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Photodegradation and Photostabilization of Poly(3-Hydroxybutyrate)

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The present work is concerned with the photodegradation and photostabilization of poly(3-hydroxybutyrate) (PHB) biopolymer. Two commercial grades of PHB were investigated, containing of 4.0% and 6.2% of hydroxyvalerate (HV) comonomer, named PHB_1 and PHB_2, respectively. Injection moulded specimens were exposed to ultraviolet radiation (UV-A) in the laboratory for periods of up to 12 weeks and then characterized by tensile testing, surface appearance, size exclusion chromatography (SEC), and scanning electron microscopy (SEM). The exposure to UV radiation caused great damaged on the surface color, reduction of molecular size and mechanical properties. The effects were more pronounced on PHB_2, probably due a lighter surface color and less packed macromolecular structure which facilitates the transmission of light throughout the samples. Specimens of PHB_1 were also injected with the addition of a UV absorber and antioxidant, resulting in a higher UV stability of PHB, as shown by a low reduction in molar mass and better mechanical properties.

Keywords: *Biodegradable polymers, PHB, ultraviolet radiation, photodegradation, photostabilization*

1. Introduction

Considering that the plastic-made products are in the center of many debates related to environmental issues, a current trend of the polymer community is the study of ways to reduce the environmental impact of these products[1-5]. Besides the development of materials with a better recyclability, the use of biodegradable polymers and plastics obtained from renewable sources are some of the main objectives to achieve this goal. Committed to this purpose, we have been investigating the poly (3-hydroxybutyrate) (PHB) which is a natural and aliphatic polyester obtained from renewable sources. Our works have been focused on its phase transformation, crystallization and melting, stress cracking, mechanical, thermal and optical properties[6-9]. PHB used in the present work was produced from sugar cane plants, and was synthesized by biotechnological processes (microbial fermentation) without environmental damages.

PHB is inherently a non-toxic material and it is considered biocompatible, being used in medical applications like prosthesis, suture threats and devices for drugs release inside the human body[10-11]. The general uses of PHB in replacement of ordinary plastics are growing, including applications like packing and other short life products like cups and cutleries for fast food restaurants. Due to its biodegradability, when discarded PHB can be attacked by microorganisms such as bacteria, and fungus which might be able to destroy its macromolecular chains producing CO_2, CH_4, H_2O and microcellular organisms. These components return to the environment and could be used in another PHB's synthesis, in a typical life cycle of PHB. These characteristics make PHB a very promising material and efforts on establishing its properties, extending its applications, and optimizing its processing conditions are reported in the literature[12-16].

Among the several possibilities of PHB application, we foresee the production of longer life consumer products. This assumption is based on the fact that the mechanical properties of this polymer are similar to usual polymers like polystyrene or polypropylene. If the product is not used or stored under conditions to withstand biodegradation, the lifetime could be compatible to the aimed application. Under this situation, the product can be exposed to ultraviolet radiation and, like the other types of polymers, suffer from this weathering condition. The photodegradation behavior of PHB, and the stabilization strategies, is scarcely reported in the literature[17]. The main objective of this work is to investigate the effects of ultraviolet radiation on PHB with different contents of hydroxyvalerate (HV) comonomers. Injection moulded specimens were exposed to weathering cycles of UV radiation, temperature and condensed water (humidity). The exposure procedure followed ASTM G-155 to simulate day (UV lights on) and night (UV lights off with water condensation)[18,19]. The effect of exposure was analyzed by scanning electron microscopy (SEM), tensile tests, and molecular weight. The use of stabilizing additives was also investigated.

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2. Experimental

2.1. Materials and specimen preparation

Two random copolymers of 3-hydroxybutyrate (HB) with different contents of 3-hydroxyvalerate (HV) were used in the present study, both supplied by PHB Industrial SA (Brazil):

- FE-141, with 4% of HV, melt flow rate MFR 23-25 dg/min (ASTM D1238, 190°C/2.16 kg), and number average molar weight M_n 52 kg/mol.
- FE-112 with 6.2% of HV, MFR 30-33 dg/min (ASTM D1238, 190°C/2.16 kg), M_n 76.2 kg/mol.

The resins were coded as PHB$_1$ and PHB$_2$, respectively. In an attempt to evaluate the effect of stabilizing additives, a UV absorber Tinuvin 791FB (0.25%) and an antioxidant Irganox B215 (0.40%) were added to PHB$_1$; this material was coded PHB$_{ABS}$. The amount of additives was chosen based on manufacturer´s recommendation. The chemicals structures of HB and HV units are shown in Figure 1.

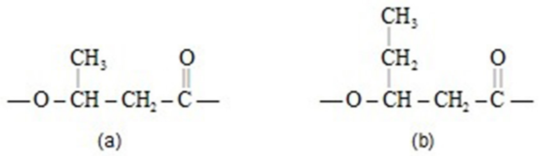

Figure 1: Structural units of 3-hydroxybutyrate HB (a) and 3-hydroxyvalerate HV (b).

Type I (ASTM D-638) tensile test specimen of PHB$_1$, PHB$_2$ and PHB$_{ABS}$ were produced in a Romi 130 injection molding machine, operating with barrel temperature ranging between 150-190°C and the mold at 20°C.

2.2. Methods

The exposure to ultraviolet (UV) radiation was done with the tensile tests specimens for up to 12 weeks in an accelerated weathering chamber Q-Lab, type QUV, containing UV-A fluorescent tubes. These lamps have a maximum irradiance of 0.89 W/m^2 at 340 nm. The weathering cycles were: 8 hours under UV light at 60°C and 4 hours in the dark under condensed water at 50°C. The exposure procedure carried out according to ASTM G-155.

Molecular weight analyses were conducted by size exclusion chromatography (SEC) using a Viscotek HT-GPC equipment at 40°C with a refractive index detector. Samples used for SEC analysis were removed from the surface (up to 1 mm) of the tensile test specimen directly exposed to UV radiation. The polymer was dissolved in chloroform and the filtered solution was injected into the equipment. The solvent flow rate was 1 mL/min and the columns were calibrated with narrow molecular weight PS.

Mechanical tests were done in accordance to ASTM D638 at 20 mm/min at 23°C, using an EMIC model DL2000 universal testing machine with load cell of 5 kN. The results reported represent averages of at least four test samples.

Scanning electron microscopy images of fractured surface were taken in a JEOL 6460, the samples were cryogenically fractured in liquid nitrogen and covered with carbon to avoid the charge accumulation.

The crystallinity degree of the exposed surface of samples was obtained by X-ray diffraction in a Rigaku-Dairix Miniflex II equipment using Cu Kα radiation (1.54 Å), and a scattering angles range of $2\theta = 4\text{-}90°$ at a rate of 3°/min.

3. Results and Discussion

Photographs of PHB$_1$ and PHB$_2$ sample tests unexposed and exposed to UV radiation for 6 and 12 weeks are showed in Figure 2. The exposed surfaces, previously brown and caramel, turned into caramel and whitish, respectively, after 12 weeks under UV exposure. According to previous works done by one of the current authors[17,18], this whitening does not result from the formation of chromophoric groups, but it is probably originated from a topological feature of the UV exposed samples, where cracks are formed on PHB$_1$ and PHB$_2$ surfaces. The occurrence of surface cracking was previously associated with polypropylene whitening during UV exposure[17], in which the cracks increase the roughness of the surface, raising the diffuse reflectance of the visible light.

Figure 2: Photographs of PHB$_1$ and PHB$_2$ tests specimens illustrating samples whitening under UV exposure. Exposing time (weeks) indicated.

The results of tensile tests for PHB$_1$ and PHB$_2$ unexposed and exposed up to 12 weeks are presented in Table 1, together with the results of molar mass determination. The average scissions number (SN) per macromolecule presented in Table 1 was determined using Equation 1:

$$SN = \frac{\overline{M_{no}}}{M_{nt}} \qquad Eq.1$$

Where: $\overline{M_{no}}$ and M_{nt} are the number-average molecular weight of the material unexposed and exposed to UV radiation for a given time, respectively.

Tensile strength and strain at break reduced with exposure time. After 12 weeks of severe weathering conditions of UV, temperature and condensed water, the tensile strength of PHB$_1$ and PHB$_2$ decreased 32% and 34%, the strain at break decreased 30% and 42%, respectively. According to work reported elsewhere[17] when PHB is under UV radiation, two mechanisms might occur in parallel, i.e., macromolecular crosslinking and chain scission; one of them will be dominant and may be visualized by the change in number-average molecular weight (M_n). Concerning the results showed in Table 1, M_n values of PHB$_1$ and PHB$_2$ decreased upon UV exposure, hence it can be deduced that the macromolecular scission is the preponderant mechanism observed here and that this is the main reason for the reduction in tensile properties.

Table 1: Mechanical properties and Mn of PHB_1 and PHB_2 before and after exposure to UV radiation.

	PHB_1				PHB_2			
Exposure time (weeks)	Tensile Strength (MPa)	Maximum elongation (%)	M_n (g/mol)	SN	Tensile Strength (MPa)	Maximum elongation (%)	M_n (g/mol)	SN
0	32.70 ± 1.26	3.17 ± 0.17	52000	-	34.14 ± 0.74	4.68 ± 0.40	76200	-
1	32.32 ± 0.62	3.52 ± 0.15	-	-	34.80 ± 0.37	5.11 ± 0.22	-	-
3	31.01 ± 0.48	3.13 ± 0.09	-	-	31.79 ± 0.87	4.41 ± 0.25	-	-
6	30.21 ± 0.58	3.09 ± 0.21	11700	4.44	26.03 ± 1.11	3.65 ± 0.16	10800	7.05
9	25.63 ± 0.72	2.54 ± 0.08	-	-	24.37 ± 1.31	3.60 ± 0.13	-	-
12	22.28 ± 0.91	2.20 ± 0.07	7500	6.93	22.84 ± 1.03	2.72 ± 0.04	6400	11.90

The HV content should be considered influencing the photodegradation of PHB. Since the HV unit is bulkier than the HB unit (see Figure 1), we have an expectation that the copolymer with a higher HV content (PHB_2) would be more susceptible to the degradation effects due to a higher free volume and hence a higher diffusion of oxygen and moisture. Commonly, PHB suffer degradation also by hydrolysis mechanisms[17-21], i.e., under humidity environment and temperature, chain scission occurs and, together with the photodegradation effects, will contribute to the deterioration in the polymer properties. If the specimen has a more open structure as it is in PHB_2 the effects of UV radiation, humidity and temperature may be more severe - as was observed for PHB_2 specimens in Figure 2, and serious damage are usually observed in the mechanical properties, as shown in Table 1. Another effect is that samples with higher content of HV is lighter and, as a consequence, the UV radiation can reach deeper regions comparing with the darker samples with low content of HV.

Scanning electron microscopy (SEM) images of PHB_1 and PHB_2 surfaces photodegraded up to 12 weeks are presented on Figure 3. As can be seen in this Figure, the sample PHB_1 did not show any significant changes at the surface; however; sample PHB_2 presented cracks after 6 weeks of exposure and the density of the cracks increased with the exposure time. As presented before, the drop in mechanical properties was more intense for PHB_2; the presence of cracks on the surface of these samples is a major reason for this behavior. The cracks formed during exposure are usually related to an increase on surface crystallinity, a phenomenon called chemi-crystallization that occurs due to rearrangement of taut molecules that are released by the chain scission events[20].

Scanning electron microscopy (SEM) images of fractured surface of PHB_1 and PHB_2 photodegraded for 12 weeks are given in Figure 4. The fracture surface of PHB_2 showed a smoother topography and similar size photodegraded zone when compared to PHB_1. By SEM images it is showed an increase in photodegraded zone with exposure time. Similar trend like that observed for 12 weeks was seen in other samples, exposed for 3, 6 and 9 weeks (results not showed here) where PHB_2 has larger photodegraded zones than PHB_1.

In an attempt to protect PHB from UV effects, antioxidant and UV absorber additives were added to PHB and samples were exposed for up to 6 weeks under the same weathering conditions described before. The molecular weight distribution curves of PHB_1 and PHB_{ABS} unexposed and exposed for different times are presented in Figure 5. It is clear that the molecular weight distribution curves for PHB_1 showed a significant modification in peak location and shape as exposure time is increased. However, PHB_{ABS} did not present a major modification on the distribution curves. A consequence of this is observed on the polydispersity values ($\overline{M}_w/\overline{M}_n$). The polydispersity of PHB_1 changes from 2.6 (unexposed) to 3.7 (6 weeks exposure), whereas PHB_{ABS} only changes from 2.2 to 2.6.

Table 2 presents the results of tensile tests, M_n and SN for PHB_1 and PHB_{ABS}. It can be observed that the mechanical properties tend to a slight decrease with the exposure time for PHB_1 whereas no significant changes could be seen for PHB_{ABS}. The molecular weight decreased as much as 77.5% after 6 weeks of exposure for PHB_1. On the other hand, the reduction of M_n for PHB_{ABS} was 43.8% after 6 weeks. The chain scissions in PHB_{Abs} were 58% and 44% lower than PHB_1 for analyses taken at 3 and 6 weeks, respectively. The results indicate that the UV absorber and antioxidant additives protected the PHB matrix from the UV radiation[18,21-24].

Table 3 shows the crystallinity degree (X_c) of the samples calculated by XRD before and after exposure to UV radiation. After three weeks PHB_1, PHB_2 and PHB_{ABS} presented an increasing on the X_c values followed by drop until 12 weeks. The first phenomenon is very known and called chemi-crystallization, it has been reported in the literature[20] and usually takes place when polymers are exposed to UV radiation. The chemi-crystallization occurs with degraded molecules (decreased on molecular weight) rearrange themselves in the form of crystals. It could be happened because the temperature inside the UV chamber (50-60°C) was higher enough to allow the cold crystallization mechanisms to develop[9]. After longer periods of exposure, it is possible that the chain becomes too defective by the presence of groups containing oxygen and, hence, further organization may be more difficult[20]. Destruction of crystals by the degradation effects has also been reported[25]. In the case of PHB_{ABS} the values of X_c increased until 6 weeks indicating that the level of the scissions was not enough to hindering the chemi-crystallization phenomenon. These results are consistent with molecular weight and mechanical properties, indicating that the UV absorber and antioxidant acted very well in PHB matrix.

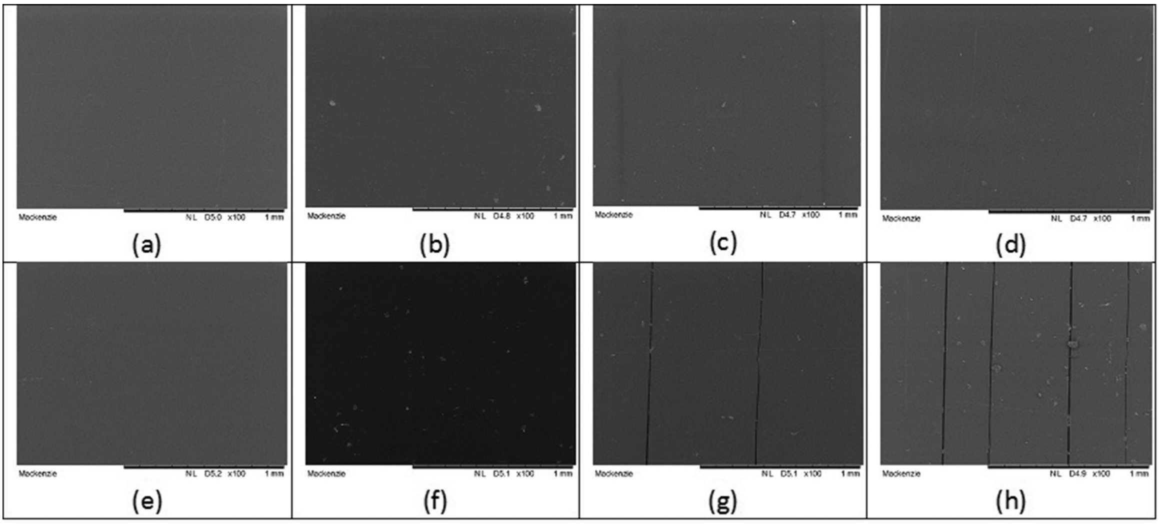

Figure 3: Scanning electron microscopy (SEM) images of PHB_1 non-exposed (a) and exposed for 3 (b), 6 (c) and 12 weeks (d); and PHB_2 non-exposed (e) and exposed for 3 (f), 6 (g) and 12 weeks (h).

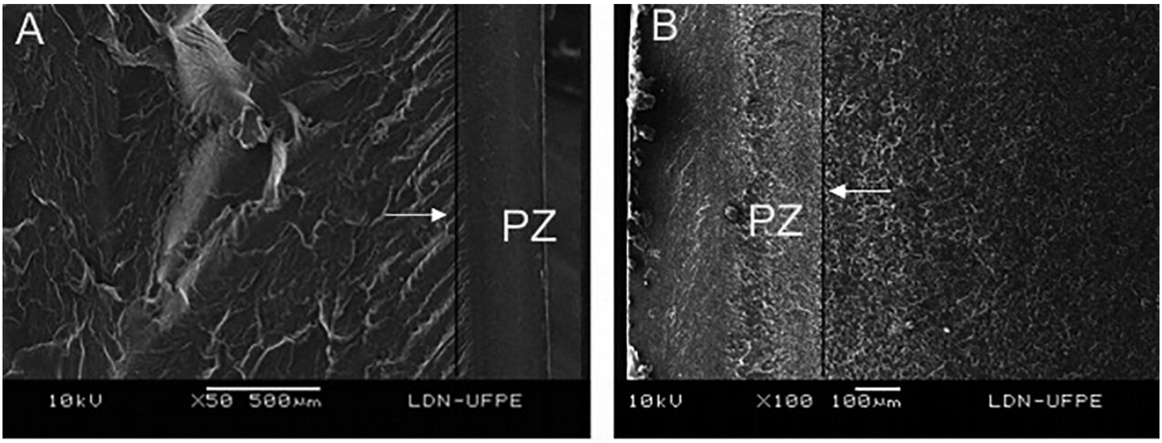

Figure 4: SEM images of fractured surface of PHB_1 (a) and PHB_2 (b) exposed to UV radiation during 12 weeks. The arrows indicate the interface between the degraded and the not-degraded material. (PZ: Photodegradaded Zone)

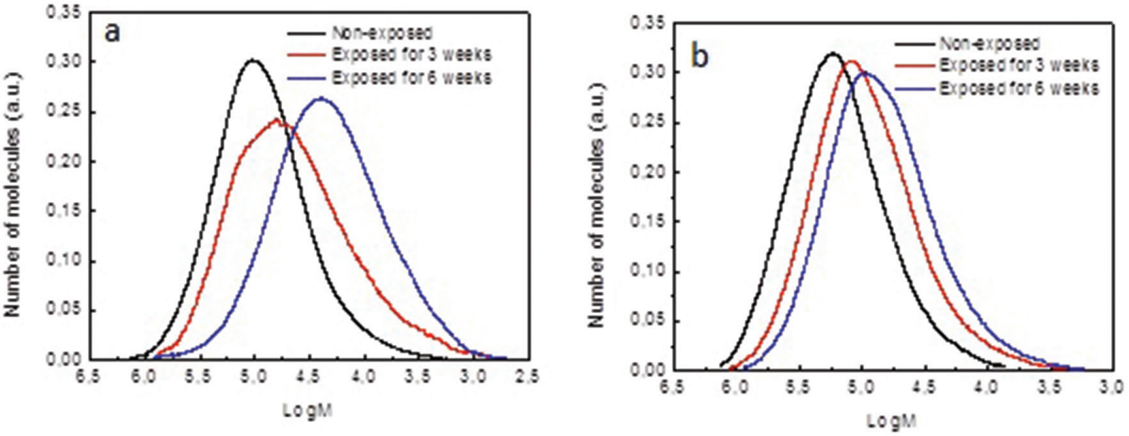

Figure 5: Molecular weight distribution curves of PHB_1 (a) and PHB_{ABS} (b) not exposure and exposed for different times.

4. Conclusion

The results presented in this work showed that there is a significant difference on the photodegradation damages of PHB depending on its HV content. This difference is not only due to the chemical structure but also to the color of the samples. The PHB with a higher HV content

Table 2: Mechanical properties and of PHB and PHB_{ABS} before and after exposure to UV radiation for different times.

	PHB_1				PHB_{ABS}			
Exposure time (weeks)	Tensile Strength (MPa)	Maximum Elongation (%)	M_n (g/mol)	SN	Tensile Strength (MPa)	Maximum Elongation (%)	M_n (g/mol)	SN
0	32.70 ± 1.26	3.17 ± 0.17	52000	-	32.15 ± 1.12	4.09 ± 0.10	85100	-
1	32.32 ± 0.62	3.52 ± 0.15	-	-	33.05 ± 0.37	4.72 ± 0.18	-	-
3	31.01 ± 0.48	3.13 ± 0.09	20600	2.52	32.68 ± 0.29	4.28 ± 0.09	57700	1.47
6	30.21 ± 0.58	3.09 ± 0.21	11700	4.44	32.41 ± 1.07	3.90 ± 0.18	43800	1.94

Table 3: Crystallinity degree (X_c) of PHB_1, PHB_2 and PHB_{ABS} before and after exposure to UV radiation for different times.

Exposure time (weeks)	PHB_1	PHB_2	PHB_{ABS}
0	56.2	51.7	49.8
3	72.3	69.5	58.0
6	64.6	56.7	59.4
12	60.7	54.7	-

is lighter than the PHB with a lower HV content and, as consequence; the penetration of UV radiation is deeper into the test bars. The results after 12 weeks showed that whiteness, mechanical properties, molecular weight and fracture surface damages were more accentuated on PHB with higher HV content. The additions of the UV absorber and the antioxidant additives have improved the UV stability of PHB, with a significant reduction on the photodegradation rate, as observed by mechanical properties, molecular weight and crystallinity degree. It is hoped that these results could be useful to design materials with more stability during processing and ultraviolet exposure while maintaining their characteristic of biodegradability.

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