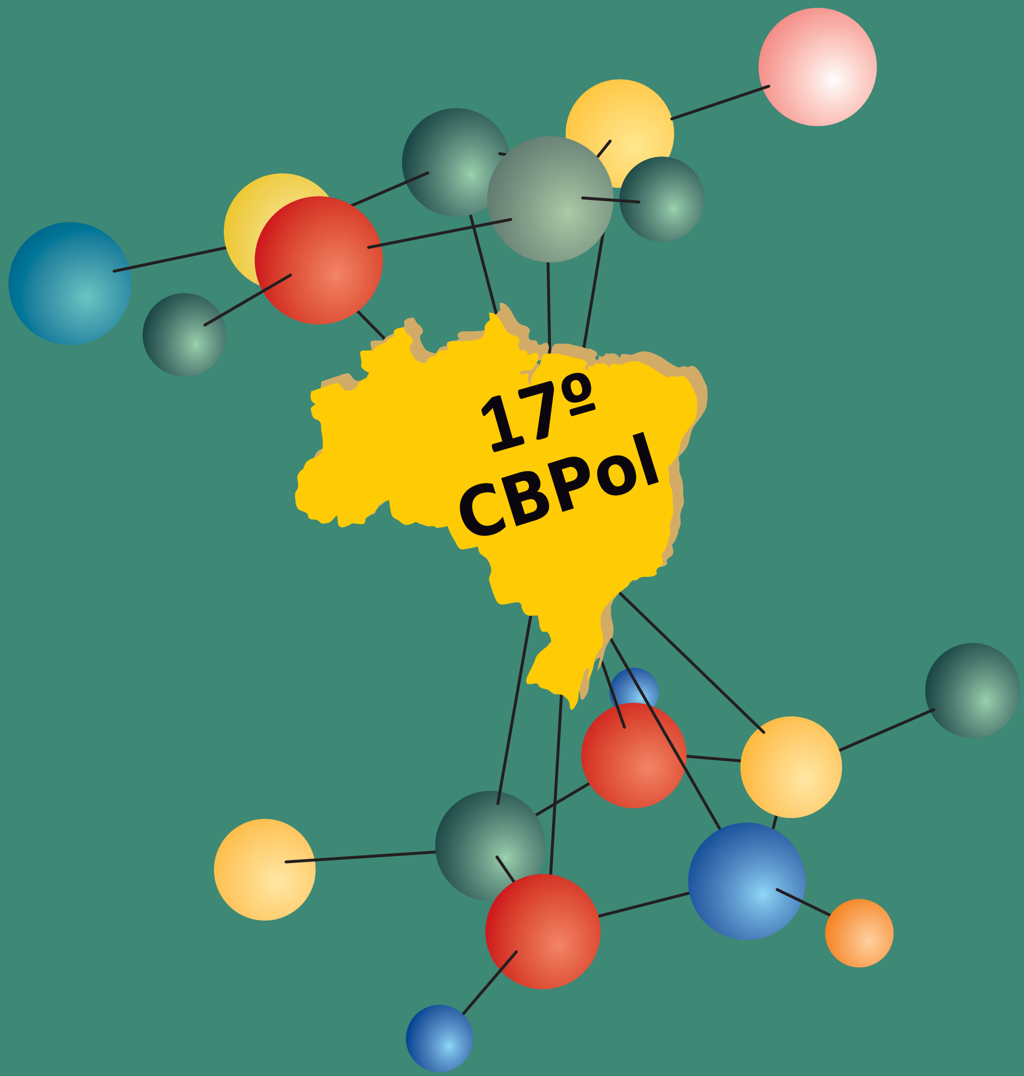

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EVALUATION OF THE MECHANICAL AND OPTICAL PROPERTIES OF LDPE INJECTION-MOLDED WITH BENZOIN IN HDPE MASTERBATCH

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Abstract – The incorporation of additives to polymers needs to be well evaluated, since, in general, it changes the matrix properties. The pro-degradant additives also accelerate the thermo-oxidation of polyolefins, therefore, this degradation is already observed in the processing, when the polymer is subjected to high temperatures, in addition to shear stress. In this work, the mechanical and optical properties of LDPE injection-molded specimens with benzoin were evaluated using a masterbatch in an HDPE matrix to compensate for the reduction of molar mass caused by thermo-oxidation and possible loss of properties. The MFI of the samples indicated that the use of HDPE causes some compensation in the chain size. Statistically, the Izod impact and tensile test results indicated that adding HDPE minimizes the impact of the loss of mechanical properties. The colorimetry, however, indicated that the benzoin acts in the oxidation of the LDPE, causing their yellowing.
Keywords: *polyethylene, oxo-biodegradable, mechanical properties, yellowing, thermo-oxidation.*

Introduction

The accumulation of polymeric waste, mainly from single-use packaging, is an environmental problem observed all over the world. The use of pro-degradant additives to obtain oxo-biodegradable polymers is a reality in facing this problem. Such additives are characterized by favouring the abiotic degradation of polyolefins, accelerating the thermo-oxidation and photooxidation of these macromolecules so that, subsequently, the oxygenated fragments can be used as nutrients by microorganisms [1].
Benzoin, a biodegradable organic compound free of transition metals, proved to be a promising pro-degradation additive in previous studies since it accelerated the thermo-oxidation [2] and photooxidation [3] of HDPE/LDPE films. However, thermo-oxidation was observed already during the processing of the films, when the polymer was exposed to temperatures that exceeded its melting point, easily reaching 200 ºC.
In this work, LDPE (low density polyethylene) injection-molded specimens with benzoin were studied. However, to compensate for the reduction of the molar mass and possible loss of mechanical and optical properties (yellowing) due to the thermo-oxidation accelerated by benzoin in the processing, the additive was incorporated from a masterbatch produced in a matrix of HDPE (high density polyethylene), known for its greater thermal stability, if compared to other polyethylenes (PE). Injection-molded specimens were produced with 0, 2, 4 and 6% of the masterbatch, which was characterized by MFI (melt flow index), to assess possible changes in the polymer chain sizes of the compound; colorimetry, to assess changes in colour and gloss, which

may be associated with the thermo-oxidation suffered during processing; Izod impact and tensile tests to assess changes in mechanical properties.

Experimental

Materials

In this work, LDPE grade EB-853, with MFI of 2.7 g/10 min (190 ºC/ 2.160 kg) and density of 0.923 g/cm3; and HDPE grade HE-150, with MFI of 1.0 g/10 min (190 ºC/ 2.160 kg) and density of 0.948 g/cm3, both manufactured by Braskem Brazil, were used. Benzoin, with a purity grade of over 99%, is produced by Merck KGaG.

Benzoin masterbatch production in HDPE matrix (pro-degradation additive)

The *masterbatch* was obtained from the mixture of HDPE with benzoin in a Haake thermokinetic mixer, model RheoDrive 7, at a temperature of 160 ºC. The first 6 minutes were to guarantee the melting of the HDPE. After that, the benzoin mass was added, with an effective mixing time of 4 minutes. Therefore, the total process lasted 10 minutes. A masterbatch with a mass ratio of 3:1 (HDPE/benzoin) was obtained. The mixture was cut with the help of pliers into granules with dimensions like those of LDPE pellets. Fig 1 shows the produced masterbatch.

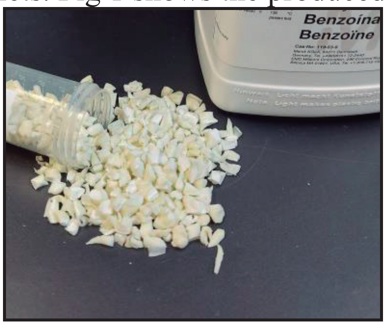

Figure 1 – Benzoin masterbatch after cutting with pliers, with dimensions like LDPE pellets.

Obtaining the injection-molded specimens

The samples were obtained in a Thermo Scientific Haake MiniJet II injection molding machine at 145 ºC, with injection pressure set at 600 bar and set back pressure at 400 bar. The samples, with 0, 2, 4, and 6% (w/w) of masterbatch of the pro-degradation additive, were named PE_0%, PE_2%, PE_4%, and PE_6%, respectively. Because it is a piston type injection molder, the mixture of LDPE with the masterbatch was previously performed in the thermokinetic mixer, for 6 minutes and at a temperature of 160 ºC. In addition to ensure a good diffusion of the additive in the LDPE, a way to establish similar conditions to those observed in industrial processes was sought, in which the material would pass through a screw for subsequent injection. Five specimens were obtained for tensile and Izod impact tests for each of the additive concentrations. The specimens are presented in Fig 2.

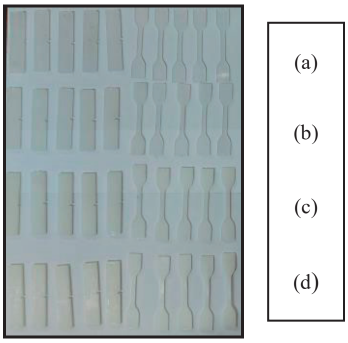

Figure 2 – Injection-molded specimens: (a) PE_0%, (b) PE_2%, (c) PE_4% and (d) PE_6%.

Determination of the melt flow index (MFI) of the injected specimens
The tests to determine the melt flow index (MFI) of the different samples, with and without the additive, were performed in CEAST modular plastomer, model 7026.000, according to ASTM D1238 standard procedures. The conditions used were 190 ºC/ 2.160 kg, with a residence time of 240 seconds.

Colorimetric test
The colorimetric test was performed using the CIE L*a*b System. In addition, the brightness was also determined. A BYK - Gardner instrument, model Spectro-guide 45/0 gloss/ Spectro-guide sphere gloss was used. In the CIE L*a*b system, it is stated that **"L"** is the luminance axis, which refers to the human perception of luminosity (on a scale from 0 to 100, where 0 is absolutely black and 100 is white); **"a"** is the axis that goes from green to red, with negative values tending to maximum green and positive values tending to maximum red; and **"b"** is the axis that goes from blue to yellow, with negative values tending to blue and positive values tending to yellow.

Tensile test
The tensile tests were performed in a universal equipment Instron, model 4200, following the procedure of ASTM D638-10, using a load cell of 5 kN and a retraction speed of 10 mm/min.

Izod Impact Test
Izod impact test was determined in Ceast equipment, model Impactor II, according to procedures described in ASTM D256-10. The specimens were notched, and a 0.5 J hammer was used for impact at room temperature.

Results and Discussion

To evaluate the thermo-oxidative degradation of macromolecules, the MFI of PE was determined in the injection-molded specimens, whose values are presented in Fig 3. Evaluating the results, it is possible to observe an increase of approximately 20% among the additivated samples, if compared to PE_0%, suggesting that the benzoin promoted the thermo-oxidation of the PE with consequent reduction of the chains, facilitating the melt flow [2, 4]. However, the MFI value remained with statistically similar values for samples PE_2%, PE_4%, and PE_6%, indicating that the reduction in the average chain size was compensated by the addition of HDPE.

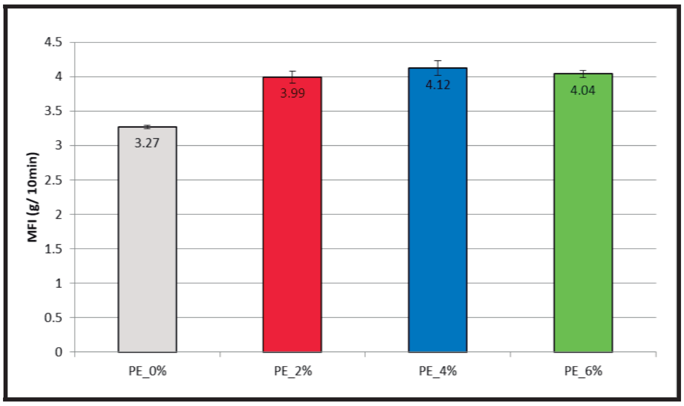

Figura 3 – MFI of PE in the injection-molded spicemens with 0, 2, 4 and 6% masterbatch.

Subsequently, to evaluate the thermo-oxidation degradation suffered by the samples, a colorimetric test was performed, whose results are presented in Table 1. It is possible to observe that there is a progressive increase in the value of **"b"**, indicating a possible formation of polymeric oxygenated fragments (containing carbonyl) and unsaturated, responsible for the yellowing of the PE [5]. The data obtained confirm the increase in the rate of LDPE thermo-oxidation in the processing with benzoin. The addition of HDPE, however, left the samples with a whiter tone (L factor), which was confirmed by the increase in the opacity of the samples (Gloss), which was expected, since the HDPE presents high crystallinity, making the thick samples more matte.

Table 1 – L*a*b and Gloss values of the PE samples obtained by colorimetric test.

Sample	L	A	b	Gloss
PE_0%	69.13 ± 0.94	0.10 ± 0.03	-1.84 ± 0.03	11.78 ± 3.20
PE_2%	67.62 ± 0.80	-1.02 ± 0.09	0.92 ± 0.19	1.68 ± 0.09
PE_4%	70.11 ± 0.77	-2.20 ± 0.20	1.77 ± 0.29	1.72 ± 0.28
PE_6%	74.02 ± 0.92	-2.69 ± 0.23	1.73 ± 0.43	2.24 ± 0.73

The results obtained in the Izod impact tests are shown in Fig 4. It can be observed that there was a reduction of approximately 8% in the strength of samples PE_4% and PE_6%, but this is not significant, showing that the addition of HDPE had a possible positive influence on the samples. The maintenance of the mechanical properties, according to Ojeda and collaborators [6], is a premise for pro-degradant additives. Thus, the masterbatch of the pro-degradant with HDPE polymer matrix is an alternative to prevent the loss of impact strength of the samples due to thermo-oxidation of LDPE.

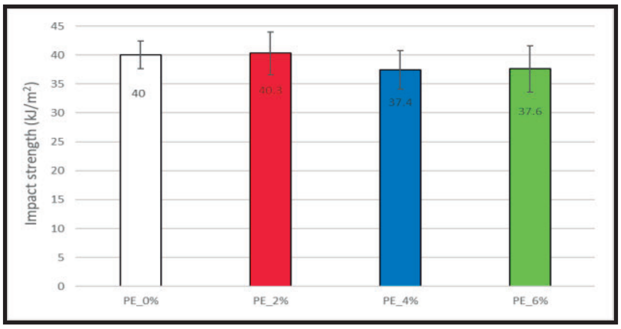

Figure 4 – Impact strength of injection-molded specimens submitted to the Izod Impact test.

Finally, Fig. 5 shows the elongation at the break of injection-molded specimens with benzoin. It can be observed that the additive may have influenced the results. It was expected that the increasing concentration of benzoin in the samples would lead to a reduction of the strain at the break due to the higher rate of thermos-oxidation of LDPE caused by the processing. But the results showed an increase in tensile strength around 10% for PE_2% and 20% for PE_4% and PE_6% compared to PE_0%. This was possibly due to the addition of HDPE, as it is known that, compared to LDPE, it has better mechanical properties [7].

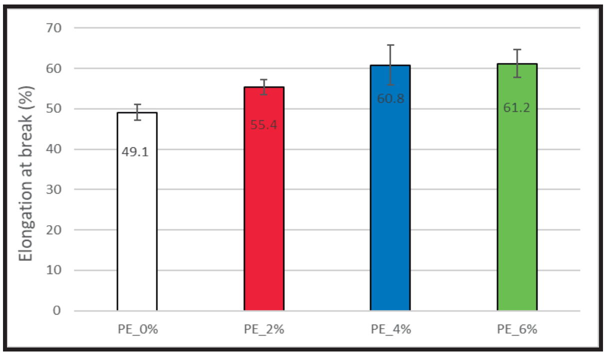

Figure 5 – Elongation at break of injection-molded specimens submitted to the tensile test.

Conclusions

Benzoin promoted LDPE thermo-oxidation, as demonstrated by the increase of MFI and the increase of the "b" value index, in the colorimetric test. However, the addition of the organic compound in HDPE matrix compensated, in parts, the degradation suffered by LDPE by thermo-oxidation and, therefore, the specimens injected with increasing concentrations of the pro-degradant masterbatch showed similar MFI values.
The addition of the additive in a matrix of HDPE maintained or even improved the mechanical properties of LDPE, proven by the results of Izod impact and tensile tests. The addition of the Masterbatch produced in this work compensates for the thermo-oxidation of LDPE macromolecules. However, the polymer is still oxo-biodegradable, being the addition of benzoin in HDPE matrix masterbatch as an alternative to reduce the loss of properties by thermo-oxidation in processing, either by extrusion or injection.

Acknowledgements

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