



EVALUATION OF THE DEGRADATION PROCESS OF POLYETHYLENE BY DILUTE SOLUTION VISCOSITY

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Abstract

The evaluation of the polymer degradation process is of great importance to predict the lifetime of artifacts produced from these materials. Numerous techniques and methodologies can be used to analyze the effects of chemical reactions on the properties of interest of macromolecules during aging, many of them costly and complex. In this context, the evaluation of the variation of the average viscosimetric molar mass by viscosimetry can be a simple and economical technique. In this work, viscosimetry was used to determine the variation of the molar mass of polyethylene in tubular HDPE/LDPE films subjected to accelerated aging in a UV chamber, which leads to polyolefin photooxidation, with production of oxygenated fragments. The reduction of the average viscosimetric molar mass was compatible with the appearance of functional groups, observed in FTIR analysis, characteristic of PE photooxidation, suggesting that the technique is possible in the evaluation of the degradation process.

Keywords: *viscosimetry, molar mass, polyethylene, photooxidation, FTIR.*

Introduction

The evaluation of the degradation process of polymers becomes necessary in the indirect determination of the lifetime of artifacts produced from this class of materials. The term "degradation" refers to any irreversible chemical reaction that alters the quality of interest of a polymeric material or polymeric compound, such as flexibility, visual aspects and mechanical strength [1]. The reactions, such as main chain scission, crosslinking reactions, and modification and/or appearance of chemical groups present, are caused by the various types of attack to which macromolecules are subjected during processing and throughout their life of use and disposal [2]. The techniques for the characterization of polymers subjected to different degradation processes are diverse, such as SEC- Size Exclusion Chromatography, which allows determining the variation of the molar mass of the polymer; TGA - Thermogravimetric Analysis, which allows evaluating the variation of the thermal stability of the degraded polymer; FTIR - Fourier Transform Infrared Spectroscopy, which allows determining the chemical changes suffered by macromolecules with insertion or removal of functional groups [3]. For a wide variety of polymers, the molar mass variation can be evaluated by dilute solution viscosimetry (DSV), a technique that involves little investment in equipment and can be easily performed [4]. Polyethylene (PE) is one of the most used thermoplastic polymers in the world, especially in the production of plastic packaging, such as supermarket bags, and whose photooxidative degradation process is well known [5], leading to the

production, among other products, of fragments containing carbonyl ($>C=O$) and terminal vinyl groups ($>C=CH_2$).

The objective of this work was to evaluate whether the dilute solution viscosity can be a simple and economical technique in the evaluation of the degradation process of PE in films obtained by tubular extrusion from a mixture of High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE), in mass percentages of 90% and 10%, respectively, when submitted to accelerated aging in a UV chambre, and also to compare it with the results obtained by FTIR analysis.

Experimental

Materials

Two polymers were used: HDPE (HE-150) and LDPE (EB-853/72), both produced by Braskem S.A; Decalin, produced by Neon, with a purity percentage above 99% and Cannon-Fenske glass viscometer (number 50), with an internal diameter of 0.44 mm, were used.

Processing by tubular extrusion

The HDPE and LDPE polymers, mixed in mass percentages of 90 and 10%, respectively, were processed in a single-core extruder, model ES 35-FR (Seibt), producing tubular film with an average thickness of 30 μ m.

Accelerated aging by UV radiation incidence

The film was exposed to 96 hours of UVA/UVB radiation in a Comexin (C-UC) chamber, according to ASTM G-154 standards.

Characterization

Dilute solution viscosimetry for determination of the molar mass of polyethylene

To determine the average viscosimetric molar mass (\overline{Mv}), five polyethylene solutions were prepared at concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0 g/dL for each film analyzed, using decalin as solvent. The dissolution of the polymer took place under stirring at 140°C for one hour. The procedures were carried out according to ASTM D445 and ASTM D446. The analyses were performed with the viscometer immersed in a thermostatic silicone oil bath of the brand SOLAB, Model SL 150, at 135°C [6], varying $\pm 0.1^\circ\text{C}$. First, the reduced specific viscosity (η_{esp}/C) and inherent viscosity ($\ln \eta_{\text{rel}}/C$) of each of the solutions were determined. Plotting the graphs of such viscosities, the intrinsic viscosity of the polyethylene used in the preparation of the solution was determined, from the extrapolation of the straight lines obtained by linear regression when the concentration tends to 0g/dL. The values found for the two straight lines tend to the same value and, for this reason, the average of them was used as intrinsic viscosity ($[\eta]$).

To determine the average viscosimetric molar mass of the polyethylene present in the samples, the Mark-Houwink-Sakurada equation was used, which relates the intrinsic viscosity and (\overline{Mv}), as presented in Eq. 1,

$$[\eta] = k. (\overline{Mv})^a \quad (1)$$

in which, $[\eta]$ is intrinsic viscosity found for that of polyethylene; k and a are the constants for the polymer-solvent system that for polyethylene-decalin. Their values are 62×10^{-5} dL/g and 0.7, respectively [6]; and (\overline{Mv}) is the average viscosimetric molar mass.

Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) analyses were performed in Perkin Elmer equipment, Frontier model. All films were evaluated in ATR (Attenuated Total Reflectance) mode. The spectra were obtained at room temperature of 25°C, air humidity controlled at 30% in absorption region ranging from 650 to 4000 cm⁻¹, with 10 scans for each sample.

The carbonyl functional group, produced in the photooxidation of polyethylene, has absorption of infrared radiation in different bands, dependent on the organic function, which are: carboxylic acids (1712 cm⁻¹), ketones (1723 cm⁻¹), aldehydes (1730 cm⁻¹) and lactones (1780 cm⁻¹) [7, 8]. From the absorption, it is possible to calculate the oxidation level of the polymeric material through the carbonyl index, CI, using Eq. 2:

$$CI = \frac{A_1}{A_2} \quad (2)$$

in which A₁ is the absorption area of the band between 1700 and 1780 cm⁻¹, referring to the peaks of the carbonyl-containing groups, and A₂ is the area of the band peaking at 1463 cm⁻¹ (1450 - 1468 cm⁻¹), considered to be one of the polyethylene bands that is invariant [8].

In addition to the carbonyl index, the terminal vinyl index, VI, due to the appearance of unsaturations, was determined using Eq. 3:

$$VI = \frac{A_3}{A_2} \quad (3)$$

where A₃ is the absorption area of the band at 908 cm⁻¹ (900-916 cm⁻¹), referring to vinyl groups [8], and A₂ is the area of the band at 1463 cm⁻¹, which is relatively constant for polyethylene [9].

Results and Discussion

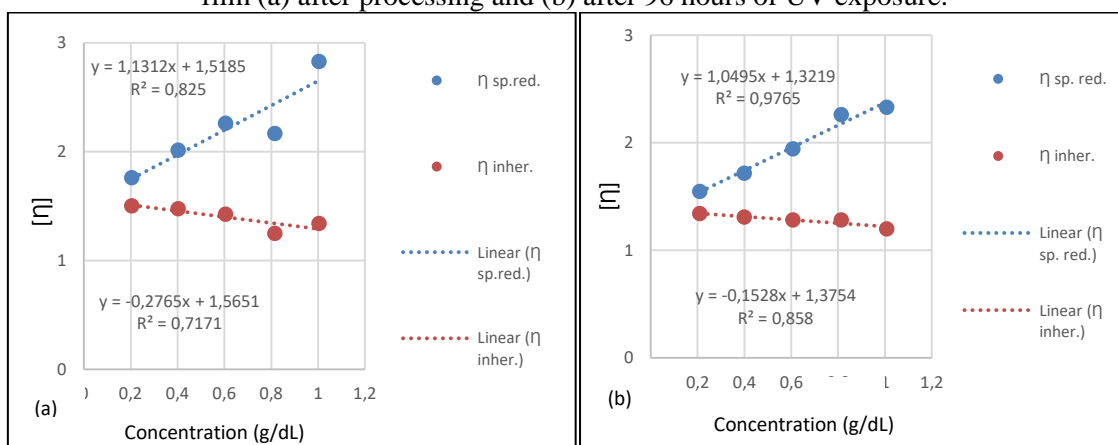
The results obtained in the viscosimetric analyses of the films after the extrusion process and after accelerated aging in UV chamber are presented in Table 1. The average solvent (decalin) flow time was 200.51 seconds (s) for the post-processing film, and 202.67 seconds (s) for the film aged in UV chamber for 96 hours.

Table 1 – Data obtained from the viscosimetric analysis of the HDPE/LDPE film after processing by tubular extrusion and after 96 hours of exposure to UV radiation.

Exposure time to UV radiation (h)	Concentration (g/dL)	Flow time (s)	η_{relative}	η_{specific}	$\eta_{\text{sp.red}}$ (dL/g)	$\eta_{\text{inher.}}$ (dL/g)
0 (Post Processing)	0.2056	273.06	1.3618	0.3618	1.7599	1.5021
	0.4040	363.62	1.8134	0.8135	2.0135	1.4734
	0.6064	475.23	2.3701	1.3701	2.2594	1.4230
	0.8164	555.30	2.7694	1.7694	2.1673	1.2477
	1.0052	770.58	3.8431	2.8431	2.8340	1.3393
96	0.2092	268.28	1.3237	0.3237	1.5475	1.3406
	0.3992	341.63	1.6856	0.6856	1.7175	1.3079
	0.6080	441.97	2.1807	1.1807	1.9420	1.2823
	0.8140	575.80	2.8411	1.8411	2.2617	1.2828
	1.0084	678.86	3.3496	2.3496	2.3300	1.1988

Fig. 1 shows the plotted graphs for the reduced specific viscosity/inherent viscosity versus concentration, from which the intrinsic viscosities of polyethylene were determined for subsequent calculation of the average viscosimetric molar mass (\bar{M}_v).

Figure 1 - Reduced specific viscosity/inherent viscosity versus concentration for HDPE/LDPE film (a) after processing and (b) after 96 hours of UV exposure.



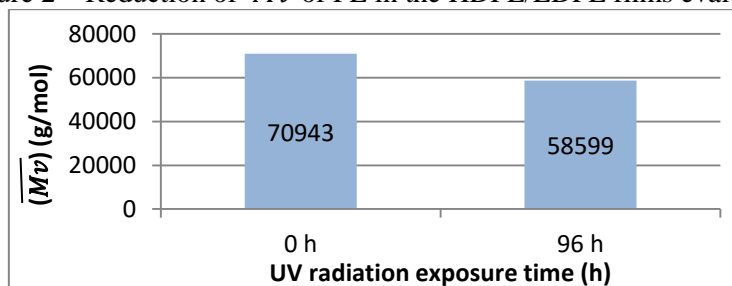
From Eq. 1 the average viscosimetric molar masses (\overline{Mv}) of the polyethylene were calculated. The results are presented in Table 2.

Table 2 - Average viscosimetric molar mass of the PE in the films evaluated.

HDPE/LDPE film	Intrinsic Viscosity (dL/g)	\overline{Mv} (g/mol)
Post Processing	$(1.5185 + 1.5651)/2 = 1.5418$	70.943
96 h UV exposure	$(1.3219 + 1.3754)/2 = 1.3487$	58.599

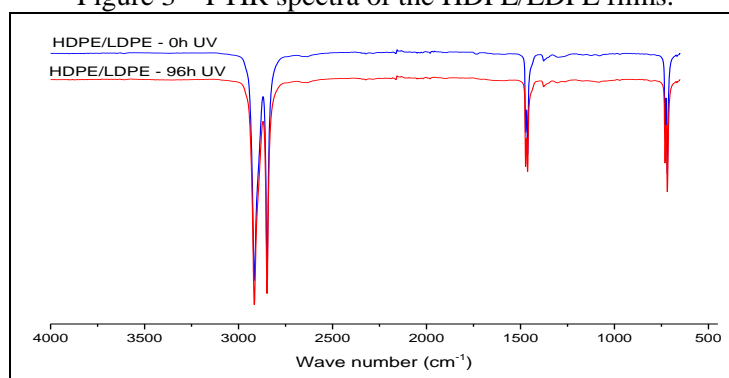
The reduction of \overline{Mv} , compatible with photooxidation of polyethylene, is graphically shown in Fig. 2.

Figure 2 – Reduction of \overline{Mv} of PE in the HDPE/LDPE films evaluated.



The FTIR spectra of the HDPE/LDPE films after processing and after 96 hours of exposure to accelerated aging are shown in Fig. 3.

Figure 3 – FTIR spectra of the HDPE/LDPE films.



The values of CI and VI, calculated from Eq. 2 and 3, are presented in Table 3.

Table 3 – CI and VI values for the HDPE/LDPE films.

HDPE/LDPE film	CI	VI
Post-processing	0.1385	0.04789
96 h UV exposure	0.2041	0.05625

The increased CI and VI confirm the degradation of PE in the films analyzed. since they provide evidence of the emergence of oxygenated (containing carbonyl groups/ $>C=O$) and unsaturated (containing terminal vinyl groups/ $>C=CH_2$) polymer fragments, which justifies the reduction of \overline{M}_v , since the PE macromolecules have undergone chain scission with unsaturation formation or insertion of functional groups containing carbonyl.

Conclusions

Dilute solution viscosimetry has been shown to be a simple and accessible method in the evaluation of PE degradation, since the decrease in the average viscosimetric molar mass occurred with increasing CI and VI after submission of the HDPE/LDPE films to photooxidation by UV incidence, as expected.

Acknowledgements

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