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# INFLUENCE OF GAMMA RADIATION ON THERMAL PROPERTIES AND WATER VAPOR TRANSMISSION OF POLY(3-HYDROXYBUTYRATE) (PHB) IN BLENDS

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## ABSTRACT

Biodegradable polymers are a newly emerging field. A vast number of biodegradable polymers have been synthesized recently and some microorganisms and enzymes capable of degrading them have been identified. Polyesters such as poly(3-hydroxybutyrate) (PHB) or other polyhydroxyalkanoates (PHAs) have attracted commercial and academic interest as new biodegradable materials. In this work, we investigated the effect of gamma radiation on the thermal properties and biodegradation behavior of PHB in blend with poly(ethyleneglicol)(PEG). The samples were irradiated at gamma radiation of 5 and 10 kGy. The thermal behaviour was investigated by utilization of differential scanning calorimetry (DSC) changes in thermal stability, glass transition and melting point were reported.

## 1. INTRODUCTION

Polyhydroxyalkanoates (PHAs) are polyesters of hydroxyalkanoates (HAS) synthesized by numerous bacteria as intracellular carbon and energy storage compounds and accumulated as granules in the cytoplasm of cells. More than 80 HAS have been detected as constituents of PHAs, which allow these thermoplastic materials to have various mechanical properties resembling hard crystalline polymer or elastic rubber depending on the incorporated monomer units. Even though PHAs have been recognized as good candidates for biodegradable plastics, their high price compared with conventional plastics has limited their use in a wide range of applications [1].

The most representative member of this family is poly(3-hydroxybutyrate) (PHB). Due to its biodegradability and biocompatibility, is intensively investigated for applications in the food industry and medicine. However, this polyester has a perfectly isotactic structure with only the (R)-configuration, PHB has high degree of crystallinity, and the obtained films are typically brittle. One of the ways to reduce this brittleness is blending PHB with PEG Poly(ethyleneglycol), therefore, blending offers much scope for expanding their range of applications. [2]

Gamma radiation is another way to change crystallinity to improve the properties of polymers. The molecular changes induced by $\gamma$-radiation in a polymer may be classified as main chain bond scission, resulting in a decrease in molecular weight and, thus, adversely affecting its mechanical properties; and chain crosslinking, resulting in an increase in molecular weight and formation of network structure. Chain scission, in general, occurs to polymeric chains at a low radiation dose. At high doses, free radicals are generated on the polymeric chains, which may cause crosslinking by forming covalent bonds between polymer chains. [3-5]

In this work we were interested in the effects of gamma irradiation on PHB in blend with PEG using different radiation doses, which may induce crosslinking in the amorphous regions of the polymer.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Poly(3-hydroxybutyrate (PHB) (lot 67 /August 2003), was supplied in powder form by Usina da Pedra PHB of Brazil S.A. (Serrana, SP, Brazil) and had an average molar mass ($M_w$) of 380000 g $mol^{-1}$, with PHB accounting for 99.9% of the dry material.

Poly(ethyleneglycol) (PEG) was supplied by Oxiteno (Mauá, SP, Brazil) and had $M_w$ of 300, g $mol^{-1}$. Chloroform was provided by Labsynth Produtos para Laboratório (Diadema, São Paulo, Brazil).

### 2.2. Film preparation

Films of PHB and PHB/PEG were prepared by casting using the following proportions of PHB/PEG: 100/0 and 95/5 (wt %). Each polymer (15%) was dissolved in chloroform (85%), the solutions were mixed in a convenient proportion and stirred at 60 ± 1°C for 10 minutes. Afterwards the solvent was allowed to evaporate at 65$^o$C in glass recipients in a saturated atmosphere of water vapour inside a stove. The blend 95/5 was irradiated and investigated.

### 2.2.1 Irradiation of films

The films were irradiated by a $^{60}$Co gamma source, operating at doses of 5 and 10 kGy under a nitrogen gas atmosphere. EMBRARAD/CBE provided the source, at dose rate of 10 kGy $h^{-1}$. Dosimetry was performed with Harwell Red Perspex 4034.

## 2.3. Differential scanning calorimetry (DSC)

Thermal analysis was performed using a DSC 822e differential scanning calorimeter (Mettler-Toledo, Switzerland) with an aluminum crucible with 10 mg of the sample, under a dynamic atmosphere of nitrogen ($N_2$), at a heating rate of 10 °C $\text{min}^{-1}$. The PHB was initially heated to 200 °C to eliminate the sample thermal history, and then cooled to room temperature before being immediately reheated to 200 °C. All DSC experiments were done in duplicate and the reported data refers to the second heating [6]. PHB crystallinity in the blends was calculated according to Equation 1.

$$Xc(\%) = \frac{\Delta Hf \times 100}{\Delta Ho \times w(PHB)} \qquad \text{Eq. (1)}$$

$\Delta H_{f}$ = melting enthalpy of the sample

$\Delta Ho$ = melting enthalpy of the 100% crystalline PHB which is assumed to be 146 $\text{J}\cdot\text{g}^{1}$[6,7]

$w$ (PHB) = weight fraction of PHB in the sample

The DSC apparatus was calibrated with In metal (m.p. 156.61 ºC; $\Delta H = 28.4\ \text{J}\cdot\text{g}^{-1}$).

## 2.4. Water vapor transmission (WVT)

The water vapor transmission (WVT) was determined in PHB films containing PEG at 5% (PEG 300). A stainless steel recipient holding silica gel was closed with a sample of film firmly fixed at the top. The recipient was subsequently placed in a desiccator with distilled water at 25 $^{o}$C. The films were removed and weighed each 24 hours for 10 days, on an Mettler analytical balance, and the water vapor transmission (*WVT*) was calculated according to Equation 2:

$$WVT = \frac{w \times x}{A\,\Delta Pv} \qquad \text{Eq. (2)}$$

Where *WVT* is the water vapor transmission (g $H_2O$ mm/ $\text{cm}^{-2}$), $x$ is the average thickness of the films (0.048 ± 0.012 mm), $A$ is the permeation area (12.57 $\text{cm}^2$), $w$ is the film weight and $\Delta$Pv is the vapor pressure difference.

### 2.4.1. Water vapor transmission rate

The water vapor transmission rate (*WVTR*) was calculated according to Equation 3:

$$WVTR = \frac{w \times x}{t \times A} \qquad \text{Eq. (3)}$$

where *WVTR* is the water vapor transmission rate (g $H_2O$ mm $cm^2$ $h^{-1}$). The term *x/t* was calculated by linear regression from the points of weight gain versus time in a constant rate period. The tests were done in triplicate.

## 3. RESULTS AND DISCUSSION

### 3.1 Differential scanning calorimetry (DSC)

The DSC results on melting and crystallization temperatures of the films, obtained in the program of heating-cooling-reheating, are showed in Table 1. According to this table the peak in the second melting was found to be due to the fusion ($T_f$) of crystals formed during the crystallization process, which happened in the cooling segment of analytical procedure of DSC.

As a consequence to the process, Table 1 show decreases of crystallinity of the PHB film, a fact which has not changed the melting temperature. The blends having PEG showed a decrease of melting temperature in almost all films, the crystallization temperature remained the same. The addition of PEG in the PHB to obtain the films resulted in films of intermediate crystallinity (between PHB powder and processed PHB).

**Table 1. DSC results of irradiated and non-irradiated PHB/PEG films.**

| PEG (%) | Concentration | Film PHB/PEG (x) - y kGy | $T_m$ (ºC) | $T_c$ (ºC) | Crystallinity (%) |
|---|---|---|---|---|---|
| 0 | | PHB powder | 172 | 89 | 38 |
| | | PHB film | 171 | 91[2] | 40[2] |
| | | PHB -5 kGy | 171 | 90 | 41 |
| | | PHB -10 kGy | 171 | 91 | 39 |
| 5 | | PHB/ PEG 300 | 157 | 70 | 33 |
| | | PHB/ PEG 300 - 5 kGy | 160 | 74 | 29 |
| | | PHB/ PEG 300 - 10 kGy | 163 | 66 | 23 |

Competition between crosslinking and scission reactions, as expected, takes place in the irradiation of polymers. Scission promotes the formation of shorter molecules that crystallize at lower temperatures, increasing the crystallinity degree, while crosslinking reactions obstruct crystallization. In Fig. 1 the results for PHB/PEG300 are reported for illustration.

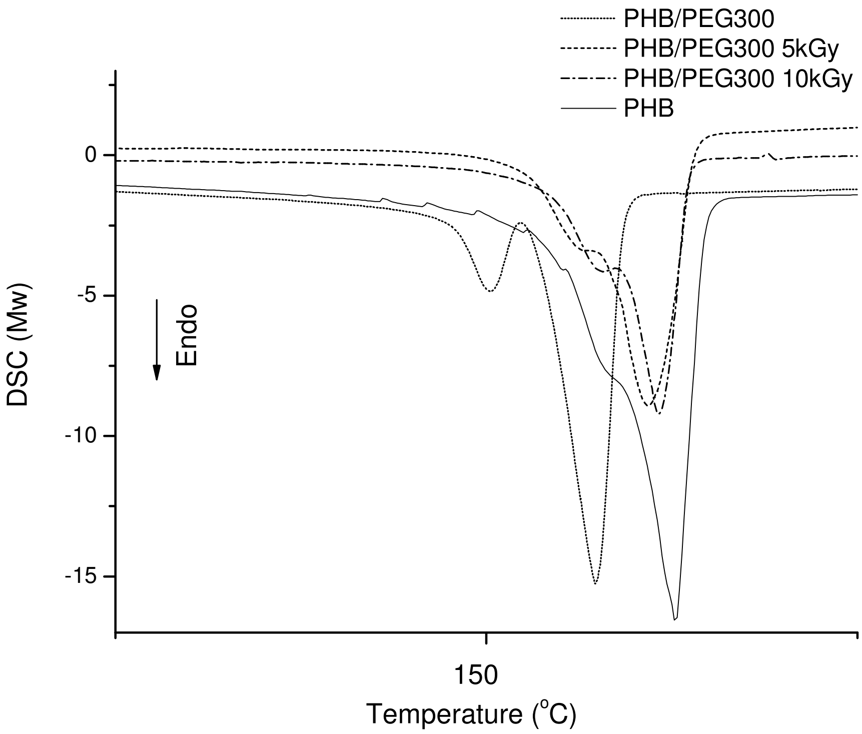

**Figure 1. DSC results of PHB/PEG blends of irradiated and non-irradiated films**.

The crystallization of irradiated films with PEG 300 are compared in Table 1: at low PEG content (5%) the observed decrease of crystallization temperature after 10 kGy means the presence of segments, a result of scission with improved mobility. The decrease of crystallinity degree (%) indicates the simultaneous occurrence of crosslinking reactions that impede the crystallization phenomenon.

The double or multiple melting behaviors sometimes occurs for PHB and its copolymers, and depends on the crystallization conditions [8]. Multiple melting behavior of a polymer is usually attributed to process of partial melting and recrystallization or melting of crystals with different lamellar thickness [9].

Parra *et al* have verified that the displacement of the melting temperatures of irradiated films occurs above 10kGy [6] . The DSC profile of PHB/PEG film irradiated at 40 kGy showed enlarged quasi-double crystallization peaks on cooling. Furthermore in the reheating a second melting peak, separated at about 17 °C from the main melting peak, was observed. At relatively low irradiation dose (below 40 kGy), this peak persists and is attributed to bimodal distribution of crystallite sizes resulting from changes in molar mass due to random scission of long PHB chains, i.e., to the decrease in the molar mass, or to unstable lamellar layers present, generally, on the surface of the crystals. After irradiation these distinct crystalline structures will become more indistinguishable with the fragmentation of the chains and the double peaks become a single enlarged peak with an increase in dose.

The second melting peak disappears only at high irradiation doses (above 50 kGy) when polymeric crystal lamellae are drastically deformed. This was verified for PHB powder at 300kGy, as reported by Oliveira *et al.* [10]. In addition to this, the plasticizer can influence lamellae formation of the polymer. PEG nucleation (crystallizing at lower temperature) reduces the mobility of PHB retarding the lamellae formation. According to Yoshie *et al.* [11], thinner lamellae have lower melting temperature. Also the crystallization temperature ($T_c$) has a little shift to lower temperature due to cold crystallization. In the presence of the PEG plasticizers, which quite efficiently reduce the intermolecular interaction in the PHB phase, the mobility of macromolecules necessary for cold crystallization may be noticed at lower temperatures, as observed by Bibers *et al* [12].

When irradiated, our films showed a decrease in crystallinity owing to the possibility of crosslinking occurring at low levels (10 kGy) of irradiation.

### 3.2 Water vapor transmission rate (WVTR)

Table 2 shows a comparison of the WVTR behaviours from all the tested samples: PHB and with PEG at irradiation 5 and 10 kGy, and non-irradiated films.

**Table 2. WVTR results of irradiated and non-irradiated PHB/PEG films.**

| PEG Concentration (%) | Film | WVTR. $10^{-8}$(g.mm.cm$^{-2}$.h$^{-1}$) | $R^2$ |
|---|---|---|---|
| | | 1.23 | 0.95 |
| 0 | PHB | | |
| | | 1.33 | 0.98 |
| 5 | PHB/PEG 300 | | |
| | PHB/PEG 300 - 5 kGy | 0.086 | 0.96 |
| | PHB/PEG 300 - 10 kGy | 0.058 | 0.93 |

The decrease in WVTR values of the irradiated films is attributed to crosslinking PHB formation, which changes the hydrophilic character of the films. The addition of plasticizer does not alter this property, table 3. These results are similar to those of Rodríguez *et al.*, who analyzed the sorption and diffusion data obtained for water vapor in four different polymers: poly(methylmethacrylate) (PMMA), poly(2-hydroxyethylmethacrylate)(PHEMA), poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(acrylonitrile) (PAN) at 35°C using a gravimetric sorption method. Highest sorption was observed in PVP, followed by PHEMA, PMMA and PAN, with very little water quantity. All polymers exhibited a type III Brunauer, Emmett and Teller (BET) isotherm sorption. The large upturn at high activity for PVP and PHEMA was probably due to plasticization of the polymers by water vapor [8].

## 4. CONCLUSION

Irradiation of the films and decreased WVT values of the samples. Crosslinking and changes of the hydrophilic character of the films have been attributed to the effects of irradiation. The evidence of crosslinking reactions in irradiated films with PEG content is the decrease of crystallization temperature that makes crystallization more difficult. The crystallinity increased with irradiation at 5 kGy and decreased at 10 kGy, but maintained a higher level than that of non-radiated films.

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## REFERENCES

1. S.Y. Lee. Bacterial polyhydroxyalkanoates. *Biotechnology and bioengineering,* **49,**pp.1-14 (1996)
2. J.A.F.R. Rodrigues, D.F. Parra, A.B. Lugão. "Crystallization on films of PHB/PEG blends", *Journal of Thermal Analysis and Calorimetry,* **79**, pp. 379-381 (2005).
3. A. Bhattacharya "Radiation and industrial polymers" *Prog. Polym. Sci.*, **25**, pp. 371-401 (2000).
4. C. J. Chen, D. C. Boose, G. S. Y. Yeh, Radiation-induced cross-linking. 2. Effect on the crystalline and amorphous densities of polyethylene *Colloid Polym Sci.,* **269**, pp. 469-476 (1991).
5. X. Lu, N. Brown, M. Shaker, L. Kamel, The effect of gamma-irradiation on slow crack-growth in polyethylene, *J Polym Sci, Polym Phys.,* **33,** pp.153-157 (1995).
6. D.F. Parra, J.A.F.R Rodrigues, A.B. Lugao. Use of gamma-irradiation technology in the manufacture of biopolymer-based packaging films for shelf-stable foods. *Nucl Instr Meth Phys Res B*; **236**, pp. 563-566 (2005).
7. M. Erceg, T. Kovacic, I. Klaric. Thermal degradation of poly(3-hydroxybutyrate) plasticized with acetyl tributyl citrate. *Polym Degrad Stab*. **90**, pp. 313-318 (2005).
8. F. Rodriguez, C. Cohen, C.K. Ober, L.A. Archen. Principles of Polymer Systems. Washington: CRC Press, Taylor & Francis; pp. 215 (2003).
9. P. Pearce, R.H. Marchessault. Multiple melting in blends of isotactic and atactic poly(beta-hydroxybutyrate). *Polymer*, **35**, pp. 3990-3997 (1994).
10. L.M. Oliveira, E.S. Araujo, S.M.L. Guedes. Gamma irradiation effects on poly(hydroxybutyrate). *Polym Degrad Stab,* **91**, pp. 2157-2162 (2006).
11. N. Yoshie, K. Nakasato, M. Fujiwara, H. Abe, Y. Doi Effect of low molecular weight additives on enzymatic degradation of poly(3-hydroxybutyrate). *Polymer*, **41**, pp. 3227-3234 (2000).
12. I. Bibers, V. Tupureina, A. Dzene, M. Kainins. Improvement of the deformative characteristics of poly-beta-hydroxybutyrate by plasticization. *Mechanics Composite Mater* **35**, 357-364 (1999).