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Influence of poly (ethylene glycol) on the thermal, mechanical, morphological, physical–chemical and biodegradation properties of poly (3-hydroxybutyrate)

D.F. Parra [a,*], J. Fusaro [a], F. Gaboardi [b], D.S. Rosa [b]

[a] *Chemical and Environmental Center (CQMA), Instituto de Pesquisas Energéticas e Nucleares (IPEN), Av. Lineu Prestes, 2242, Cidade Uiversitaria 05508-900, São Paulo, SP, Brazil*

[b] *Laboratório de Polímeros Biodegradáveis e Soluções Ambientais, Universidade São Francisco, Rua Alexandre Rodrigues Barbosa, no. 45, Centro, 13251-900, Itatiba, SP, Brazil*

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Abstract

Blends of poly (3-hydroxybutyrate) (PHB) with poly (ethylene glycol) (PEG), (PHB/PEG), in different proportions of 100/0, 98/2, 95/5, 90/10, 80/20 and 60/40 wt%, respectively, were investigated for their thermal properties (using differential scanning calorimetry and thermogravimetric analysis), tensile properties, water vapor transmission rate, enzymatic biodegradation (using light microscopy) and mass retention. The addition of plasticizer did not alter the thermal stability of the blends, although an increase in the PEG content reduced the tensile strength and increased the elongation at break of pure PHB.

Keywords: Poly (3-hydroxybutyrate); Plasticizers; Mechanical and thermal properties; Physical–chemical properties

1. Introduction

The detrimental effects of synthetic polymers on the environment have become increasingly evident in recent decades, mainly because of the resistance of these materials to peroxidation and to degradation by water and microorganisms, all of which contribute to limited recycling [1]. The final disposal of biodegradable materials is an important consideration in the ecological balance of materials. Once biobased material has been recycled through composting and the compost applied to land, significant energy stores can accumulate, thereby increasing the value of the compost for sustainable agriculture [2]. The advantage of renewable resources is that the carbon dioxide burden in the atmosphere is neutral for biobased polymers, but attention is claimed to the oil-based energy involved in the growing transport and processing of biological materials to produce polymers [3]. Although the costs of producing "in developing" biopolymers are currently high, this is expected to decrease with time [4].

Biodegradable polymers are necessary to overcome the problems on fossil resources, recycling limitations and global environment [5].

The biodegradation of polymers involves distinct mechanisms, depending on the nature of the polymer. One mechanism involves hydrolysis (biotic or abiotic) followed by bioassimilation (hydrodegradation) and is the primary pathway involved in the biodegradation of heterochain polymers such as starch, cellulose and polyesters, including poly (L-lactide) (PLA) and PHA. The second mechanism is peroxidation followed by bioassimilation of low molar mass products (oxo-biodegradation), and is typical for carbon chain polymers. Bioassimilation after peroxidation occurs as soon as low molar mass oxidation products are formed [6].

* Corresponding author. Tel.: +55 01138169341; fax: +55 01138169325.
E-mail addresses: duclercp@iq.usp.br (D.F. Parra), derval.rosa@saofrancisco.edu.br (D.S. Rosa).
URL: http://www.dervalrosa@yahoo.com.br

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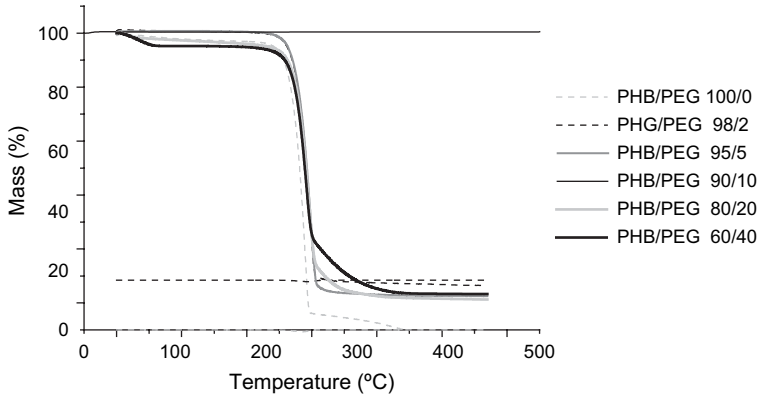

Fig. 1. TGA curves for the thermal decomposition of PHB and the PHB/PEG blends.

Among biodegradable polymers, polyesters of microorganism origin are derived from renewable resources, such as starch and fats, and are completely biodegraded in soil and rivers. Poly (3-hydroxybutyrate) (PHB) is a natural, linear, homochiral, thermoplastic polyester produced by microorganisms as intracellular fat deposits in response to limited nutrient availability. PHB belongs to a polyhydroxyalkanoate class of shorter pendant groups that confers a high degree of crystallinity [7].

PHB is well-known for its mechanical properties that are similar to those of polypropylene. This polymer provides a better oxygen barrier than PP and polyethylene terephthalate, with a water barrier performance lower than PP and good resistance to solubility in water and thermal resistance. PHB is highly biodegradable and biocompatible.

The degradation of PHB depends on the microbial activity of the environment and on the surface area of the sample. In addition, the crystallinity, molecular weight of the sample, and temperature are important factors that influence the growth of microorganisms on the polymer surface.

Poly (ethylene glycol) (PEG) has been used to form various block copolymers with poly(ε-caprolactone) (PCL) and poly (L-lactide) (PLA) [8,9]. PEG has outstanding properties, including good solubility in water and in organic solvents, a lack of toxicity, and no antigenicity, and, consequently, no immunogenicity, all of which are essential properties for drug formulations. In addition, PEG is hydrophilic and not biodegradable.

In this study, we examined the influence of different concentrations of PEG on the thermal properties (using differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA)), mechanical properties (tensile strength at maximum and elongation at break), permeability to water steam, enzymatic biodegradability (based on light microscopy (LM)) and mass retention of PHB.

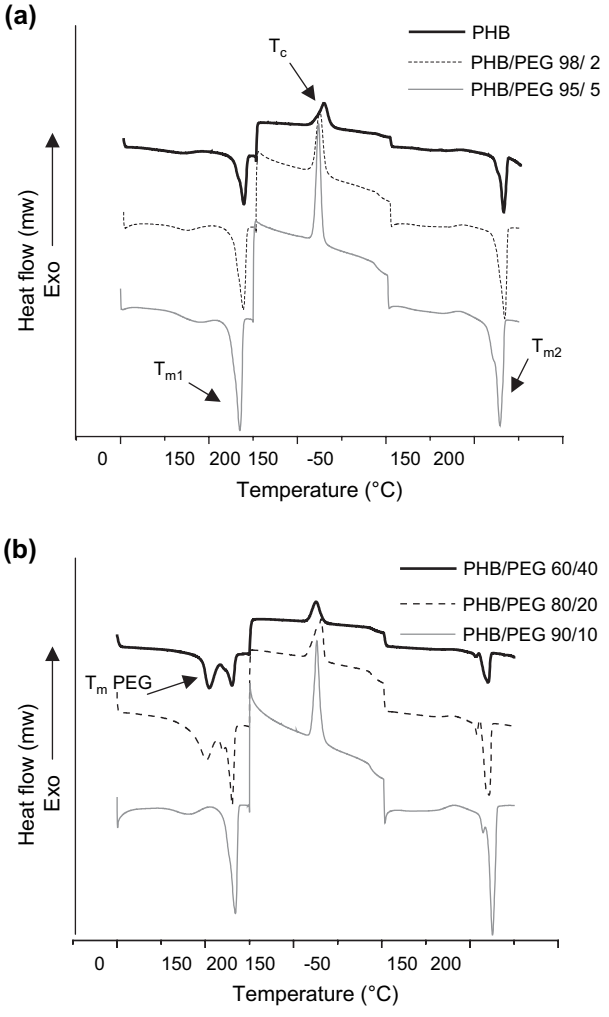

Fig. 2. DSC curves of PHB and PHB/PEG blends. (a) Blends with 2% and 5% PEG; (b) blends with 10%, 20% and 40% PEG.

Table 1
DSC results of the various PHB/PEG blends

Blend	T_{m1} (°C)	T_c(°C)	T_{m2} (°C)	Crystallinity (%)
PHB/PEG 100/0	178.7	91.3	171.0	30.7
PHB/PEG 98/2	175.5	79.9	169.4	32.0
PHB/PEG 95/5	174.3	77.3	164.6	31.5
PHB/PEG 90/10	167.0	74.2	150.1	25.0
PHB/PEG 80/20	166.2	64.8	152.4	26.1
PHB/PEG 60/40	173.4	72.8	159.1	29.8

Table 2
Tensile mechanical properties of the various PHB/PEG blends

Blend	Tensile strength at maximum (MPa)	Elongation at break (%)
PHB/PEG 100/0	28 ± 3	9 ± 3
PHB/PEG 98/2	26 ± 8	25 ± 6
PHB/PEG 95/5	11 ± 3	25 ± 10
PHB/PEG 90/10	12 ± 3	25 ± 8
PHB/PEG 80/20	13 ± 8	32 ± 8
PHB/PEG 60/40	13 ± 4	31 ± 10

The values are the mean value of eight determinations.

2. Experimental

2.1. Materials

2.1.1. PHB

It was supplied in powder form by Usina da Pedra PHB do Brazil S.A. (Serrana, SP, Brazil) and had an weight average molecular weight (M_w) of 380,000 g/mol, with PHB accounting for 99.9% of the dry material.

Poly(ethylene glycol) (PEG) was supplied by Oxiteno (Mauá, SP, Brazil) and had an M_w of 300 g/mol.

2.2. Film preparation

Films of PHB with and without PEG were prepared by casting using the following proportions of PHB/PEG: 100/0, 98/2, 95/5, 90/10, 80/20 and 60/40 (wt%). Pure PHB is represented by 100/0. The materials were dissolved in chloroform to give 15% (w/w) solutions that were stirred thoroughly at 60 ± 1 °C for 10 min and then poured into Pyrex recipients after which the solvent was allowed to evaporate in a saturated atmosphere.

2.3. Thermal analysis

2.3.1. TGA

TGA scans were obtained using samples of about 30 mg in sapphire crucibles, under a nitrogen atmosphere (50 ml min^{-1}), at a heating rate of 5 °C min^{-1} in an SDTA-822 thermobalance (Mettler Toledo, Switzerland). The initial decomposition temperatures (T_{onset}) were determined directly from the thermograms.

2.3.2. DSC

Thermal analysis was done using a DSC 821^e differential scanning calorimeter (Mettler Toledo, Switzerland) under an atmosphere of nitrogen, at a heating rate of 10 °C min^{-1}. Two heating cycles were used for each film. The PHB was initially heated from −50 °C to 200 °C to eliminate the thermal history of the sample, and then cooled to −50 °C at a cooling rate at 10 °C min^{-1} before being immediately reheated to 200 °C. The second scan (−50 °C to 200 °C) was done at the same heating rate. All DSC experiments were done in duplicate and the thermograms shown refer to the second heating. The crystallinity (X_c) of PHB in the blends is calculated according to Eq. (1).

$$X_c = \Delta H_f \times 100 / \Delta H_o \times w(\mathrm{PHB}) \quad (1)$$

ΔH_f = melting enthalpy of the sample (J g^{-1}). ΔH_o = melting enthalpy of the 100% crystalline PHB which is assumed to be 146 J g^{-1}[10] and w (PHB) is the weight fraction of PHB in the sample.

The DSC apparatus was calibrated with Indium (m.p. 156.61 °C; $\Delta H = 28.54$ J g^{-1}).

2.4. Determination of the tensile properties

Type I specimens (ASTM D-638/99) were stamped with a cutting tool. The tests were done using an Instron model 4400R universal testing machine (Instron Materials Testing, Canton, MA, USA) with a 50 N load cell. The specimens were 4.0 mm long and the speed of stretching was 1.0 mm/s. The test specimens were cut in the shape of Die F dumbbells, according to the standard ASTM method. The tensile strength

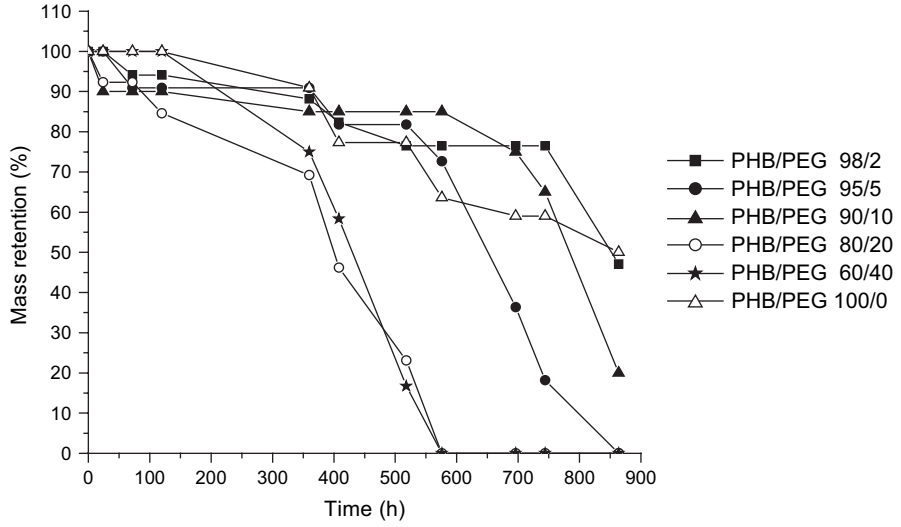

Fig. 3. Results for the enzymatic biodegradation of the films.

at maximum (σ_{rmax}) and elongation at break (ε_{rup}) were determined and are shown as the averages of five specimens.

2.5. Enzymatic biodegradation

2.5.1. Light microscopy (LM)

The morphology and behavior of the materials during phase separation were assessed by light microscopy using a Laborana Model XP-500 microscope fitted with a CCD photographic camera (Laborana Ltda., São Paulo, Brazil) with a resolution of 330/460 lines and a range of enlargement from 10× to 400×. The samples were examined after 0, 24, 72, 120, 576, 744 and 864 h. Photographs of the initial and final stages of each samples are shown.

2.5.2. Enzymatic degradation

Each sample was placed in a vial filled with 5.7 g of α-amylose and 10 ml of acetate buffer (pH 6) was added, after which the vials were placed in a thermostatted oven at 60 °C. The enzyme/buffer system was changed every 24 h to restore the original level of enzymatic activity. After 0, 24, 72, 120, 576, 744 and 864 h, the samples were removed from the incubation medium, washed with distilled water, wiped dry, and then weighed and examined by light microscopy. Control samples were prepared in buffer without enzyme.

2.6. Water vapor transmission rate

The water vapor transmission rate (WVTR) was calculated according to Eq. (2).

$$\mathrm{WVTR} = \frac{w \times x}{t \times A} \tag{2}$$

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

3. Results and discussion

The PHB/PEG films were transparent, homogeneous and flexible compared to the brittle, pure PHB film. PHB was completely miscible with PEG during the preparation of the films.

3.1. Thermal analysis

3.1.1. TGA

Fig. 1 shows the thermal behavior (TGA curves) of pure PHB and its blends containing 0%, 2%, 5%, 10%, 20% and 40% PEG. The T_{onset} of the PHB films were 257 °C, 256 °C, 258 °C, 246 °C and 235 °C for PEG contents of 2%, 5%, 10%, 20%, and 40%, respectively, whereas for PHB film without PEG the temperature was 257 °C. These temperatures were very close to each other, indicating that the addition of plasticizer to a final concentration of up to 10% did not alter the thermal stability of the blends. Blends obtained with addition of 20 and 40% of PEG showed displacement of the T_{onset} value. Probably in higher concentrations the diffusion of the plasticizer to the surface is enhanced by heating and the T_{onset} of

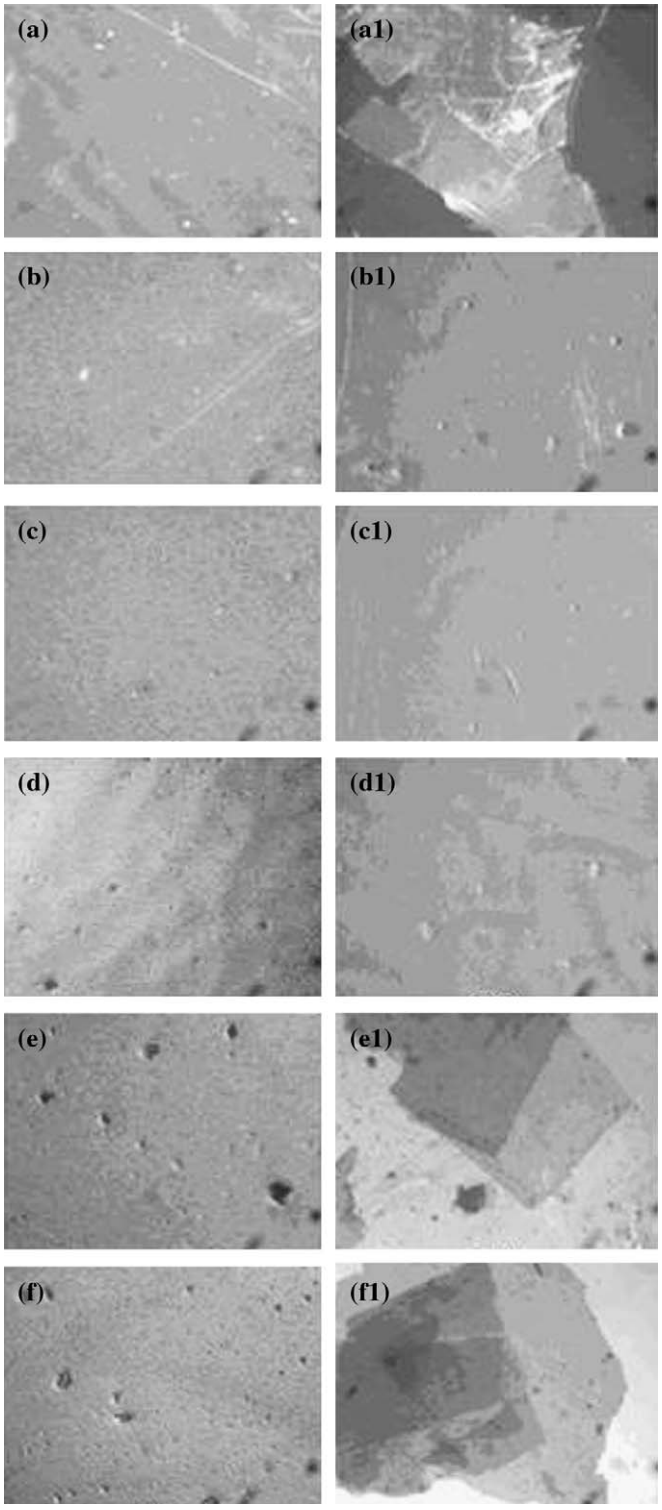

Fig. 4. Light microscopy (40×) of the sample before and after the biodegradation test. (a) pure PHB (before), (a1) pure PHB (after); (b) PHB 2% (0 h), (b1) PHB 2% (744 h); (c) PHB 5% (0 h), (c1) PHB 5% (744 h); (d) PHB 10% (0 h), (d1) PHB 10% (744 h); (e) PHB 20% (0 h), (e1) PHB 20% (408 h); (f) PHB 40% (0 h), (f1) PHB 40% (408 h).

the blend decreases. In the TG curves shown in Fig. 1, the mass loss observed at around 50 °C was caused by the presence of solvent in the film.

3.1.2. DSC

The DSC results (Fig. 2) showed that the melting temperatures (T_{m1} and T_{m2}) of the blends decreased with increasing concentration of PEG when compared to the pure PHB. The plasticizer probably weakened the intermolecular forces between the adjacent polymer chains. Consequently, there was a change in free volume that reduced the melting temperatures of the system (T_{m1} and T_{m2}). Results are shown in Table 1. On the other hand plasticizer that crystallizes before the PHB (T_c of PEG = 50–60 °C) can influence the lamellae formation of the polymer. The performed nucleation of the additive probably reduces the mobility of the PHB retarding the lamellae formation. According to Yoshie et al., thinner lamellae have lower melting temperature [11]. The crystallinity of PHB in the sample was determined according to Eq. (1) and the results are shown in Table 1. The films showed lower crystallization temperatures (T_c) than the pure PHB (91.3 °C) for all the blends. During non-isothermal crystallization, the crystallization rate decreased in the presence of the plasticizer. Consequently, nucleation was hindered and promoted the formation of small spherulites, thereby increasing the flexibility of the blends compared to the pure material. The crystallinity was altered in the films of 90/10 or 80/20 blends but considering the information by Luo et al. [9], also in this case the additive has little effect on the crystallinity.

3.2. Determination of the tensile properties

Table 2 shows the tensile strength and elongation at break for pure PHB and for the samples with plasticizer. Compared to pure PHB film, tensile strength was reduced by the addition of PEG. These results indicated that the plasticizer reduced any restraint imposed on the separation of the lamellae during the mechanical test. PEG probably inhibited the relative chain motion or reduced the force of secondary intermolecular bonds between the PHB chains [12]. In addition, the blends with plasticizer had a higher elongation at break than the pure PHB film.

3.3. Enzymatic biodegradation

The results of enzymatic degradation are shown in Fig. 3. The hydrophilic plasticizer enhanced the biodegradation, and increasing the content of plasticizer increased the rate of enzymatic degradation. Amylase, the enzyme used in this degradation test, reduces the activation energy in the hydrolysis of polymers and increases the reaction rates by facilitating the bioassimilation and biodegradation of low molecular weight fragments [13].

The results of enzymatic degradation, together with the data for mass loss and light microscopy findings, are shown in Figs. 3 and 4, respectively. Samples containing 20% and 40% PEG lost 50% of their mass after 401 and 431 h of aging with amylase. The same amount of mass loss was seen after 853, 650 and 784 h for 2%, 5% and 10% PHB, respectively (Fig. 5). The addition of larger amounts of PEG (20% and 40%) increased the number of polar groups in the samples, and promoted the interaction of these groups with water molecules in the hydrolysis that preceded biodegradation. These results agree with the permeability to water, which tended to increase with rising concentrations of the plasticizer.

Increasing concentrations of plasticizer also caused morphological alterations in the surface of PHB, and reduced the interaction between the chains of PHB and PEG in the

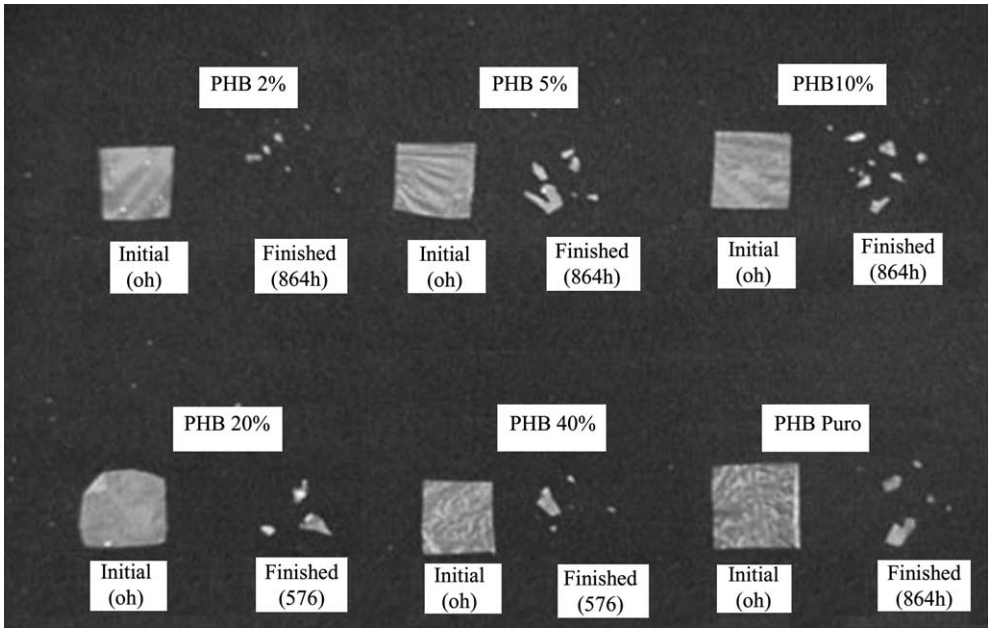

Fig. 5. Visual aspect of the PHB and PHB/PEG blend samples before and after enzymatic aging.

Table 3
Water vapor transmission rate of the various PHB/PEG blends

Blend	WVTR $\times 10^{-8}$ (g H_2O mm/h cm^2)
PHB/PEG 100/0	0.347
PHB/PEG 98/2	0.628
PHB/PEG 95/5	1.058
PHB/PEG 90/10	1.189
PHB/PEG 80/20	1.549
PHB/PEG 60/40	1.585

blends, thereby accelerating biodegradation. Similar results were also obtained by Bragança and Rosa [14] in studies of poly(ε-caprolactone) and cellulose acetate blends. Another explanation could be the natural incompatibility between PEG and PHB, already mentioned by Chiellini and Solaro [15], and could account for the extensive biodegradation of samples containing 40% PEG because of the migration of this plasticizer to the surface of the polymeric material.

3.4. Water vapor transmission rate (WVTR)

The permeability steam water vapor rate shown in Table 3 indicates that the permeability reached a maximum value and stabilized at a PEG concentration of 20%.

4. Conclusions

The PHB/PEG films were transparent and flexible compared to the pure, brittle PHB film. The initial temperatures of decomposition of these films were very close to each other, indicating that the addition of plasticizer to a concentration of up to 10% did not alter the thermal stability of the final blends. The plasticizer probably weakened the intermolecular forces between the adjacent polymer chains. Consequently, there was a change in free volume with reduction of the melting temperatures (T_{m1} and T_{m2}). The hydrophilic nature of the plasticizer improved the water vapor permeability and the biodegradation such that permeation of water and rate of enzymatic degradation were greater with increasing concentrations of plasticizer.

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