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The Yellowness Index as an Adjuvant Tool for Assessing the Recyclability of Two Different Types of Oxo-Biodegradable HDPE

***João Augusto Osório Brandão*[a*], *Bianca da Silva Schumacher*[b], *Edson Luis Francisquetti*[c], *Ruth Marlene Campomanes Santana*[a]**

[a]*Universidade Federal do Rio Grande do Sul, Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e Materiais, Porto Alegre, RS, Brasil.*
[b]*Universidade Federal do Rio Grande do Sul, Departamento de Materiais, Porto Alegre, RS, Brasil.*
[c]*Instituto Federal do Rio Grande do Sul, Programa de Pós-Graduação em Tecnologia e Engenharia de Materiais, Farroupilha, RS, Brasil.*

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The use of pro-oxidant additives in the processing of HDPE is a viable alternative for reducing the impacts caused by the accumulation of polymer waste in the environment, since they favor the thermal oxidation and photooxidation of macromolecules. However, these additives can affect the mechanical recyclability of the polymer, as they are exposed to high temperatures during reprocessing. This study evaluated the consequences of the presence of these additives in the multiple reprocessing of two different types of oxo-biodegradable HDPE, obtained by adding d2w™ and benzoin. After 5 reprocessing cycles, these additives caused a greater increase in oxygenated functional groups, which reduced the contact angle with distilled water. Additionally, thermal oxidation led to a greater loss of mechanical properties in samples with pro-oxidant additives when compared to HDPE reprocessed without these additives. These alterations were accompanied by a progressive increase in the yellowness index, compatible with the changes observed.

Keywords: *HDPE, Pro-oxidants, Thermal oxidation, Yellowness index, Recyclability.*

1. Introduction

High density polyethylene (HDPE) is widely used around the world due to its mechanical properties, low cost, durability and ease of processing[1-5], especially in the production of packaging[6]. However, its high durability is because it only consists of carbon and hydrogen atoms, which give the macromolecules high chemical inertness and resistance to degradation[7-11], which contributes to the accumulation of polymer waste in the environment.

To reduce this problem, saturated polyolefins, including HDPE, can be processed with pro-oxidant additives and are then called oxo-biodegradable polymers[10,12-15]. These additives are generally transition metals (e.g., Mn, Co, Fe) in the form of organic salts, especially stearates[8,12,14,16-19]. They favor the thermal oxidation and photooxidation of macromolecules, known as the abiotic step of oxo-biodegradation[10,12,20-22]. In oxidation, whether by exposure to heat or UV radiation in the presence of oxygen from the air, functional groups containing carbonyls (e.g., carboxylic acids, esters, aldehydes, lactones and ketones), hydroxyls and unsaturated molecular fragments are also formed, reducing the molar mass of the polymer[1,2,7,10,12,18,23]. After oxidation, the oxygenated molecular fragments with a smaller chain size are used as nutrients by microorganisms such as bacteria, fungi and algae[14,15,24-27], known as the biotic or biodegradation step, which can occur in the presence or absence of oxygen. On the other hand, the use of pro-oxidant additives can have an impact on the mechanical recycling of these polymers, since the waste is exposed to high temperatures and high shear rates in reprocessing and, therefore, thermal oxidation will occur at higher rates in their presence. Thermal oxidation results in the modification of chemical bonds in the polymer, which consequently affects the chemical functional groups, leading to yellowing of the material[28,29] and alteration of other properties, which can be a limiting factor in recycling the waste.

In this work, two different types of oxo-biodegradable HDPE were obtained. The first was obtained by extruding HDPE filament with 1% (w/w) of the commercial additive d2w™, consisting of an organic manganese salt[27,30,31]. The second was obtained by adding 0.25% (w/w) benzoin, an organic substance free of transition metals that has been shown to be effective in promoting the thermal oxidation and photooxidation of polyolefins[10,12,15]. The samples were then subjected to multiple extrusion cycles (reprocessing) and the changes to the HDPE were evaluated using dilute solution viscometry (DSV) to assess changes in average viscosimetric molar mass $\left(\overline{Mv}\right)$; Fourier transform infrared spectroscopy (FTIR) to determine the carbonyl index (CI); contact angle to assess changes in the interaction of the material with distilled water; colorimetry to determine the

*e-mail: jaobrandao@yahoo.com.br
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yellowness index (YI); tensile strength and Izod impact tests to assess changes in mechanical properties. The aim of the work was to assess whether the YI is proportional to the degree of oxidation of the macromolecules and to the changes in the properties assessed, so that it can be used as a parameter in the analysis of the recyclability of HDPE.

2. Materials and Methods

2.1. Materials

High density polyethylene (HDPE), HE150 grade, with a melt flow index of 1.0 g/10 min (190 ºC/ 2.16 kg) and a density of 0.948 g/cm^3, produced by Braskem Brazil; Decalin with a purity level above 99%, produced by Neon; d2w™ pro-oxidant additive, produced by Symphony Plastic Technologies and marketed in Brazil for RES Brazil; Benzoin, with a purity level above 99%, produced by Merck KGaG.

2.2. Oxo-biodegradable HDPE sample preparation via extruder

The oxo-biodegradable HDPE samples were obtained in a single-screw extruder manufactured by CIOLA, model MEP-18. The thread had a diameter of 18 mm, and the L/D ratio was 22. The equipment had 3 heating zones, and the following temperature profile was used: 140 ºC for Zone 1 (feed), 150 ºC for zones 2 and 3 (die). A simple filament die was used. The screw motor was kept at a constant speed of 52 rpm. The samples were granulated immediately after extrusion in a granulator manufactured by SEIBT, model PS 50, with the reference speed maintained at 4.0.

The first oxo-biodegradable HDPE was obtained by adding 1% (w/w) of the commercial additive d2w™. The second oxo-biodegradable HDPE was obtained by adding 0.25% (w/w) benzoin. The oxo-biodegradable HDPE samples were then subjected to 5 reprocessing cycles by filament extrusion, with the initial process parameters in the extruder and granulator remaining constant. For comparison purposes, virgin HDPE was also subjected to 6 processing cycles (1 referring to the cycle for obtaining oxo-biodegradable HDPE and the other 5 for evaluating oxidative thermomechanical degradation). Under these conditions, the names shown in Table 1 were adopted. Virgin HDPE, which was not exposed to any type of processing, was also characterized and will be referred to as HDPE_Virgin in the results.

2.3. Sample preparation via injection molding

To carry out the characterizations, injection molded specimens were obtained to assess changes in chemical, surface, optical and mechanical properties A Thermo Scientific Haake MiniJet II mini injection molding machine was used at 170 ºC, with injection pressure set at 400 bar and repression pressure at 350 bar. Two types of injection molded specimens were obtained for each sample. The first type had dimensions specified by ASTM D256-23e1[32], for carrying out the Izod Impact test (rectangular-shape). The second type had dimensions specified by ASTM D638-22[33], for tensile strength test (dumbbells-shape).

Table 1. Composition of samples, with and without pro-oxidant additives.

Sample name	HDPE (%w/w)	d2w™ (%w/w)	Benzoin (%w/w)
HDPE_NA*	100	-	-
HDPE_d	99	1	-
HDPE_B	99.75	-	0.25

* no pro-oxidant additive.

2.4. Sample characterization

2.4.1. Carbonyl index (CI)

The injection molded samples with virgin HDPE and with the different HDPE granules after the first, third and fifth reprocessing cycles, with a rectangular shape, were evaluated by FTIR in Perkin Elmer equipment, model Polymer ID Analyzer. The measurements were carried out in an environment with a constant temperature of 25 ˚C and relative humidity of 30%. The evaluations were made in ATR mode, in bands between 4000 and 450 cm^{-1}. 32 scans were taken per sample. To assess the degree of oxidation of the HDPE macromolecules, the carbonyl indexes (CI) were calculated using Equation 1.

$$CI = A_{1780-1700} / A_{1500-1420} \quad (1)$$

The integrated area between 1780 and 1700 cm^{-1} ($A_{1780-1700}$) refers to functional groups containing carbonyls[10,12,34], such as carboxylic acids (1712 cm^{-1}), ketones (1723 cm^{-1}), aldehydes (1730 cm^{-1}) and lactones (1780 cm^{-1}). The integrated area between 1500 and 1420 cm^{-1} ($A_{1500-1420}$) refers to the methylene group (CH_2), which is invariable in the HDPE degradation process[35,36].

2.4.2. Contact angle

The contact angles were determined for rectangular injection molded specimens made from virgin HDPE and granules of different types of HDPE after the first, third and fifth reprocessing cycles. The analysis was carried out using distilled water as the liquid, which allows the hydrophilia or hydrophobia of the substrate to be determined. For each sample, 10 repetitions were carried out, in which drops of water were placed on the surface. The images were taken on equipment manufactured by SEO, model Phoenix - P10001, after 3 seconds of dripping. Surftens 4.3 software was used to determine the values.

2.4.3. Yellowness index (YI)

The rectangular injection molded specimens made from virgin HDPE and different types of HDPE after the first, third and fifth reprocessing cycles were evaluated by colorimetry using the CIE Lab System. A BYK - Gardner instrument was used, model Spectro-guide 45/0 Gloss/ Spectro-guide Sphere Gloss. Three measurements were taken for each sample. With the values of L, a and b, the yellowness indexes (YI) were determined using Equation 2[37,38]:

$$YI = \frac{0.72a + 1.79b}{L} .100 \quad (2)$$

where YI is the yellowness index; *a* and *b (*red and yellow, respectively) and L is the luminosity measurement. YI was therefore calculated in triplicate.

2.4.4. Tensile strength test

The tensile strength tests were carried out on the samples injected with virgin HDPE and with the different types of HDPE after the first, third and fifth reprocessing cycles, in Instron universal testing equipment, model 4200, following a procedure adapted from the ASTM D638-22 standard[33], using a 5000 N load cell and 100 mm/min removal speed. Five specimens were used for each sample.

2.4.5. Izod Impact test

The Izod impact tests were carried out on the specimens injected with virgin HDPE and the different types of HDPE after the first, third and fifth reprocessing cycles. Equipment manufactured by Ceast, model Impactor II, was used in accordance with ASTM D-256-23e1[32] procedures. Five previously notched specimens were used for each analysis, with an 11.0 J hammer, at an ambient temperature of 25 ºC.

2.4.6. Dilute solution viscometry (DSV) for evaluation of intrinsic viscosity ([η]) and average viscosimetric molar mass $\left(\overline{Mv}\right)$

The [η] of HDPE was determined for the virgin polymer (pellet) and for the granules after the fifth reprocessing cycle, to evaluate the variation in the average viscosimetric molar mass. A Cannon-Ubbelohde capillary viscometer, number 50, with a capillary diameter of 0.44 mm, was used. Initially, a solution of the polymer was prepared in decalin, with a concentration of 1.0 g/dL, at a temperature of 135 ºC. The flow time for this solution was measured in duplicate using a viscometer immersed in a temperature-controlled silicone bath at 135 ºC, varying by ± 0.1 ºC. Subsequently, successive 4 mL aliquots of decalin were added, obtaining solutions with the following approximate concentrations: 0.7, 0.55, 0.45, 0.38 and 0.33 g/dL. For all of them, the flow time was measured in duplicate. The relative (η_{rel}), specific (η_{esp}) and reduced (η_{red}) viscosities were determined. The graph of η_{red} versus concentration was plotted and the [η] of the HDPE was determined by extrapolating the lines obtained by linear regression when the concentration tends to 0. To determine the average viscosimetric molar mass $\left(\overline{Mv}\right)$, the Mark-Houwink-Sakurada equation was used, presented here as Equation 3:

$$[\eta] = k.\left(\overline{Mv}\right)^{a} \quad (3)$$

in which [η] is the intrinsic viscosity found for polyethylene; k and α are the constants for the polymer-solvent system, which for polyethylene-decalin are 62 x 10^{-5} dL/g and 0.7, respectively; and $\overline{Mv}$ is the average viscosimetric molar mass (g/mol)[10,39,40].

2.5. Statistical analysis

The statistical analysis of the variance (ANOVA) of the obtained results was conducted using the software Origin. A one-way ANOVA and a Tukey's test were used to check for statistical differences among groups ($p \leq 0.05$). This analysis was performed for the results obtained for contact angles, yellowing index, elongation at break, and Izod impact resistance.

Figure 1 is a schematic representation of the methodology used in this work.

3. Results and Discussion

3.1. Carbonyl index (CI)

Figure 2 shows the FTIR spectra obtained for the specimens injected with virgin HDPE and HDPE granules after the first, third and fifth reprocessing cycles, limited to the areas investigated, between 2000 and 1400 cm^{-1}. The degree of oxidation can be followed by an increase in the peaks, mainly in the region between 1780 and 1700 cm^{-1},

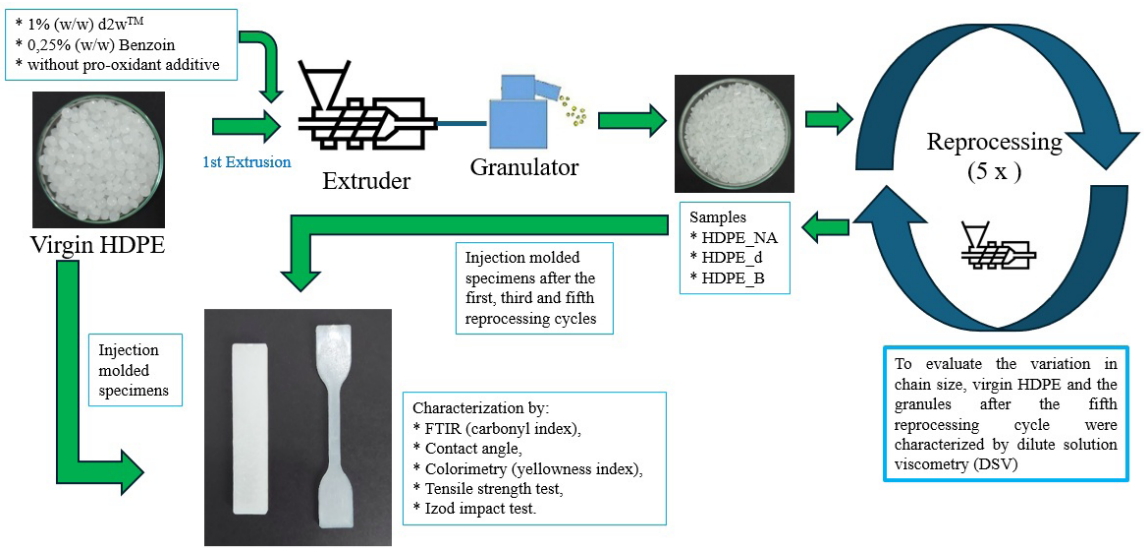

Figure 1. Schematic representation of the methodology used in this study, showing the production of two different types of oxy-biodegradable HDPE and the analysis performed to characterize the samples before and after 1, 3 and 5 reprocessing cycles.

referring to functional groups containing carbonyls, such as carboxylic acids, ketones, aldehydes and lactones.

The spectra show that thermal oxidation has occurred due to the reprocessing cycles and even the injection process. However, it is only clearly noticeable for the HDPE_d sample after the fifth reprocessing cycle. It is important to note that, among the saturated polyolefins, HDPE is the most resistant to the oxidative degradation process[13,19,41] and, for this reason, the carbonyl indexes (CI) were determined using Equation 1. The results are shown in Figure 3.

The CI values show that the d2w™ additive is responsible for higher rates of oxidation of HDPE in the reprocessing cycles evaluated, in addition to exposure to high temperatures in the injection process, with a greater increase in functional groups containing carbonyls. However, although at lower rates than d2w™, benzoin also favored the oxidation of macromolecules, since the CI values for the different cycles are higher than those observed for HDPE_NA. The presence of a pro-oxidant additive favors a higher oxidation rate during processing and reprocessing[42].

3.2. Contact angle

Table 2 shows the values determined for the contact angle with distilled water for the injection molded specimens (rectangular) with virgin HDPE and with HDPE granules after the first, third and fifth reprocessing cycles. The results evidence that all the HDPE samples showed a reduction in the contact angle, demonstrating the occurrence of thermal oxidation due to the reprocessing cycles and also due to the injection process used to obtain specimens. However, for all cycles, it is most evident in the presence of the d2w™ additive, followed by samples containing benzoin as a pro-oxidant additive. Thermal oxidation at higher rates for the samples containing the additives is corroborated by the CI values presented above. It should be noted that, in addition to functional groups containing carbonyls, thermal oxidation inserts hydroxyls and unsaturations into the polymer matrix, which contributes to a reduction in the contact angle[12,41], due to the increase in intermolecular interactions between the water molecules and the oxidized HDPE macromolecules.

3.3. Yellowness index (YI)

It is assumed that the yellowing of HDPE is a consequence of the oxidative thermomechanical degradation[43] of the polymer when subjected to repeated reprocessing cycles, in addition to the oxidation that occurs during injection processing. However, due to the presence of pro-oxidant additives, oxidation rates tend to be higher, causing the material to yellow more clearly, as can be seen in Figure 4.

Yellowing can be quantified by determining the YI (yellowness index) values, using the L, a and b values obtained by colorimetry and from Equation 2 and the results are shown in Table 3. The values confirm that thermal oxidation rates are higher in the presence of the d2w™ additive, with higher YI values in all reprocessing cycles. YI values in the presence of benzoin are also higher than when HDPE is processed and reprocessed without pro-oxidant additives, but at lower rates than when in the presence of the commercial additive. The values are consistent with the carbonyl indexes and the values presented for the contact angles. It should be noted that the injection process used to obtain the test specimens contributed to the oxidation of the HDPE molecules.

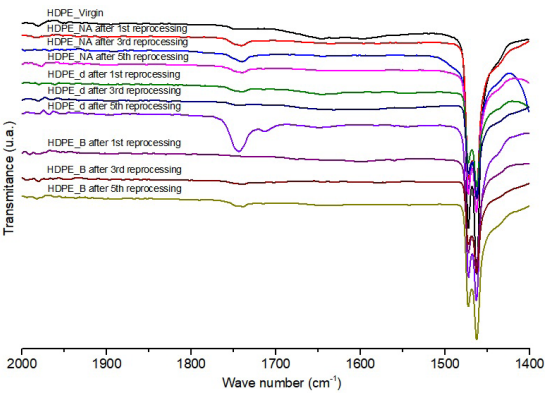

Figure 2. FTIR spectra of injection molded specimens of virgin HDPE and those obtained with HDPE granules after the first, third and fifth reprocessing cycles.

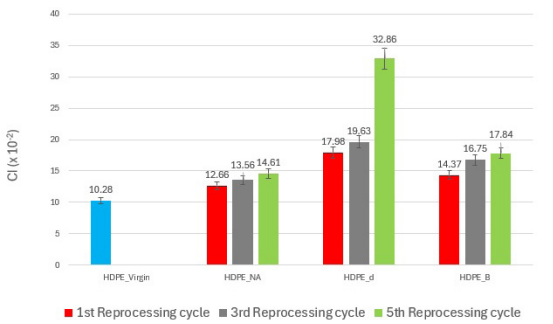

Figure 3. CI for the injection molded specimens made of virgin HDPE and HDPE granules after the first, third and fifth reprocessing cycles.

Table 2. Contact angle (º) of injection molded specimens made of virgin HDPE and HDPE granules after the first, third and fifth reprocessing cycles.

Sample	HDPE_Virgin	HDPE_NA	HDPE_d	HDPE_B
Before extrusion	81.30 ± 1.99	-	-	-
After 1st reprocessing	-	72.51 ± 3.07[a]	69.95 ± 2.51[a]	70.20 ± 1.83[a]
After 3rd reprocessing	-	71.33 ± 3.59[a]	65.81 ± 5.89[b]	69.06 ± 5.12[ab]
After 5th reprocessing	-	69.75 ± 4.60[a]	64.04 ± 2.80[b]	68.48 ± 5.00[ab]

[a,b] Different letters on the same line indicate statistically significant differences between experimental groups ($p < 0.05$).

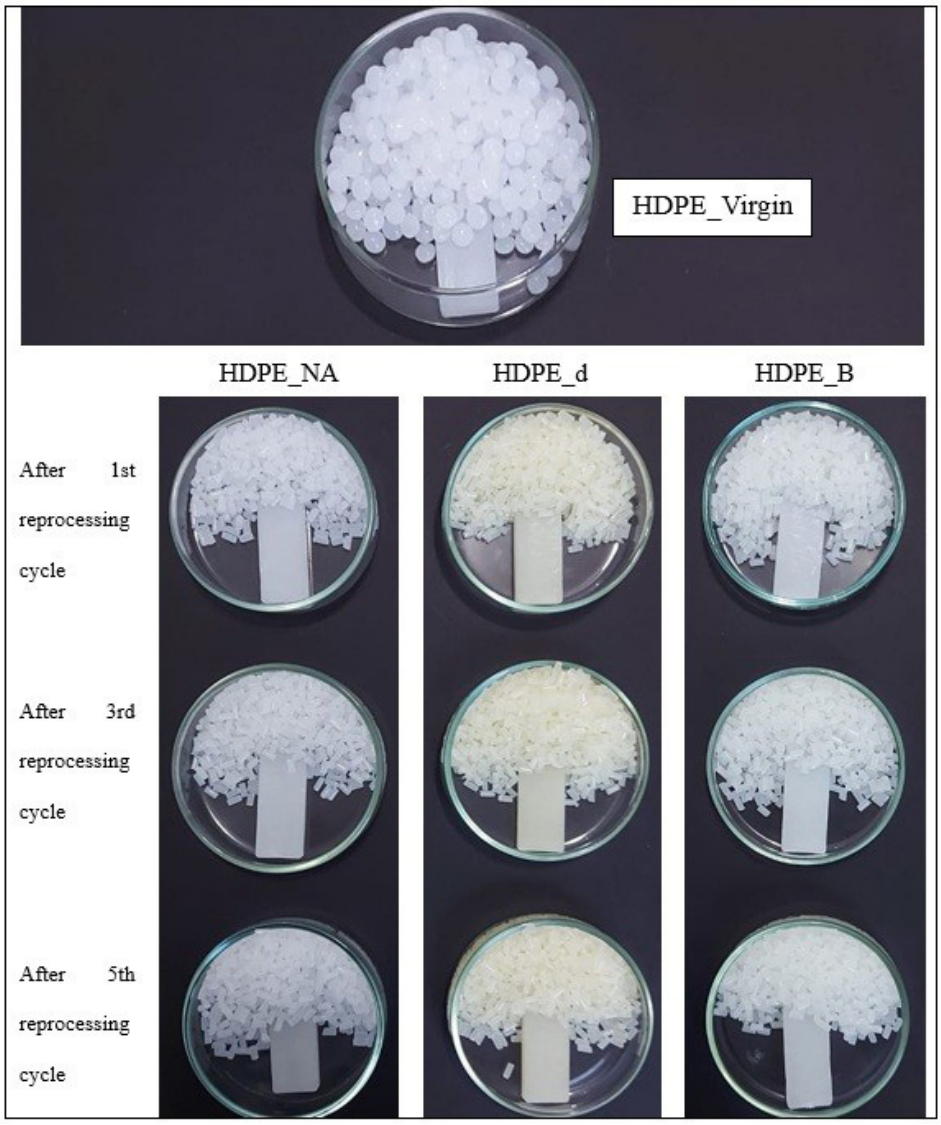

Figure 4. Granules and injection molded specimens of virgin HDPE and the different HDPE samples after the first, third and fifth reprocessing cycles.

Table 3. YI determined by colorimetry of injection molded specimens made of virgin HDPE and granules after the first, third and fifth reprocessing cycles.

Sample	HDPE_Virgin	HDPE_NA	HDPE_d	HDPE_B
Before extrusion	-7.02 ± 0.89	-	-	-
After 1st reprocessing	-	-4.49 ± 0.16[a]	24.24 ± 0.15[b]	8.39 ± 0.40[c]
After 3rd reprocessing	-	-0.59 ± 0.08[a]	25.99 ± 0.28[b]	8.31 ± 0.31[c]
After 5th reprocessing	-	2.66 ± 0.16[a]	26.49 ± 0.96[b]	9.49 ± 0.83[c]

[a,b,c] Different letters on the same line indicate statistically significant differences between experimental groups ($p < 0.05$).

3.4. Tensile strength test

The average results obtained for maximum tensile stress, tensile stress at break and Young's Modulus in the tensile strength test for all samples evaluated are summarized in Table 4.

However, considering the importance of deformation until rupture, especially in the production of packaging such as disposable bags and sacks, this will be the property discussed here. Table 5 shows the average values of deformation until the rupture of virgin HDPE and different types of HDPE after the

first, third and fifth reprocessing cycles, properly statistically processed. The values confirm the loss of mechanical properties of HDPE, especially in the presence of pro-oxidant additives, however, with little statistical significance. The two additives had a similar effect on this property after five reprocessing cycles. The loss of deformation capacity when subjected to tension is a consequence of the reduction in molar mass and is characteristic of the HDPE degradation process[17,31,36,44].

Figure 5 shows the representative stress versus strain curves for virgin HDPE and the different types of HDPE after the first, third and fifth reprocessing cycles. The various reprocessing cycles lead to substantial losses in the polymer mechanical properties, especially in the presence of pro-oxidant additives.

3.5. Izod impact test

Table 6 shows the average Izod impact resistance values of injection molded samples made from virgin HDPE and HDPE granules after the first, third and fifth reprocessing cycles. As in the tensile strength test, a loss of this mechanical property was observed in all samples. However, considering the evaluation of the averages, this loss is more evident in samples containing pro-oxidant additives. Nevertheless, they are statistically similar. For each of the reprocessing cycles, the reduction in impact resistance is more evident in the presence of d2w™, followed by samples processed with benzoin. The values are therefore consistent with those presented for CI and contact angle, confirming higher rates of thermal oxidation when pro-oxidant additives are present.

3.6. Dilute solution viscometry

To assess the change in the polymer molar mass, virgin HDPE and HDPE granules after the fifth reprocessing cycle were characterized by dilute solution viscometry (DSV), with determination of the intrinsic viscosity and, using Equation 3, the average viscosimetric molar masses were determined, as shown in Table 7. After 5 reprocessing cycles, the HDPE processed with the d2w™ additive had a reduction of approximately 17%. When processed with the benzoin additive, the reduction was approximately 10%, while for HDPE reprocessed without pro-oxidant additives, the reduction was less than 7%. The variations in molar mass are consistent with the results presented throughout this work and with other related studies when HDPE is processed with pro-oxidant additives[8,10,12].

Table 4. Average values of max. tensile stress, tensile stress at break and Young's Modulus obtained for the different samples evaluated in this study.

Sample	Max. tensile stress (MPa)	Tensile stress at break (MPa)	Young´s Modulus (MPa)
HDPE_Virgin (before extrusion)	30.12 ± 0.70	8.01 ± 3.68	612.55 ± 20.69
HDPE_NA (after 1st reprocessing)	31.06 ± 0.64	12.32 ± 0.51	627.46 ± 36.53
HDPE_NA (after 3rd reprocessing)	31.20 ± 0.39	12.09 ± 1.80	531.51 ± 42.53
HDPE_NA (after 5th reprocessing)	30.9 ± 0.41	6.57 ± 3.16	481.07 ± 19.40
HDPE_d (after 1st reprocessing)	62.71 ± 0.77	22.91 ± 1.24	1143.01 ± 19.60
HDPE_d (after 3rd reprocessing)	32.86 ± 0.56	9.40 ± 1.45	509.71 ± 14.18
HDPE_d (after 5th reprocessing)	31.34 ± 0.39	7.44 ± 2.33	491.68 ± 18.73
HDPE_B (after 1st reprocessing)	30.71 ± 0.31	12.13 ± 0.41	568.68 ± 17.33
HDPE_B (after 3rd reprocessing)	31.50 ± 0.82	9.92 ± 2.93	473.60 ± 35.96
HDPE_B (after 5th reprocessing)	32.68 ± 0.57	7.49 ± 3.55	476.27 ± 7.58

Table 5. Average values of the elongation at break (%) of the injection molded specimens of virgin HDPE and HDPE granules after the first, third and fifth reprocessing cycles.

Sample	HDPE_Virgin	HDPE_NA	HDPE_d	HDPE_B
Before extrusion	315.6 ± 147.2	-	-	-
After 1st reprocessing	-	289.1 ± 95.6[a]	186.1 ± 44.1[a]	229.5 ± 74.8[a]
After 3rd reprocessing	-	327.8 ± 134.1[a]	99.9 ± 59.3[b]	111.6 ± 49.4[b]
After 5th reprocessing	-	124.8 ± 13.5[a]	100.1 ± 12.7[a]	90.4 ± 20.0[b]

[a,b] Different letters on the same line indicate statistically significant differences between experimental groups ($p < 0.05$).

Table 6. Average Izod impact resistance (kJ/m^2) values of injection molded specimens made from virgin HDPE and HDPE granules after the first, third and fifth reprocessing cycles.

Sample	HDPE_Virgin	HDPE_NA	HDPE_d	HDPE_B
Before extrusion	58.89 ± 3.08	-	-	-
After 1st reprocessing	-	48.59 ± 2.75[a]	47.25 ± 1.41[a]	50.55 ± 2.78[a]
After 3rd reprocessing	-	42.63 ± 1.64[a]	41.93 ± 1.76[a]	46.16 ± 5.22[a]
After 5th reprocessing	-	41.59 ± 1.60[a]	35.92 ± 6.21[a]	39.61 ± 1.99[a]

Means followed by the same letter do not differ significantly according to Tukey's test at $p < 0.05$.

Despite being subjected to multiple reprocessing cycles, the polymer still has a high molar mass, which suggests that it can be recycled[2,45]. However, considering the changes to its properties, the investigation of suitable dilution factors with virgin polymer should be considered. Yellowing can be assessed by determining YI and has proved to be a simple parameter to obtain and is directly related to the rate of thermal oxidation suffered by HDPE, which can be used as a criterion in assessing the recyclability of waste.

3.6. Evaluating the correlation between YI and the other parameters evaluated in the thermo-oxidative degradation of HDPE

The results found in this study show that YI values increase as HDPE is thermo-oxidized. In this sense, it is directly proportional to CI and inversely proportional to the contact angle, molar mass, elongation at break and Izod impact resistance. Figure 6 shows graphs demonstrating the

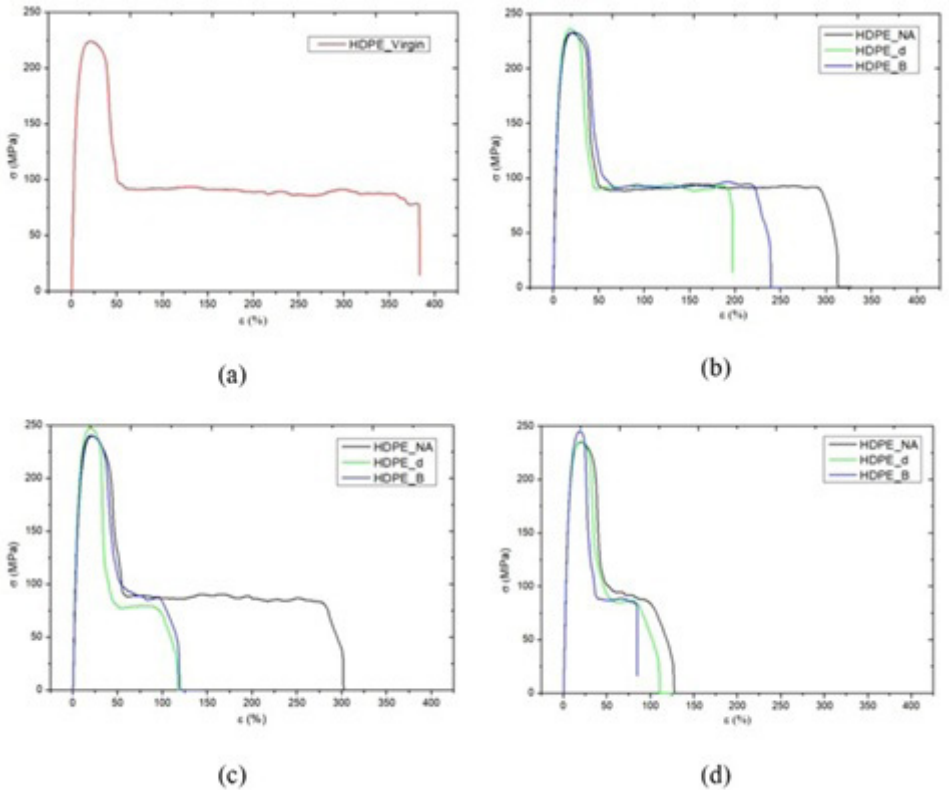

Figure 5. Stress-strain curves of injection molded specimens made of (a) virgin HDPE and HDPE granules after the (b) first (c) third and (d) fifth reprocessing cycles.

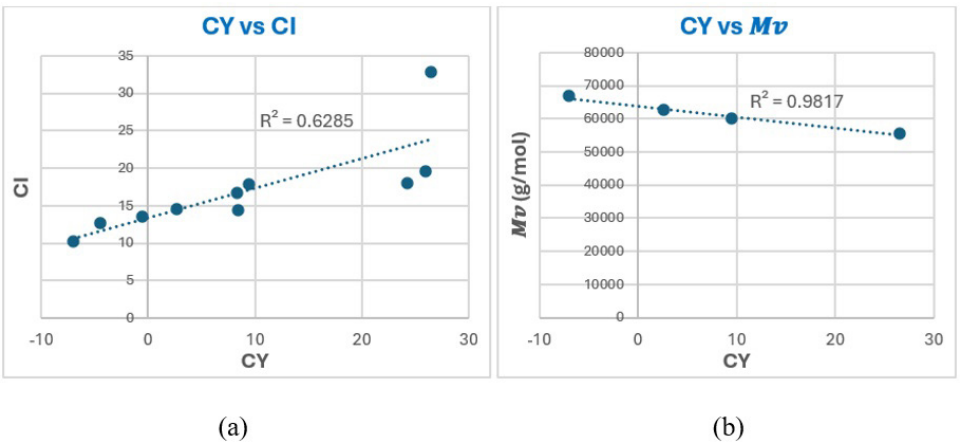

Figure 6. Graphs showing the trend line between (a) YI *vs.* CI and (b) YI *vs.* $\overline{Mv}$.

Table 7. Values determined for the intrinsic viscosity [η] and average viscosimetric molar mass ($\overline{Mv}$) for the different HDPE samples.

Sample	[η] (dL/g)	$\overline{Mv}$ (g/mol)
HDPE_Virgin	1.4797	6.69×10^4
HDPE_NA	1.4146	6.27×10^4
HDPE_d	1.2994	5.55×10^4
HDPE_B	1.3720	6.00×10^4

relationship between YI vs. CI (a) and YI vs. $\overline{Mv}$. However, the R^2 values show that further tests need to be carried out to establish mathematical mechanisms for using YI as a parameter in assessing the recyclability of different types of HDPE, including oxo-biodegradable HDPE.

4. Conclusions

The results obtained in this study show that pro-oxidant additives act by increasing the rate of thermal oxidation of HDPE when they are subjected to multiple reprocessing cycles. At the concentrations evaluated, d2w™ acted more clearly on the degradation of HDPE than benzoin, when compared to the polymer reprocessed without these additives, as demonstrated by the CI results. The insertion of oxygenated functional groups improves the interaction of HDPE with distilled water, reducing the contact angle. Similarly, the reduction in molar mass leads to a loss of mechanical properties, according to the results presented for the tensile strength and Izod impact tests. All these changes are accompanied by progressive yellowing of the samples, which can be assessed by YI. It was possible to observe that the yellowness indexes increased in proportion to the changes observed.

The results of the DSV test, however, show little reduction in molar mass for all the samples after 5 reprocessing cycles, evidencing that this material can be recycled and the yellowness index can be used as a parameter for determining the dilution factor with virgin polymer or even using the waste to obtain other single-use items such as bags and other packaging that does not come into direct contact with food. In this context, the authors suggest that further studies be conducted with other concentrations and different types of pro-oxidant additives, including other grades of HDPE, in order to establish the correct mathematical relationships between YI and one of the parameters that assesses the thermal oxidation of HDPE (CI, contact angle, for example), assisting in the correct determination of the dilution factor to be used, mainly in the manufacture of disposable bags.

5. Acknowledgments

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7. References

1. Benítez A, Sánchez JJ, Arnal ML, Müller AJ. Monitoring abiotic degradation of branched polyethylenes formulated with pro-oxidants through different mechanical tests. Polym Degrad Stabil. 2013;98(9):1705-16. http://doi.org/10.1016/j.polymdegradstab.2013.06.004.
2. Babetto AS, Antunes MC, Bettini SHP, Bonse BC. A recycling-focused assessment of the oxidative thermomechanical degradation of HDPE melt containing pro-oxidant. J Polym Environ. 2020;28(2):699-712. http://doi.org/10.1007/s10924-019-01641-6.
3. Cuesta F, Camacho AM, Rúbio EM. Influence of the main blown film extrusion process parameters on the mechanical properties of a high-density polyethylene hexene copolymer and linear low-density polyethylene butene copolymer blend used for plastic bags. Appl Sci (Basel). 2023;13(22):12164. http://doi.org/10.3390/app132212164.
4. Shahsavari-Badvestani T, Jahanmardi R, Tayouri M-I, Fathi M. Acceleration of thermo-oxidative degradation of high-density polyethylene using oxidized polyethylene. Polyolefins J. 2023;10(3):149-57. http://doi.org/10.22063/POJ.2023.3288.1246.
5. Moreno-Serna V, Ubilla M, Montoille L, Saavedra M, Corrales T, Muñoz L, et al. Influence of modified SiO2 nanoparticles on the photostability of recycled HDPE. J Polym Environ. 2024;32(5):2045-58. http://doi.org/10.1007/s10924-023-03126-z.
6. Mastalygina E, Abushakhmanova Z, Poletto M, Pantyukhov P. Biodegradation in soil of commercial plastic bags labelled as “biodegradable”. Mater Res. 2023;26:e20220164. http://doi.org/10.1590/1980-5373-mr-2022-0164.
7. De la Orden MU, Montes JM, Urreaga JM, Bento A, Ribeiro MR, Pérez E, et al. Thermo and photo-oxidation of functionalized metallocene high density polyethylene: effect of hydrophilic groups. Polym Degrad Stabil. 2015;111:78-88. http://doi.org/10.1016/j.polymdegradstab.2014.10.023.
8. Antunes MC, Agnelli JAM, Babetto AS, Bonse B, Bettini SHP. Abiotic thermo-oxidative degradation of high density polyethylene: effect of manganese stearate concentration. Polym Degrad Stabil. 2017;143:95-103. http://doi.org/10.1016/j.polymdegradstab.2017.06.012.
9. Ghatge S, Yang Y, Ahn J-H, Hur H-G. Biodegradation of polyethylene: a brief review. App Biol Chem. 2020;63(1):27. http://doi.org/10.1186/s13765-020-00511-3.
10. Brandão JAO, Morisso FDP, Francisquetti EL, Santana RMC. Influence of the nature of pro-oxidants on the photooxidation of polyethylene blown films. Heliyon. 2022;8(8):e10217. http://doi.org/10.1016/j.heliyon.2022.e10217.
11. Ghanadi M, Padhye LP. Revealing the long-term impact of photodegradation and fragmentation on HDPE in the marine environment: origins of microplastic and dissolved organics. J Hazard Mater. 2024;465:133509. http://doi.org/10.1016/j.jhazmat.2024.133509.
12. Brandão JAO, Morisso FDP, Francisquetti EL, Santana RMC. Structural changes of polyethylene in blown films with different pro-oxidants. Polímeros. 2021;31(3):e2021029. http://doi.org/10.1590/0104-1428.20210058.
13. Padermshoke A, Kajiwara T, An Y, Takigawa M, Nguyen TV, Masunaga H, et al. Characterization of photo-oxidative degradation process of polyolefins containing oxo-biodegradable additives. Polymer. 2022;262:125455. http://doi.org/10.1016/j.polymer.2022.125455.
14. Sciscione F, Hailes HC, Miodownik M. The performance and environmental impact of pro-oxidant additive containing plastic in the open unmanaged environment – a review of the evidence. R Soc Open Sci. 2023;10(5):230089. http://doi.org/10.1098/rsos.230089.
15. Brandão JAO, Martin PT, Morisso FDP, Francisquetti EL, Santana RMC. Characterization of the abiotic degradation of oxo-biodegradable polypropylene obtained from transition metal-free pro-oxidant. Polym Degrad Stabil. 2024;223:110741. http://doi.org/10.1016/j.polymdegradstab.2024.110741.

16. Nguyen T-A, Gregersen OW, Männle F. Thermal oxidation of polyolefins by mild pro-oxidant additives based on iron carboxylates and lipophilic amines: degradability in the absence of light and effect on the adhesion to paperboard. Polymers. 2015;7(8):1522-40. http://doi.org/10.3390/polym7081468.
17. Antunes MC, Agnelli JAM, Babetto AS, Bonse BC, Bettini SHP. Correlating different techniques in the thermooxidative degradation monitoring of high-density polyethylene containing pro-degradant and antioxidants. Polym Test. 2018;69:182-7. http://doi.org/10.1016/j.polymertesting.2018.05.008.
18. Grause G, Chien M-F, Inoue C. Changes during the weathering polyolefins. Polym Degrad Stabil. 2020;181:109364. http://doi.org/10.1016/j.polymdegradstab.2020.109364.
19. Mamin EA, Pantyukhov PV, Olkhov AA. Oxo-additives for polyolefin degradation: kinetics and mechanism. Macromol. 2023;3(3):477-506. http://doi.org/10.3390/macromol3030029.
20. Gomes LB, Klein JM, Brandalise RN, Zeni M, Zoppas BC, Grisa AMC. Study of oxo-biodegradable polyethylene degradation in simulated soil. Mater Res. 2014;17(Suppl. 1):121-6. http://doi.org/10.1590/1516-1439.224713.
21. Antelava A, Constantinou A, Bumajdad A, Manos G, Dewil R, Al-Salem SM. Identification of commercial oxo-biodegradable plastics: study of UV induced degradation in an effort to combat plastic waste accumulation. J Polym Environ. 2020;28(9):2364-76. http://doi.org/10.1007/s10924-020-01776-x.
22. Zhang F, Zhao Y, Wang D, Yan M, Zhang J, Zhang P, et al. Current technologies for plastic waste treatment: a review. J Clean Prod. 2021;282:124523. http://doi.org/10.1016/j.jclepro.2020.124523.
23. Montazer Z, Najafi MBH, Levin DB. Challenges with verifying microbial degradation of polyethylene. Polymers. 2020;12(1):123. http://doi.org/10.3390/polym12010123.
24. Montagna LS, Catto AL, Forte MMC, Chiellini E, Corti A, Morelli A, et al. Comparative assessment of degradation in aqueous medium of polypropylene films doped with transition metal free (experimental) and transition metal containing (commercial) pro-oxidant/pro-degradant additives after exposure to controlled UV radiation. Polym Degrad Stabil. 2015;120:186-92. http://doi.org/10.1016/j.polymdegradstab.2015.06.019.
25. Arráez FJ, Arnal ML, Müller AJ. Thermal and UV degradation of polypropylene with pro-oxidant: abiotic characterization. J Appl Polym Sci. 2018;135(14):46088. http://doi.org/10.1002/app.46088.
26. Vazquez YV, Ressia JA, Cerrada ML, Barbosa SE, Vallés EM. Prodegradant additives effect onto commercial polyolefins. J Polym Environ. 2019;27(3):464-71. http://doi.org/10.1007/s10924-018-01364-0.
27. Abdelmoez W, Dahab I, Ragab EM, Abdelsalam O, Mustafa A. Bio- and oxo-degradable plastics: insights on facts and challenges. Polym Adv Technol. 2021;32(5):1981-96. http://doi.org/10.1002/pat.5253.
28. Doriat A, Gigliotti M, Beringhier M, Lalizel G, Dorignac E, Berterretche P, et al. Assessment of a color measurement-based method for the characterization of polymer thermo-oxidation. Polym Degrad Stabil. 2024;229:110950. http://doi.org/10.1016/j.polymdegradstab.2024.110950.
29. Plota-Pietrzak A, Masek A. Functionalized metal oxide particles with antioxidant as new carriers providing higher stability of polyolefin products. Sustain Mater Tech. 2024;40:e00885. http://doi.org/10.1016/j.susmat.2024.e00885.
30. Ammala A, Bateman S, Dean K, Petinakis E, Sangwan P, Wong S, et al. An owerview of degradable and biodegradable polyolefins. Prog Polym Sci. 2011;36(8):1015-49. http://doi.org/10.1016/j.progpolymsci.2010.12.002.
31. Babetto AS, Agnelli JAM, Bettini SHP. Avaliação de sistemas pró-degradantes na degradação termooxidativa do PEAD. Polímeros. 2015;25(spe):68-76. http://doi.org/10.1590/0104-1428.2022.
32. ASTM: American Society for Testing and Material. ASTM D256-23e1: standard test method for determining the izod pendulum impact resistance of plastic. West Conshohocken: ASTM; 2018.
33. ASTM: American Society for Testing and Material. ASTM D638-22: standard test method for tensile properties of plastics. West Conshohocken: ASTM; 2022.
34. Corti A, Muniyasamy S, Vitali M, Imam SH, Chiellini E. Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. Polym Degrad Stabil. 2010;95(6):1106-14. http://doi.org/10.1016/j.polymdegradstab.2010.02.018.
35. Almond J, Sugumaar P, Wenzel MN, Hill G, Wallis C. Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. E-Polymers. 2020;20(1):369-81. http://doi.org/10.1515/epoly-2020-0041.
36. Zha S, Lan H, Lin N, Meng T. Degradation and characterization methods for polyethylene gas pipes after natural and accelerated aging. Polym Degrad Stabil. 2023;208:110247. http://doi.org/10.1016/j.polymdegradstab.2022.110247.
37. Balköse D, Egbuchunam TO, Okieimen FE. Formulation and properties' evaluation of PVC/(dioctyl phthalate)/(epoxidized rubber seed oil) plastigels. J Vinyl Addit Technol. 2008;14(2):65-72. http://doi.org/10.1002/vnl.20142.
38. Pagacz J, Chrzanowski M, Krucinska I, Pielichowski K. Thermal aging and accelerated weathering of PVC/MMT nanocomposites: structural and morphological studies. J Appl Polym Sci. 2015;132(24):42090. http://doi.org/10.1002/app.42090.
39. Mortazavi SMM, Jafarian H, Ahmadi M, Ahmadjo S. Characteristics of linear/branched polyethylene reactor blends synthesized by metallocene/late transitional metal hybrid catalysts. J Therm Anal Calorim. 2016;123(2):1469-78. http://doi.org/10.1007/s10973-015-5072-4.
40. Brandup J, Immergut EH, Grulke EA. Polymer handbook. 2nd ed. New York: Wiley-Interscience Publication; 2009.
41. Chiellini E, Corti A, D'Antone S, Baciu R. Oxo-biodegradable carbon backbone polymers – oxidative degradation of polyethylene under accelerated test conditions. Polym Degrad Stabil. 2006;91(11):2739-47. http://doi.org/10.1016/j.polymdegradstab.2006.03.022.
42. Samsudin MSF, Wahab MAA, Ahamid Z. Effect of recycled HDPE with pro-oxidant on the photodegradation of HDPE film. Prog Rubber Plast Recycl Technol. 2013;29(2):69-80. http://doi.org/10.1177/147776061302900201.
43. Zeng S-F, Guo P, Hu C-Y, Wang Z-W. Effects of mechanical recycling on optical properties and microstructure of recycled high-density polyethylene pellets and bottles. J Appl Polym Sci. 2023;140(6):e53446. http://doi.org/10.1002/app.53446.
44. Suresh B, Maruthamuthu S, Khare A, Palanisamy N, Muralidharan VS, Ragunathan R, et al. Influence of thermal oxidation on surface and thermo-mechanical properties of polyethylene. J Polym Res. 2011;18(6):2175-84. http://doi.org/10.1007/s10965-011-9628-0.
45. Reyes JCS, Uribe OAC, Méndez LDG, Rodrígues AMP, Piñales RAP. A scoping and critical review of properties, standards and regulations of oxo-biodegradable plastics. Univ Sci. 2023;28(1):65-139. http://doi.org/10.11144/Javeriana.SC281.asac.

Data Availability

The entire dataset supporting the findings of this study is available from the author, João Augusto Osório Brandão, upon request.