Yan S, and Takahashi I, A study on the crystallization behavior of poly(β-hydroxybutyrate) thin films on Si wafers, Polymer, 2011; 52(17): 3865-3870. https://doi.org/10.1016/j.polymer.2011.06.024

[43] Janigová I, Lacík I, and Chodák I, Thermal degradation of plasticized poly(3-hydroxybutyrate) investigated by DSC, Polymer Degradation and Stability, 2002; 77(1): 35-41. https://doi.org/10.1016/S0141-3910(02)00077-0

Received on 13-07-2021 Accepted on 03-09-2021 Published on 28-09-2021

DOI: https://doi.org/10.12974/2311-8717.2021.09.02