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Correlating different techniques in the thermooxidative degradation monitoring of high-density polyethylene containing pro-degradant and antioxidants

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ABSTRACT

Different techniques were used to assess the effect of a primary and a secondary antioxidant, separately, and in combination with a pro-degradant (manganese stearate) on the thermooxidative abiotic degradation of high-density polyethylene (HDPE). The parameters measured over time at three temperatures (60, 70 and 80 °C) were variation in carbonyl index (CI), by means of infrared spectroscopy; reduction in tensile strain at break, by means of mechanical testing; reduction in molar mass distribution by means of size exclusion chromatography (SEC). Regardless of the presence of primary or secondary antioxidants, the same levels of degradation were attained. However, contrary to the secondary antioxidant, the primary antioxidant significantly increased induction time of HDPE oxidative degradation processes, evidenced by the shift in the “CI versus time” curve and by the considerably longer time for the strain at break to reach minimal values. Increase in thermooxidation temperature reduced induction time significantly.

1. Introduction

High-density polyethylene (HDPE) is widely used in the manufacture of many products, including plastic bags. These single-use plastics have a relatively small shelf life and, after use, are frequently disposed of in the environment, both terrestrial and marine [1–3]. Pro-degrading additives are commonly added to HDPE to accelerate the oxidative abiotic degradation and thereby promote biodegradation of the material after its disposal [4–12]. However, the pro-degradant should not impair the physical, chemical and mechanical properties of the product during its service life. Using these additives creates a conflict between optimum product performance during service life and efficiency of the biodegradation process after disposal. Nevertheless, a balance between these opposite forces can be achieved with the use of antioxidants, which, when properly formulated, can guarantee the performance of the product during its service life without interfering with the oxidative abiotic degradation of the polymer after product disposal [4,13–19]. Hence, the main function of combining antioxidant and pro-degradant is to delay, but not cancel the abiotic degradation process of polymers [20–23].

The conflict between antioxidant and pro-degradant additives occurs because the chemical species involved in the respective reaction

mechanisms are the same. The action of pro-degradants, based on transition metals, is satisfactorily explained by the Haber-Weiss reactions and mechanisms, in which the main chemical species is hydroperoxide. On the other hand, primary antioxidants are hydrogen donors, mainly to peroxy radicals to form hydroperoxides. Hence, the formation of new alkyl macroradicals is reduced and, consequently, HDPE degradation is delayed. Secondary antioxidants decompose hydroperoxide into more stable species, such as alcohols, through redox reactions. Thus, both additives (metallic salts and secondary antioxidants) act on the hydroperoxide radical, but the secondary antioxidant stabilizes the auto-catalytic oxidation cycle of HDPE, while the metallic salts promote the formation of new peroxy radicals, intensifying the HDPE degradation reactions [24–31].

The addition of metal salts (Fe, Mn and Co), at levels considered residual, may accelerate the thermo- and photooxidation processes of the different polyethylene (PE) types [5,30–42]. Due to chemical and morphological characteristics, the different types of PE present relatively different susceptibilities to the oxidative degradation processes, e.g., studies have shown that LDPE and LLDPE are more susceptible to thermooxidative degradation than HDPE [43–45].

Regarding the behavior of the transition metals in the thermo-oxidation of PE, Co and Mn presented approximately the same pro-

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degrading performance, but Fe presented a significantly lower performance, whereas in photooxidation the pro-degrading performance of Fe was very similar to that of Co and Mn [39,46,47]. According to Focke et al. [20] the catalytic effect on the photooxidation of LDPE can be reduced with the addition of relatively high concentrations of secondary antioxidants associated with a UV stabilizer, such as sterically hindered amines (HALS). The addition of primary antioxidants was, however, less effective in minimizing the effects of photooxidation of LDPE. When degradation was conducted under thermooxidation, the addition of primary antioxidant in both Fe-based and Mn-based pro-degrading systems and the increase in their concentrations increased the induction times for degradation [20,22,48].

Antunes et al. [25] studied the influence of manganese stearate concentration (pro-degradant) on the thermooxidative degradation of HDPE at three different temperatures (60, 70 and 80 °C), and the carbonyl index results showed that Mn concentration does not significantly affect the maximum degradation levels of the polymer. However, the results indicate that the time to reach the maximum degradation levels is dependent on Mn concentration.

This study assesses the influence of primary and secondary antioxidants on the thermooxidative degradation of HDPE containing pro-degradant manganese stearate (Mn), at three temperatures (60, 70 and 80 °C). Degradation was monitored by means of variations in carbonyl index (CI) using infrared spectroscopy, molar mass distributions using SEC, as well as tensile strain at break using mechanical testing. The aim of this study was to evaluate the interaction between antioxidant and pro-degradant in the thermooxidation of HDPE, and propose formulations that guarantee the service life of HDPE products without impairing the purpose of the pro-degradant.

2. Experimental

2.1. Materials

The HDPE (GM9450F) used in this study was supplied by Braskem, obtained through polymerization with Ziegler catalysts, with bimodal molar mass distribution, melt flow index (ASTM D1238) of 0.33 g/10min (190 °C, 5 kg) and density of 0.952 g/cm³. Manganese stearate (pro-degradant) was purchased from Rhett Comércio Exterior e Logística, (CAS 3353-05-7), molecular formula C₃₆H₇₀O₄Mn, purity 99.99%, melt temperature between 100 and 110 °C and particle size of 200 mesh. The primary and secondary antioxidants were Songnox 1010 (based on sterically hindered phenols) and Songnox 1680 (based on phosphites), respectively, supplied by Songwon.

2.2. Methods

2.2.1. Preparation of the formulations and manufacture of the specimens

To improve distribution of the additives in the PE films, formulations have been prepared in two extrusion steps. First, three HDPE concentrates in the form of pellets were prepared, denominated Con.1, Con.2, and Con.3. All contained 5000 ppm Mn, however Con.2 also contained 12500 ppm primary antioxidant and Con.3 12500 ppm secondary antioxidant, i.e., Con.1: 5000 ppm Mn; Con.2: 5000 ppm Mn + 12500 ppm pAO; Con.3: 5000 ppm Mn + 12500 ppm sAO. In the second stage, these concentrates were used to prepare flat films containing 200 ppm Mn (HDPE/200Mn); 200 ppm Mn plus 500 ppm

primary antioxidant (HDPE/200Mn/pAO); and 200 ppm Mn plus 500 ppm secondary antioxidant (HDPE/200Mn/sAO). Table 1 lists the nominal and experimental compositions, obtained via X-ray fluorescence in a FISCHERSCOPE[®] X-RAY XDV[®]-SDD instrument by Fischer do Brasil.

All extrusion processes were carried out in a co-rotating twin-screw extruder (MP19 B&P Process Equipment and Systems), with screw diameter of 19 mm and L/D = 25, and exchangeable dies that allowed changing dies for pellet production to flat film production, used in the first and second stages, respectively. The temperature profile used in both stages was 170 °C, 175 °C, 180 °C and 185 °C; and die temperature 195 °C. Flat films produced in the second stage had average thickness of 45 ± 7 µm.

2.2.2. Thermooxidative abiotic degradation

HDPE/200Mn, HDPE/200Mn/pAO and HDPE/200Mn/sAO films were subjected to accelerated thermooxidative aging in air circulation ovens at three different temperatures (60, 70 and 80 °C). The consequences of these thermal treatments on film degradation were monitored by three analysis techniques at different predetermined time intervals for each assay type. Degradation monitoring was conducted in a way that enabled assessment of the formation of degradation products (functional carbonyl groups) by infrared spectroscopy (FTIR); the variation in molar mass by size exclusion chromatography (SEC); and tensile tests to assess mechanical properties.

2.2.3. Infrared spectroscopy (FTIR)

Films were analyzed in triplicate by absorbance spectra in the region between 4000 and 400 cm⁻¹, resolution of 2 cm⁻¹ and 64 scans, in a Varian 640-IR Fourier Transform Infrared Spectrometer from Agilent Technologies. The carbonyl index (CI) was calculated from the ratio between the absorptions at 1713 cm⁻¹ and 730 cm⁻¹ as reference. The former is attributed to the stretching vibration of the ketone C=O bond and the latter to the concerted rocking vibrational mode of all CH₂ groups, when four or more CH₂ groups are in a chain [49].

2.2.4. Mechanical testing

The mechanical property strain at break was assessed by means of tensile tests performed in an Instron 5569 universal tester, in accordance with ASTM D882, with distance between grips of 50 mm and testing speed of 500 mm/min. Specimen width and thickness were 25.4 mm and 45 ± 7 mm, respectively.

It should be mentioned that strain at break is used in polymer degradation because of the great sensitivity of this property to any structural change. At very high molar masses such as that of HDPE, tensile strength and elastic modulus are significantly affected only when there are very significant variations in molar mass.

2.2.5. Size exclusion chromatography (SEC)

Molar mass analyses were performed at 135 °C in a high temperature Viscotek HT-GPC size exclusion chromatograph from Malvern Panalytical with main and auxiliary pump flows of 1 and 0.5 mL/min, respectively. Shodex HT-806M columns were used, with exclusion limit of 20,000,000 g/mol (permeation range between about 500 g/mol and 10,000,000 g/mol). The samples were solubilized at 140 °C for 2 h in 1,2,4-trichlorobenzene (TCB) solvent pre-stabilized with 1% 2,6-di-tert-

Table 1

Experimental compositions, determined by X-ray fluorescence.

Formulation	Primary antioxidant (ppm)	Secondary antioxidant (ppm)	Mn Nominal (ppm)	Mn Experimental (ppm)	Fe Experimental (ppm)
HDPE/200Mn	–	–	200	227.9	1.31
HDPE/200Mn/pAO	500	–	200	193.6	–
HDPE/200Mn/sAO	–	500	200	185.6	1.76

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