Degradability of linear polyolefins under natural weathering

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ABSTRACT

High density polyethylene (HDPE), linear low density polyethylene (LLDPE), and isotactic polypropylene (PP) containing antioxidant additives at low or zero levels were extruded and blown moulded as films. An HDPE/LLDPE commercial blend containing a pro-oxidant additive (i.e., an oxo-biodegradable blend) was taken from the market as supermarket bag. These four polyolefin samples were exposed to natural weathering for one year during which their structure and thermal and mechanical properties were monitored. This study shows that the real durability of olefin polymers may be much shorter than centuries, as in less than one year the mechanical properties of all samples decreased virtually to zero, as a consequence of severe oxidative degradation, that resulted in substantial reduction in molar mass accompanied by a significant increase in content of carbonyl groups. PP and the oxo-bio HDPE/LLDPE blend degraded very rapidly, whereas HDPE and LLDPE degraded more slowly, but significantly in a few months. The main factors influencing the degradability were the frequency of tertiary carbon atoms in the chain and the presence of a pro-oxidant additive. The primary (sterically hindered phenol) and secondary (phosphite) antioxidant additives added to PP slowed but did not prevent rapid photo-oxidative degradation, and in HDPE and LLDPE the secondary antioxidant additive had little influence on the rate of abiotic degradation at the concentrations used here.

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1. Introduction

Polyolefins are a class of polymers synthesised by addition reactions of unsaturated monomers (alkyl-ethylenes), of which high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and propylene (PP) are good representatives. HDPE, LLDPE and PP differ structurally in the number and length of branches, whose presence tends to reduce the amount and size of crystals, as well as their melting and crystallisation temperatures [1,2]. While HDPE has molecules with a very low number of short and long branches (typically <2 CH₂ groups/1000 C atoms), LLDPE has more short branches (10–30 CH₂/1000 C), obtained through the introduction of one or more co-monomers to ethylene such as 1-butene, 1-hexene and 1-octene [1]. As a result of these branches, HDPE has a high degree of crystallinity (typically 60–80%) and a high melting temperature of ~135 °C, while LLDPE has lower crystallinity (40–60%) and melting temperature (~125 °C) [1]. Isotactic PP contains one methyl branch per monomer unit (333 CH₃/1000 C), but the spatial organisation of these branches results in degrees of crystallinity of 40–60% and a melting temperature of ~163 °C [2]. The tertiary carbon atoms that are present at the branch sites are more susceptible to attack by free radicals, because they form more stable radicals when they lose a hydrogen atom. Some structural defects such as unsaturation and carbonyl and hydroperoxide groups may also be present in all polymers, formed during polymerisation and subsequent processing, but are present at very low levels [3–5].

Polyolefins are the most produced and consumed synthetic polymers worldwide, with many uses such as packaging, toys, appliances, and disposable items. Although chemical and biological inertness was originally seen as an advantage, the high stability of these compounds and resistance to degradation has led to their accumulation in the environment, considerably increasing visible pollution and contributing to the clogging of drains during heavy rains, among other problems [6–8]. Biodegradation represents a solution for the treatment of packaging and disposable items.
wastes with low thicknesses, which are usually difficult to recycle. However, the principle of microbial infallibility formalised by Alexander [9] has serious limitations when it comes to xenobiotics consisting of polyolefin polymers, which are resistant to biodegradation (recalcitrant) for a number of reasons: they are hydrophobic and have high molar masses, dramatically reducing their bioavailability; they usually form crystals, which are less vulnerable to degradation; and they usually have varying amounts of branches, increasing the recalitrance of these materials by blocking the action of enzymes of the β-oxidation route on the fatty acids formed by abiotic and biotic oxidation of hydrocarbons [10].

Physical and chemical treatments leading to polymer oxidation (abiotic degradation) can be effectively used as a pretreatment strategy before subjecting the material to biodegradation (biotic degradation) [11,12]. Natural weathering, which includes solar radiation, wind and ambient temperature leads to the formation of free radicals, which may combine with oxygen at the surface and form peroxides and hydroperoxides, following the known reactions of oxidative degradation. As a consequence, alkenes, alkenes, ketones, aldehydes, alcohol, carboxylic acids, keto-acids, linear esters and lactones are formed [13], decreasing the polymer reactivity of oxidative degradation. As a result, alkanes, and form peroxides and hydroperoxides, following the known strategy before subjecting the material to biodegradation (abiotic degradation) can be effectively used as a pretreatment formed by abiotic and biotic oxidation of hydrocarbons [10].

Another objective was to understand how the different chemical treatments leading to polymer oxidation (abiotic degradation) can be effectively used as a pretreatment strategy before subjecting the material to biodegradation (biotic degradation) [11,12]. Natural weathering, which includes solar radiation, wind and ambient temperature leads to the formation of free radicals, which may combine with oxygen at the surface and form peroxides and hydroperoxides, following the known reactions of oxidative degradation. As a consequence, alkenes, alkenes, ketones, aldehydes, alcohol, carboxylic acids, keto-acids, linear esters and lactones are formed [13], decreasing the polymer hydrophobicity and molar mass, thus increasing the bioavailability and biodegradability of the polymer [3]. Some browning and crosslinking reactions may also occur, but chain scission dominates over crosslinking for all materials [8,14,15]. Abiotic degradation can be understood by certain organic salts of transition metals (Co, Mn, Fe, Ni, Cu, etc.), which participate in redox reactions, generating free radicals on the hydrocarbon chains or decomposing previously formed hydroperoxides. Such compounds may be purposely added to the polymer as pro-oxidant additives or may be present as catalytic residues or impurities [28,16,17]. The polymeric materials containing pro-oxidant (or pro-degrading) substances are known as oxo-biodegradable polymers [18].

On the other hand, antioxidant additives are usually added to slow the abiotic degradation of polyolefins, and these additives can be generally classified as primary and secondary [19]. Primary antioxidants work efficiently at ambient temperature (and at processing temperatures in synergism with secondary antioxidants), providing protection during the polymer’s service life (long-term thermal stability). These are free radical scavengers such as sterically hindered phenols, and are added at levels of around 200–1000 mg kg⁻¹ of polymer. Secondary antioxidants act efficiently at the high processing temperatures (melt-processing stability). These are hydroperoxyde decomposers, and are mainly certain phosphites, phosphonites and thioesters, and are added at levels of around 400–2000 mg kg⁻¹ of polymer. In addition to these additives, there are UV stabilisers, including the UV absorbers that shield the polymer from UV light, and the sterically hindered amine light stabilisers (HALS) that scavenge the radical intermediates formed in the photodegradation process. Abiotic degradation only becomes significant after the consumption of the antioxidant additives, and results in the breakdown of the polyolefin molecules into smaller segments and in the incorporation of oxygenated groups, significantly increasing the bioavailability and biodegradability of the polymer [2,17,18].

Considering the enormous and growing worldwide consumption of linear polyolefins and the worrying pollution caused by their accumulation in the environment, this study aimed to assess the abiotic degradability of HDPE, LLDPE and PP extruded blown films with low or zero concentrations of antioxidant additives, as well as an HDPE/LLDPE blend containing a pro-oxidant additive (oxo-biodegradable blend), during one year of natural weathering. Another objective was to understand how the different chemical structures of the polyolefins studied here affect their abiotic degradability.

2. Materials and methods

2.1. Experimental conditions and materials

HDPE was obtained directly from the polymerisation reactor output (Braskem, Spherilene technology). The HDPE used here had melt indices [20] of 0.35 (190 °C, 5.0 kg) and 8.5 dg min⁻¹ (190 °C, 2.16 kg), with <2 CH₃/1000 C atoms and a density of 0.947 g cm⁻³ (23 °C). The virgin resin was mixed with 0, 100 and 300 mg kg⁻¹ of tris (2,4-di-tert-butylphenyl) phosphite (Irgafos 168, Ciba, a secondary antioxidant) and blown extruded into films (Carnevalli CHD 60 extruder) with a thickness of 25 ± 5 μm. LLDPE, an ethylene-1-butene copolymer (15 CH₃/1000 C atoms), was taken from the reactor (Braskem, Unipol technology) with a melt index of 0.70 dg min⁻¹ (190 °C, 2.16 kg) and a density of 0.921 g cm⁻³, and was mixed with 0, 100 and 300 mg kg⁻¹ of Irgafos 168 prior to being blown extruded into films with a thickness of 80 ± 5 μm. Isotactic PP was taken from the reactor (Braskem, Spheripol technology) with a melt index of 7.0 dg min⁻¹ (230 °C/2/16 kg) and a density of 0.905, and was mixed with 0, 100 and 300 mg kg⁻¹ of Irganox B-215 (a blend of 2 mass parts of Irgafos 168 and 1 part of Irganox 1010, from Ciba). Irganox 1010 is tetrakis [3,5-di-tert-butyl-4-hydroxyhydrocinnamate] methane, a primary antioxidant. Subsequently, these mixtures were extruded to form 70 ± 5 μm thickness films. Unlike PE resins, PP always needs primary and secondary antioxidants, because it is extremely sensitive to oxidative degradation under environmental conditions, due to its high content of tertiary carbon atoms. PE bag samples (HDPE/LLDPE — around 70/30 in mass) containing a pro-oxidant additive (dye additive from Symphony, at approximately 80 mg cobalt per kg of resin), with 15 μm thickness and 3.66 ± 0.05 g each bag were obtained in supermarkets in São Paulo, Brazil. These bags were painted on one side. In this work, the priority was to obtain films with thicknesses of normal market applications for each resin, using the process of blown film extrusion, which was recommended for all resins used.

2.2. Abiotic degradation

The blown extruded films were inserted into transparent polypropylene envelopes as rectangular samples of approximately 75 × 35 cm. The exposure of the samples to natural weathering was conducted from February, 2007 to February, 2008 on platforms built with an angle of 30° to the ground, facing the equator, in Porto Alegre, RS (Brazil), 30° 02'S, 51° 12'W. The envelopes used to support the samples on the platform for sun exposure were made of polypropylene, and they were prepared by blown film extrusion, with a wall thickness of 50 ± 5 μm, containing anti-blocking and anti-oxidant additives but no light stabiliser. The envelopes were changed monthly to avoid losses in transparency and mechanical properties. The transmittances of the envelopes to visible and ultraviolet radiation were higher than 90% in the 285–800 nm range. The transparencies of the film samples used in this work followed the order: PP >> LLDPE > HDPE >> HDPE/LLDPE blend (opaque, painted). The supermarket bag films were exposed with the side without ink to the sun. The envelopes were opened weekly for several hours of aeration. At regular intervals up to 280 days, the exposed samples were analysed as follows. a) Visual inspection of fragmentation, documented by photography. b) Molar masses were determined by size exclusion chromatography (SEC) in a gel permeation chromatograph model Waters GPC 150C with tri-chlorobenzene as the solvent at a temperature of 140 °C with refraction index detection. c) Changes in chemical structure were monitored through Fourier transform infrared spectroscopy (FTIR) with a Nicolet 470 Nexus instrument. The samples were pressed
into films at 35–70 kPa and 175 °C under nitrogen flow. The content of carbonyl groups, formed by the oxidation of polyolefins, was quantified by a "carbonyl index" [21], obtained by dividing the stretching carbonyl band area (≈ 1718 cm⁻¹) by the area of reference bands. In this work, bands in the near-infrared region (4100–4200 cm⁻¹) were taken as reference. They are due to overtones and combinations of the fundamental C=H stretching and bending vibration bands [22].

d) Crystallinity was monitored using differential scanning calorimetry (DSC; TA Instruments 2910) at a heating rate of 5 °C min⁻¹ over a temperature range from 20 to 150 °C (PEs) or to 200 °C (PP). The second heating run after a previous cycle of heating and cooling (used to destroy thermal histories) was used to determine melting and crystallisation temperatures, and melting enthalpies. The degree of crystallinity was the obtained by dividing the melting enthalpy by the enthalpy of crystallisation (T. Ojeda et al. / Polymer Degradation and Stability 96 (2011) 703–707)

3. Results and discussion

The polymers were rapidly oxidised, as seen by the rapid increase in carbonyl levels (Table 1). PP was strongly oxidised at a much higher rate than those observed for HDPE and LLDPE, making it impossible to carry out analyses with reproducible results after 48 days. The oxidation rates (incorporation of carbonyl groups) of LLDPE were slightly higher than those of HDPE, despite the higher thicknesses of the LLDPE film samples that limit oxygen diffusion. For these three polyolefins, antioxidant additives at the concentrations used here slowed but did not prevent oxidation, even in the case of PP formulated with a synergistic combination of primary and secondary antioxidants. These results indicate the need for light stabilisers and other additives and pigments for the protection of polyolefins exposed to the outside during their service lives. In the case of HDPE and LLDPE, the absence of a primary antioxidant contributed to the similar high levels of degradation found in samples with different concentrations of the secondary antioxidant.

The secondary antioxidant was inefficient without the presence of a primary antioxidant at the ambient temperatures of the test. The pro-oxidant containing HDPE/LLDPE (oxo-biodegradable) sample showed much faster oxidation than the samples of HDPE and LLDPE, indicating that the addition of the pro-oxidant additive was efficient in promoting the oxidation of the polyolefines.

HDPE samples at all three additive concentrations showed a sharp decrease in molar mass during the first 48 days of exposure, with a less pronounced decrease after this period (Table 2). After nine months, the weight average molar masses (Mw) were still over 30,000 g mol⁻¹. Nevertheless, fragmentation occurred after 5–7 months as a result of the low fracture and tear resistance of the material. The HDPE samples at all three additive concentrations presented very similar decreases of molar masses, showing that the antioxidants used here were insufficient to reduce the abiotic degradation. However, the fragmentation of the sample with 300 mg kg⁻¹ occurred about two months later than that of the samples with 0 and 100 mg kg⁻¹.

LLDPE showed a less pronounced decrease in molar mass than HDPE (Table 2), with Mw values higher than 40,000 g mol⁻¹ after nine months of exposure. However, this behaviour may be a consequence of the higher thicknesses of the LLDPE film samples. Some authors reported faster degradation for HDPE [9,26], whereas others reported LLDPE degrading faster [27,28]. Again, the added levels of secondary antioxidants were not sufficient to prevent the collapse of molar masses, with the three evaluated concentrations resulting in similar behaviour. The PP profile was very similar to that of HDPE, with a sharp decrease of molar mass in the first 48 days, decreasing more slowly after this period. However, the PP samples presented lower molar masses than those observed for HDPE and LLDPE after nine months of exposure, with Mw values below 10,000 g mol⁻¹. As already observed for HDPE and LLDPE, PP did not show a marked difference in molar mass between samples with different concentrations of antioxidants. The oxo-biodegradable HDPE/LLDPE blend showed a large drop in molar mass after five months, and the lowest values (~8000 g mol⁻¹) among the tested polyolefins after nine months of natural weathering (Table 2). The molar mass distribution curves for PP after 48 days of exposure narrowed and shifted to molar mass values that were about ten times lower than the initial ones (Fig. 1). This behaviour suggests that chain rupture occurred in both the non-crystalline and crystalline phases. The most likely oxidation sites correlated to the crystalline phase are fold surfaces, loose chain

### Table 1

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<th>Polyoilefin</th>
<th>Additive (mg kg⁻¹)</th>
<th>Exposure time (days)</th>
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<th>161</th>
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<tr>
<td></td>
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<td></td>
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<td>0.000 0.054 nd 0.517</td>
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<td>PP</td>
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<tr>
<td></td>
<td>100 (PA + SA)⁺</td>
<td>0.000 0.310 nd nd</td>
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a SA = Secondary Antioxidant.
b PA + SA = Primary Antioxidant (1 part) + Secondary Antioxidant (2 parts).
c Not determined.

### Table 2

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<tr>
<th>Polyoilefin</th>
<th>Additive (mg kg⁻¹)</th>
<th>Exposure time (days)</th>
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<tr>
<td></td>
<td>100 (PA + SA)⁺</td>
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<tr>
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<td>nd³</td>
<td>183,000 112,000 14000 8300</td>
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</table>

a SA = Secondary Antioxidant.
b PA + SA = Primary Antioxidant (1 part) + Secondary Antioxidant (2 parts).
c Not determined.
ends and interlamellar tie molecules, because the inner crystal is impermeable to oxygen.

The melting and crystallisation temperatures (after thermal history destruction) of PP significantly decreased with exposure time (Fig. 2). The lowering of the melting and crystallisation temperatures results from the increase in crystal defects occurring with oxidative degradation, such as oxygenated groups, double bonds, chain ends and branch sites, which results in smaller crystals with more imperfections. The concentration of impurities can be obtained from Flory’s equation for melting temperature depression [29]. The values obtained for PP ranged from 0 mol% (initial situation supposed) to 7–10 mol% (after 280 days) of defective units (crystalline defects) per sequence of polymer repeating units, representing a significant structural change. Nevertheless, it is important to realise that the Flory equation tends to predict higher-than-actual impurity concentrations.

In spite of the relatively large standard errors, opposing trends in crystallinity behaviour are observed during exposure to natural weathering of PP without antioxidants compared with the HDPE/LLDPE blend with a pro-oxidant additive (Fig. 3). PP showed a decline in degree of crystallinity, while the crystallinity of the blend increased. Rabello and White [30] proposed two phenomena to explain these trends: a) an increase in crystallinity as a result of the decreasing molecular size (and thus increasing chain mobility) dominating in the blend; and b) a decrease of crystallinity as a result of the increasing concentration of chemical impurities dominating in PP. This is in agreement with Guadagno et al. [10], who found an increase in crystalline fraction and crystal size and perfection with progressive degradation for an LLDPE sample.

In tensile tests in films (Fig. 4), PP showed the most rapid loss of mechanical properties due to its extremely high frequency of tertiary carbon atoms, which resulted in a substantial reduction in molar mass accompanied by a significant increase in carbonyl group content. The sample without antioxidants started fragmentation in the second month, while the samples with 100 and 300 mg kg\(^{-1}\) began to disintegrate in the third month. The mechanical strength of these samples was negligible after 48 days of exposure. HDPE also lost its mechanical properties rapidly (Fig. 4). The mechanical strength of its samples fell to zero in about two months of exposure, contributing to the subsequent disintegration. The observed decrease in strength is mainly related to the small fraction of non-crystalline material, which is largely responsible for elastic and plastic deformations, and consequently for the material toughness. It is assumed that fewer tie molecules connect the crystalline

![Fig. 1. Molar mass (g mol\(^{-1}\)) distribution obtained by SEC of the PP samples after 48 days of natural weathering: A) with 0 mg kg\(^{-1}\) antioxidant; B) with 100 mg kg\(^{-1}\) antioxidant; C) with 300 mg kg\(^{-1}\) antioxidant; as well as of D) a sample with 0 mg kg\(^{-1}\) antioxidant, without any exposure.](image1)

![Fig. 2. Second melting (Tm2) and crystallisation (Tc) temperatures from DSC analyses of PP with 0, 100 and 300 mg kg\(^{-1}\) of Irganox B-215 as a function of exposure time.](image2)

![Fig. 3. Degree of crystallinity (from DSC, after thermal history destruction) of PP samples without antioxidant compared to a commercial oxo-biodegradable HDPE/LLDPE sample as a function of exposure time (standard errors indicated by bars).](image3)

![Fig. 4. Strain at rupture from tension tests for HDPE, LLDPE and PP films with 0, 100 and 300 mg kg\(^{-1}\) of antioxidants, compared to a commercial oxo-biodegradable HDPE/LLDPE film as a function of exposure time. HDPE and PP curves are partially overlapping.](image4)
lamellae in HDPE than in LLDPE, because the tie molecules are related to the frequency of branches, which is much lower in HDPE [6,8]. Furthermore, as mentioned before, HDPE films were thinner than the LLDPE films studied here, facilitating the access of oxygen to the interior chains of the HDPE samples, and thus their oxidation. PP and HDPE curves for different contents of antioxidants are partially overlapping. LLDP was the only polymer without cracks or fragmentation after 280 days of exposure, because its mechanical properties declined more slowly than the other polymers tested (Fig. 4). The good retention of the mechanical properties of LLDP was due, besides the high thickness of the films, to the number of tertiary carbon atoms, low enough to avoid significant oxidative attack (as it occurs in PP), but on the other hand high enough to promote the formation of interlamellar tie molecules. Guadagno et al. [10] and Naddeo et al. [14] observed a slow decrease of the mechanical properties of an LLDPE sample, which accelerated after 6–7 months of exposure, followed by rapid increase in carbonyl and unsaturated groups. The loss of mechanical properties by the oxo-biodegradable blend was less rapid than the losses by PP and HDPE (Fig. 4), probably due to the (supposed) higher level of antioxidants used with the blend, and the presence of LLDPE in the blend. Fragmentation was observed after three months, and the mechanical properties were virtually nonexistent by 5.5 months.

This study assesses the degradability of three linear polyolefin samples containing low or zero levels of antioxidant additives and a polyolefin blend containing a pro-oxidant additive, after one year of natural weathering. The results showed that PP and the oxo-bio HDPE/LLDPE blend are rapidly degrading materials, whereas HDPE and LLDPE degrade more slowly, but also significantly in a few months, in the form of film. The main factors influencing the degradability were the frequency of tertiary carbon atoms in the chain and the presence of a pro-oxidant additive.

The abiotic degradability decreased the crystallinity of PP and increased the crystallinity of the oxo-biodegradable HDPE/LLDPE blend. The low or zero concentrations of primary (sterically hindered phenol) and secondary (phosphate) antioxidant additives used in this study had little influence on the abiotic degradation of the polyolefins and PP samples. Reduction of the content of antioxidant additives and/or combination of antioxidant with pro-oxidant additives could increase the abiotic degradability and reduce the pollution caused by these polyolefins. In a forthcoming study, the fragments obtained from the oxidative degradation of the linear polyolefins in this work were subjected to biodegradation.

4. Conclusions

Films of polyolefins with low or zero content of antioxidant additives degrade severely in less than one year of exposure to natural weathering. The oxidative degradation results in substantial reduction in molar mass accompanied by a significant increase in content of carbonyl groups, having as a consequence loss of mechanical properties. PP and oxo-bio HDPE/LLDPE blend degrade very rapidly as film, whereas HDPE and LLDPE degrade more slowly, but significantly in a few months. The main factors influencing the degradability were the frequency of tertiary carbon atoms in the polymer chain and the presence of a pro-oxidant additive. The primary (sterically hindered phenol) and secondary (phosphate) antioxidant additives added to PP slow but do not prevent rapid photo-oxidative degradation at the concentrations used here. In HDPE and LLDPE, the secondary antioxidant additives have little influence on the rate of abiotic degradation at the concentrations tested here. During exposure to natural weathering, PP shows decline in degree of crystallinity after thermal history destruction, whereas the HDPE/LLDPE oxo-biodegradable blend tested here shows increase in crystallinity.

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