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Influence of oxidized polyethylene wax (OPW) on the mechanical, thermal, morphological and biodegradation properties of PHB/LDPE blends

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Abstract Blends of poly(β-hydroxybutyrate) (PHB) and low density polyethylene (LDPE) were prepared in proportions of 100/0, 75/25, 50/50, 27/75 and 0/100 (PHB/LDPE wt.%), with and without oxidized polyethylene wax (OPW, 5 wt.%), and the mechanical, thermal (differential scanning calorimetry and melting flow index, morphological (scanning electron microscopy) and biodegradation (aging in simulated soil) properties were evaluated. The addition of OPW increased the tensile strength and Young's modulus but decreased the elongation at break of the blends. Similarly, OPW increased the T_g of the pure LDPE and enhanced the melt flow index. Scanning electron microscopy showed that OPW reduced the phase separation of LDPE and increased the biodegradation during aging in simulated soil.

Introduction

The resistance of plastics to attack by microorganisms markedly increases the time required for complete degradation. As a result, the accumulation of plastics in the environment, including oceans [1], can markedly influence the compactation of other waste and create impermeable layers that can affect liquid and gas exchange during the decomposition of biodegradable material in soil and sediment. The use of biodegradable polymers is an alternative for reducing the environmental impact of plastic waste [2].

Poly(β-hydroxybutyrate) (PHB) is a polymer synthesized by bacteria, such as *Alcaligenes eutrophus*, during sugar cane fermentation and is stored in the cell cytoplasm where it serves as a carbon and energy reserve [3, 4]. Despite advantages such as good biodegradability, the commercial production of this polymer is expensive compared to synthetic polymers. An alternative to reduce the cost of this polymer is to produce blends with lower-priced polymers such as low-density polyethylene (LDPE) [5]. However, LDPE is resistant to microbial attack [4], and its biodegradation must be enhanced by incorporating an additive.

Biodegradation is a natural process that is initiated by the action of microorganisms on the polymer surface, with the microorganisms secreting enzymes capable of converting polymers into water and carbon dioxide (CO_2) that can be recycled into carbon and nitrogen under appropriate conditions [6, 7]. Oxidized polyethylene wax (OPW) is an additive that facilitates biodegradation because of the presence of oxidized elements in its chemical structure.

Prooxidant additives represent a promising solution to the problem of the environment contamination with polyethylene film litter. Prooxidants accelerate photo- and thermo-oxidation and consequent polymer chain cleavage rendering the product apparently more susceptible to biodegradation [8]. In addition, nuclear magnetic resonance (NMR) has revealed significant amounts of organic substances derived from polyethylene oxidized by exposure to aqueous medium and bacteria, and also from stearate [8]. Kawai et al. [9] showed that polyethylene wax fragments with a molar mass distribution close to 1000 Da were rapidly consumed by microorganisms.

The biodegradation of LDPE by acetylcetonate, cobalt stearate (Co) and manganese in compost was studied and

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confirmed that metal catalyst disappeared or was inactive during compostage. X-ray diffraction showed that Co/acetylacetonate complexes migrated out of the film whereas Mn remained within the film, although the metal had been inactived by an unknown mechanism [10].

Chiellini et al. [11] analyzed carbon dioxide (CO_2) production during the biodegradation of polyethylene containing a thermally-treated prooxidant in soil and compostage. There was a decrease in the molar mass of polyethylene during thermal degradation, with the rates of biodegradation being 50–60% in soil and 80% in compostage.

The aim of this study was to assess the influence of OPW on the biodegradation of PHB/LDPE blends in simulated soil based on the mechanical properties (tensile strength, elongation at break and Young's modulus), thermal analysis (differential scanning calorimetry (DSC) and melt flow index (MFI)), and morphology assessed by scanning electron microscopy (SEM).

Experimental

Materials

Low density polyethylene (LDPE, type PB-208) was supplied in pellet form by Braskem (Triunfo, RS, Brazil). The melt flow at 190 °C was 22 g/10 min (ASTM D-1238) with a density of 923 kg/m^3 (ASTM D-1505).

Poly(β-hydroxybutyrate) (PHB, type Biocycle 1170-1) was supplied in powder form by PHB Industrial S.A. (Biocycle, Serrana, SP, Brazil). The melt flow index at 190 °C was 18 g/10 min with a density of 1230 kg/m^3 (ASTM D-792) and a weight average molecular weight (M_w) of 600,000 g/mol.

Oxidate polyethylene wax (OPW, type Meghwax OPW 416) was supplied in flake form by MEGH Indústria e Comércio Ltda. (São Paulo, SP, Brazil).

Blend preparation

Blends of PHB/LDPE (100/0, 75/25, 50/50, 25/75 and 0/100, w/w) were prepared with and without OPW (final content, 5%) using a single-screw extruder with an L/D 25. The thermal profile was 150, 170, 180 and 190 °C for zones 1, 2 and 3 and the headstock, respectively, and the screw speed was 50 rpm.

Film preparation

Films were compression molded into sheets (180 mm × 180 mm × 1 mm) using a model MA 098 Marconi press (Marconi-Equipamentos e Calibração para Laboratórios, Piracicaba, SP, Brazil). Approximately 20 g of each formulation was pressed with a closure force of 49030 N and the temperature was kept at 190 ± 5 °C for 4 min. The resulting sheets were cooled to room temperature.

Injection of the specimens

The specimens for mechanical analysis were injected into a model PIC 62 machine (Petersen & Cia Ltda., SP, Brazil) at a pressure of 118 MPa and a total cycle time of 40 s. The temperatures used in zones 1, 2, 3 and 4 were 170, 170, 160 and 130 °C, respectively, for the formulation containing more than 50% PHB, and 150, 150, 140 and 130 °C, respectively, for the remaining formulations.

Mechanical properties

Tensile tests to determine the elongation at break, tensile strength and Young's modulus were done with a model DL 2000 EMIC universal testing machine (EMIC Equipamentos e Sistemas de Ensaio Ltda., São José dos Pinhais, PR, Brazil), according to ASTM D638 [12] (Type III). The specimens were strained at a rate of 0.83 mm/s at room temperature.

Melt flow index (MFI)

The melt flow indices of PHB, LDPE and their blends were determined using a model MI-1 plastometer (DSM Instrumentação Cientifica Ltda., São Paulo, SP, Brazil), according to ASTM-D-1238 (190 °C/2.160 kg) [13].

Differential scanning calorimetry (DSC)

Thermal analysis was done using a DSC 204 TASC 414/3A differential scanning calorimeter (Netzsch-Geraütebau GmbH, Bavaria, Germany) in a nitrogen atmosphere, at a heating rate of 10 °C/min. Two heating cycles were used for each film. The samples were first heated from room temperature to 200 °C to eliminate their thermal history and then cooled to 150 °C and immediately reheated to 200 °C.

Scanning electron microscopy (SEM)

Specimens were fractured after freezing in liquid nitrogen and micrographs of the fractured surfaces were obtained using a JEOL model JSM-5900LV scanning electron microscope. The cross-sections were coated with gold in a Baltec SCD 050 sputter coater (40 mA current for 60 s) and then examined by SEM. Representative images were selected for analysis.

Light microscopy

The morphology and behavior of the materials during enzymatic degradation were also assessed by light microscopy (Model XP-500 microscope, Laborana Ltda., São Paulo, SP, Brazil) fitted with a CCD camera (resolution of 330/460 lines). Photographs were taken before and after aging in simulated soil.

Biodegradation in simulated soil

The simulated soil consisted of 23% loamy silt, 23% organic matter (cow manure), 23% sand and 31% distilled water (all w/w). The specimens (20 mm × 20 mm) were weighed and buried, in triplicate, in simulated soil at 24 °C in the dark. Biodegradation was monitored every 30 days for approximately 8 months by measuring the mass retention. At each interval, the buried samples were recovered, washed with distilled water and dried at room temperature until there was no further variation in weight, after which they were weighed. The specimens were buried again in their respective trays until the next weighing.

Results and discussion

Mechanical properties

Table 1 shows the tensile strength, elongation at break and Young's modulus for PHB, LDPE and their blends with and without OPW.

In this study, the tensile strength of break of PHB was higher than the LDPE (29 MPa and 10 MPa, respectively), and the addition of OPW did not change this property of pure PHB. In contrast, Quental and Felisberti [14] studied blends of linear low density polyethylene (LLDPE) and ethene-propene-1-butene copolymer (t-PP) with different compositions and find tensile strength of break of 23 MPa for LLDPE, higher than the values of the LDPE evaluated in this work, of 10 MPa.

The addition of OPW increased the tensile strength and Young's modulus compared to the respective blends without OPW. In contrast, the elongation at break decreased with the addition of OPW. The incorporation of OPW into pure LDPE reduced the tensile strength and the elongation at break but increased the Young's modulus compared to LDPE without OPW. A possible explanation for this finding is that the lower molar mass of OPW, i.e., the short chains produced during degradation of the polymer, resulted in fewer interactions among the chains of polyolefin (LDPE). OPW may have altered the crystallinity of LDPE, as shown by DSC analysis, making it more rigid and less susceptible to elongation. Pedroso and Rosa [15] observed the same behavior with recycled LDPE and found a lower resistance to tensile strength at break and greater rigidity when compared to the pure polymer. This effect was greater for blends containing a higher amount of PHB, as shown by the increase in the Young's modulus of the blends, probably because of the rigidity of PHB. Our findings corroborated those of Pedroso and Rosa [15] for starch and LDPE blends in which an increase in the starch content of the blends reduced the tensile strength and the elongation at break but increased Young's modulus. In the latter case, starch acted as a reinforcing load in a different manner to LDPE in the PHB/LDPE blends.

Thermal properties

Figure 1 shows the MFI of the pure polymers and their blends.

The incorporation of OPW increased the MFI of the blends, particularly in blends containing at least 50% LDPE. The increase in MFI probably resulted from a combination of several factors, including: (a) the incorporation of oxidized wax that acted as a lubricating agent between the chains of PHB and LDPE, (b) a slight degradation of LDPE by the oxidized wax and (c) the possibility that the incorporation of a compound with a smaller molar mass caused fewer interactions between LDPE and PHB. El-Hadi et al. [16] also suggested similar behavior in rheological studies of PHB with wood powder.

Table 1 Tensile strength, elongation at break and Young's modulus of PHB/LDPE blends without and with OPW

PHB/LDPE blend	Tensile strength (MPa)		Elongation at break (%)		Young's modulus (MPa)	
	Without OPW	With OPW	Without OPW	With OPW	Without OPW	With OPW
100PHB/0LDPE	29 ± 2	29 ± 2	0.6 ± 0.1	0.6 ± 0.1	8,265 ± 806	8265 ± 2063
75PHB/25LDPE	18 ± 2	21.6 ± 0.8	11 ± 2	1.2 ± 0.2	367 ± 20	4498 ± 1289
50PHB/50LDPE	10.5 ± 0.6	11.8 ± 0.4	19 ± 5	3.8 ± 0.9	142 ± 30	3334 ± 509
25PHB/75LDPE	8.6 ± 0.2	9.1 ± 0.2	186 ± 5	23 ± 3	82 ± 22	1143 ± 130
0PHB/100LDPE	10 ± 0.2	7.9 ± 0.1	310 ± 5	68 ± 6	41 ± 11	355 ± 58

The values are the mean ± S.D. of 10 determinations

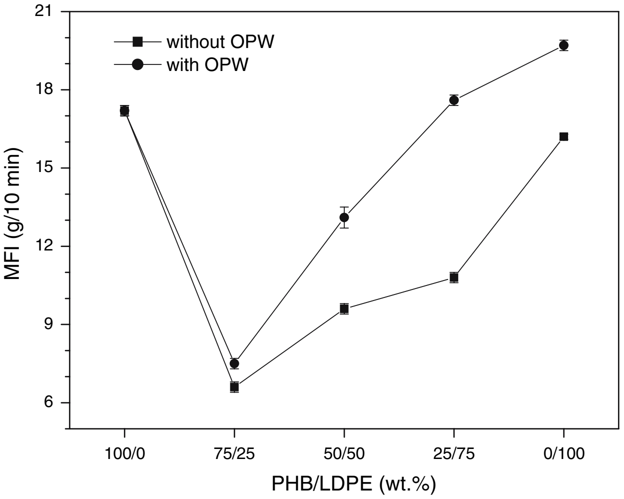


Fig. 1 MFI for PHB, LDPE and their blends with and without OPW. The points are the mean + S.D. of 10 determinations

Figures 2 and 3 show the thermal behavior of PHB, LDPE and their blends without OPW.

LDPE and PHB had glass transition temperatures (T_g) of –104.7 °C and 0.7 °C, respectively. The difference between the T_g values of LDPE and PHB were related to the chemical structure of PHB, which contains polar groups such as carbonyls that tend to approach the polymeric chains, thereby increasing the strength of secondary forces and the T_g and melting temperature (T_m) of the material [17]. The incorporation of PHB into LDPE increased the T_g of the blends, which suggested only slight interaction between the polymers.

Figure 3 shows the thermal melting curves for PHB, LDPE and their blends without OPW. The T_m of blends without OPW and of pure PHB were higher than for pure LDPE, with temperatures of 172.1 °C and 109.1 °C, respectively. The similarity between the T_m of the PHB/LDPE blends and those of pure polymers indicated that there was little interaction between the polymers in the blends.

Figure 4 shows the thermal behavior for PHB, LDPE and their blends with OPW and Table 2 presents the values of T_g and T_m for al the polymers.

The T_g of pure LDPE was lower than that of LDPE with OPW (12.6 °C). This change in T_g probably resulted from the insertion of OPW between the polymeric chains that tended to reduce the force of the molecular attraction between the chains [17]. OPW did not alter the T_g of PHB, which suggested little interaction between OPW and the chains of PHB, perhaps because OPW was incorporated directly into the polyolefin, with little contact with PHB. However, the T_g of these blends was lower than that of blends without OPW.

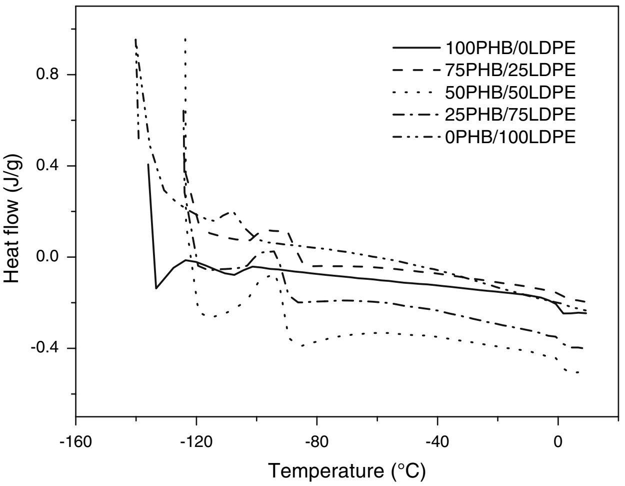


Fig. 2 DSC curves for PHB, LDPE and their blends without OPW

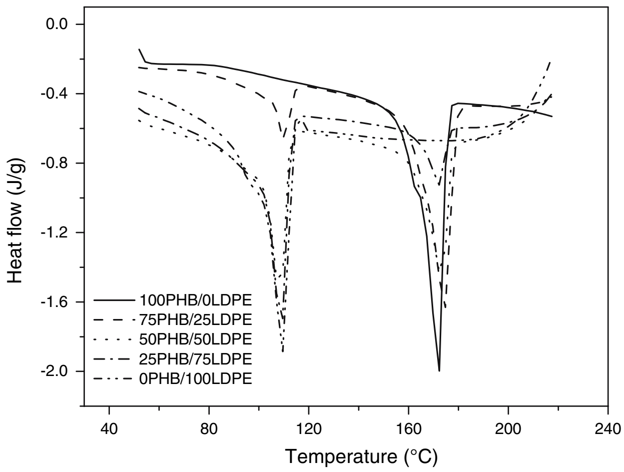


Fig. 3 DSC curves showing the melting temperature peaks for PHB, LDPE and their blends without OPW

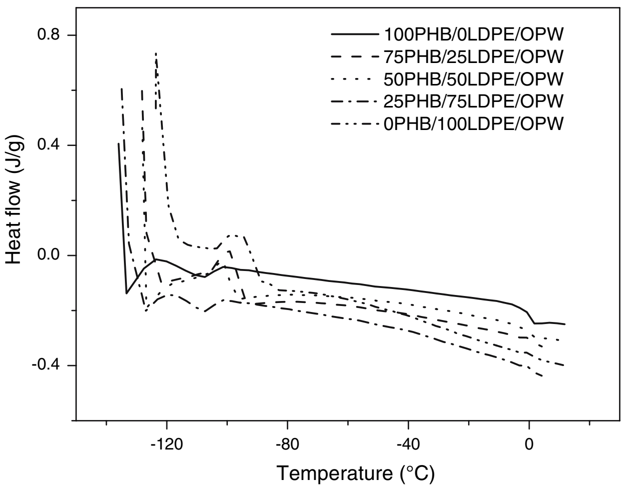


Fig. 4 DSC curves for PHB, LDPE and their blends with OPW

Table 2 T_g and T_m for PHB, LDPE and their blends without and with OPW

PHB/LDPE blend	T_g (°C)				T_m (°C)			
	Without OPW		With OPW		Without OPW		With OPW	
	LDPE	PHB	LDPE	PHB	LDPE	PHB	LDPE	PHB
100PHB/0LDPE	–	0.7	–	0.7	–	172.1	–	172.1
75PHB/25LDPE	–86.9	2.1	–96.1	1.7	109.9	174.1	108.1	173.7
50PHB/50LDPE	–90.5	1.9	–101.7	0.7	108.3	173.3	107.5	169.1
25PHB/75LDPE	–90.8	1.7	–108.8	1.3	108.9	172.5	108.1	169.5
0PHB/100LDPE	–104.7	–	–92.1	–	109.5	–	109.3	–

Figure 5 shows the melting thermogram for PHB, LDPE and their blends with OPW.

The T_m values were unaltered by OPW; PHB had a higher T_m than LDPE whereas the polymer blends has similar values to those of the pure polymers, probably because the 5% OPW incorporated into LDPE was insufficient to significantly change the melting process.

Morphological analysis

PHB and LDPE were immiscible and showed phase separation (Fig. 6b–g). The polymeric spheres in the blend containing 25% LDPE were larger than in the other blends, whereas the blend containing 50% LDPE had higher polymer dispersion and smaller spheres. The LDPE matrix was more homogenous, with no phase separation of the two polymers.

There was poor interfacial adhesion between PHB and LDPE, and the spheres of LDPE were not retained in the PHB matrix (Fig. 6b); indeed, the concave regions seen in SEM probably corresponded to areas from which spheres of LDPE were removed or lost when the samples were fractured in liquid nitrogen.

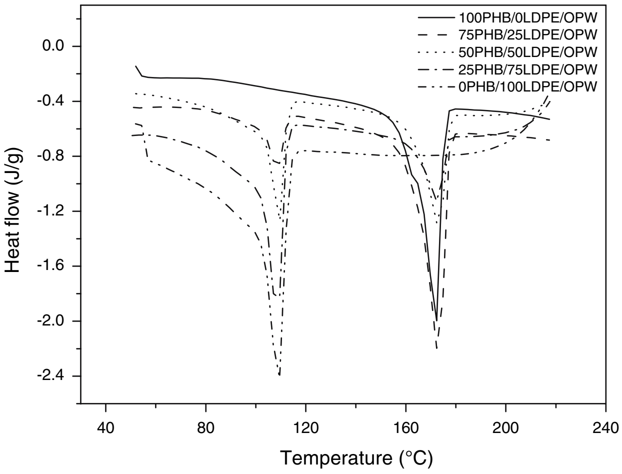


Fig. 5 DSC curves showing the melting temperature peaks for PHB, LDPE and their blends with OPW

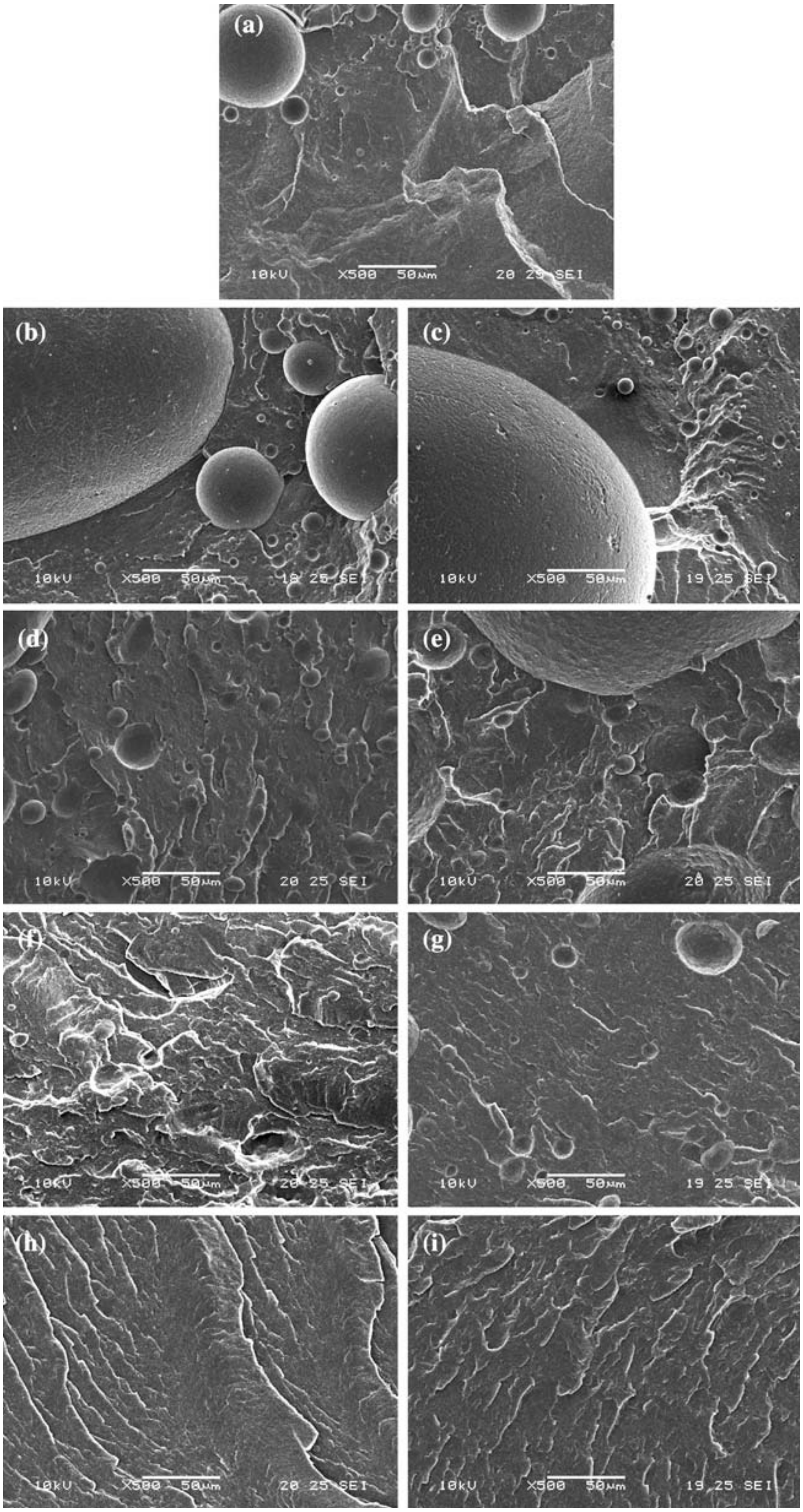
The incorporation of OPW into the blends improved the interfacial adhesion between the two polymers, as shown in Fig. 6b and c for 75PHB/25LDPE and 75PHB/25LDPE/OPW, respectively. The increased interfacial adhesion seen in the blends agreed with the mechanical properties in which the addition of wax increased the tensile strength of the blends by 20%, 12% and 6% in blends containing 25%, 50% and 75% LDPE, respectively.

Biodegradation based on mass retention in simulated soil

Figures 7 and 8 show the percentage of mass retention of PHB, LDPE and their blends with and without the addition of OPW, respectively, during aging in simulated soil.

Figure 7 shows that up to 150 day of aging in simulated soil, the PHB showed higher biodegradation, however, after this period, the 75PHB/25LDPE blend had the highest loss of mass (90%) during aging in simulated soil followed by pure PHB (84%). This means that the polymers may present different behavior during their biodegradation. So, to compare the biodegradation of different kind of polymer it is necessary maintaining the monitoring during al the stages of biodegradation process, that is, the lag phase [18] with the adaptation and selection of the degrading microorganisms; the second phase, from the end of the lag phase until about 90% of the maximum level of biodegradation, which is characterized by a drastic reduction in mass retention in all of the blends; and the last phase, which the plateau phase extend from the end of the biodegradation phase until the end of the test [18]. In contrast, pure LDPE and the blends 25PHB/75LDPE and 50PHB/50LDPE showed little or no loss of mass, which probably reflected the inertness of LDPE. Similar behavior was observed in samples containing OPW, with the 75PHB/25LDPE/OPW blend and pure PHB losing 88% and 84% of their mass, respectively. The 50PHB/50LDPE/OPW blend showed a slight loss of mass that was greater than that seen without

Fig. 6 Photomicrographs of PHB/LDPE blends with and without OPW (500×): (**a**) 100PHB/0LDPE, (**b**) 75PHB/25LDPE, (**c**) 75PHB/25LDPE/OPW, (**d**) 50PHB/50LDPE, (**e**) 50PHB/50LDPE/OPW, (**f**) 25PHB/75LDPE, (**g**) 25PHB/75LDPE/OPW, (**h**) 0PHB/100LDPE, (**i**) 0PHB/100LDPE/OPW



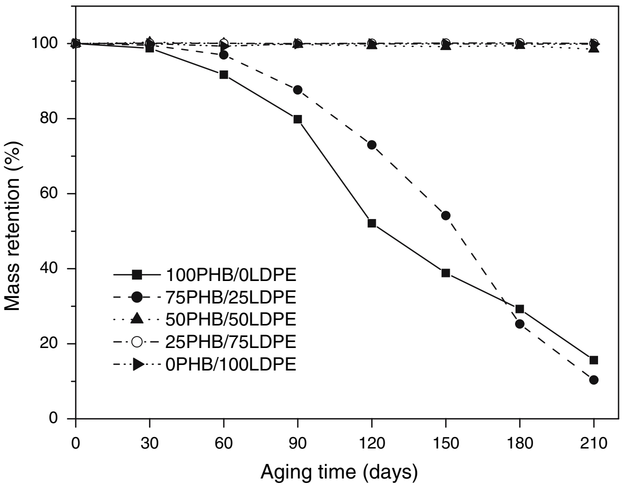


Fig. 7 Mass retention of PHB, LDPE and their blends without OPW during aging in simulated soil. The points are the mean + S.D. of three determinations

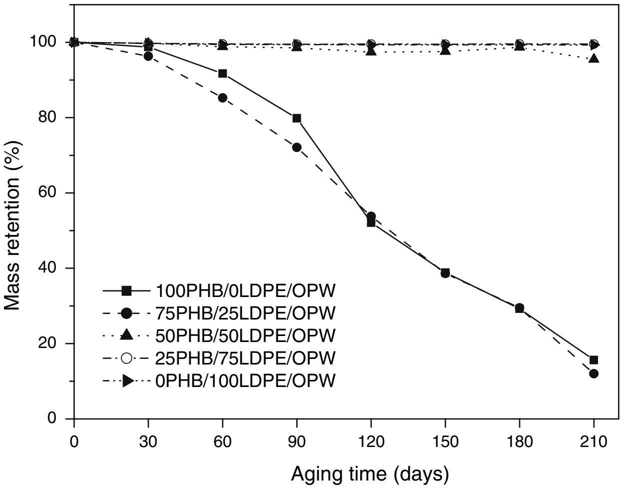


Fig. 8 Mass retention of PHB, LDPE and their blends with OPW during aging in simulated soil. The points are the mean + S.D. of three determinations

OPW. The presence of OPW enhanced the biodegradation of the 75PHB/25LDPE/OPW blend, particularly after 100–150 days of aging (Figs. 7 and 8).

The biodegradation of PHB varies according to the experimental conditions. Kim et al. [19] reported that PHB lost ~98%, 69%, 10% and 7% of its mass after incubation for 25 days at 37 °C in silt, farm soil, arenaceous soil and forest soil, respectively. In a separate study, Rosa et al. [20] found that PHB lost 100% of its mass when aged at pH 7 in simulated soil for 120 days.

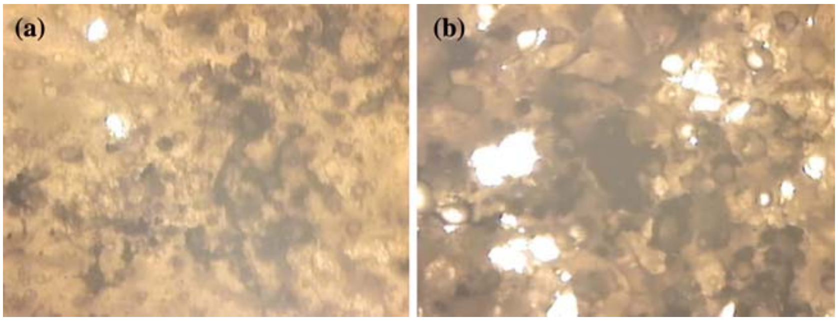
The incorporation of OPW made the samples more susceptible to attack by microorganisms (Fig. 9), as shown by the colonies of microorganisms on the polymer surface (Fig. 10).

Morphological analysis of PHB confirmed that fungi colonized the surface of the polymers and that the initial phase of biodegradation involved the formation of small holes on the surface of the film. In addition, the color of the polymer changed from yellow to green with increasing age, and eventually to black prior to fragmentation.

Conclusion

The incorporation of OPW into blends of PHB/LDPE increased the tensile strength and Young's modulus, but reduced the elongation at break of the blends. In contrast, the addition of OPW to pure LDPE reduced the tensile strength and the elongation at break, but increased Young's modulus. The addition of OPW increased the MFI and the T_g of LDPE, which suggested changes in the structure of the LDPE chains. SEM showed that OPW reduced the phase separation between the polymers and slightly increased the rate of biodegradation of the blends in simulated soil, with the effect being greatest for the blend containing 25% LDPE.

Fig. 9 Light micrographs of 75PHB/25LDPE blends without (**a**) and with (**b**) OPW aged in simulated soil



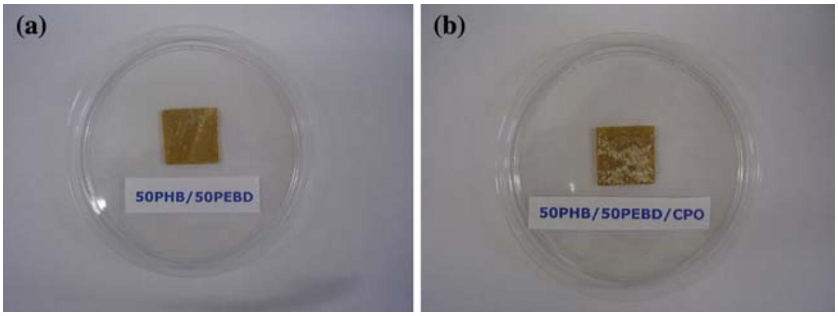


Fig. 10 Surfaces of the 50PHB/50LDPE blend without (**a**) and with (**b**) OPW after seven months of aging in simulated soil

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