

Thermal oxidation of metallocene ethylene-1-olefin copolymer films during one year oven aging

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A B S T R A C T

Metallocene ethylene homopolymer, ethylene-1-hexene and ethylene-1-octadecene copolymer films were characterized and analysed during their aging in a forced draft oven at 60 °C and compared to commercial polymers (HDPE and LDPE). Each polymer is essentially different in its structure, and the variables used in the present study are comonomer size and content in the main linear backbone polymer. The polymers were characterized initially using GPC, DSC, FTIR, and tensile tests. Later, at different time intervals, samples were removed from the oven and characterized using FTIR and GPC in order to detect changes in chemical structure, size, and molecular weight distribution due to thermo-oxidative aging. At the end of aging, films were subjected to tensile tests to quantify the effect of time on their useful life. As a qualitative reference parameter, the carbonyl index, the ratio of the infrared absorbance of the CO stretching band at 1715 cm⁻¹ and the absorbance of a reference band at 718 cm⁻¹, was determined. Kinetic thermo-oxidation is related to comonomer size and content in the main backbone polymer. As comonomer size decreases or comonomer content increases, degradation rate increases. The scission factor (*S*) and carbonyl index (*CI*) graphs of each material show a slope increase which is related to the autocatalytic rate of oxidation.

Keywords:

Thermal oxidation
Degradation
Metallocene
Polyethylene
1-Olefin
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1. Introduction

The advent of metallocene catalysts has made possible the production of various tailor-made polymers [1] to satisfy industrial and end user requirements. This is due to the fact that metallocene catalysts are single-site catalysts that lead to narrower molecular weight distribution and more uniform structure than traditional Ziegler–Natta catalysts. The use of this new family of catalysts has allowed the synthesis of polyolefins with added value with respect to traditional commodity production of polyethylene (HDPE and LDPE). In particular, the copolymerization of ethylene with higher α -olefins has given rise to linear low-density polyethylene (LLDPE), yielding copolymers with homogenous comonomer content [2,3].

Metallocene linear low-density polyethylenes (mLLDPE) are characterized by their high resistance and tenacity compared to other thermoplastics. They are used mostly for packaging and in greenhouses (with mulching films as the new trend), standing out because of their lightness, inertness and durability. Their accumulation, however, causes environmental pollution.

One property of all these materials is their resistance to thermal degradation, a characteristic that determines possible material applications. Therefore, the study of their degradation is an area of continuous development [4–7]. Thermal degradation of polymers can be carried out in an inert environment (pyrolysis) or in an oxidative environment (air), and it is described by a random scission mechanism which does not follow first order degradation kinetics [7]. Reich and Stivala [8] describe how initiators (alkyl and peroxy radicals) are formed during the degradation in an autocatalytic degradation reaction, scissioning the macromolecule into fragments of lower molecular weight, and thereby affecting the material's mechanical properties [9]. Therefore, the need to study the influence of 1-olefin comonomer type and content in the thermal oxidation of metallocene ethylene-1-olefin copolymer films arises naturally.

2. Experimental

2.1. Reagents, materials and methods

rac-Ethylenebis(indenyl)zirconiumdichloride (Et(Ind)₂ZrCl₂) catalyst from Crompton Corporation (Bergkamen, Germany) and methylaluminoxane co-catalyst (MAO) at 10 vol% in toluene from

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Witco GMBH (Bergkamen, Germany) were used for the polymerisation reaction. Ethylene >99.99% purity from AGA S.A. (Chile) was purified by passing the gas through two columns of 4 Å molecular sieves to remove traces of water, oxygen and sulphur. Toluene solvent from J.T. Baker (Xalostoc, Mexico) and comonomers 1-hexene and 1-octadecene from Aldrich (Milwaukee, WI, USA) were purified by refluxing for 3 h over metallic sodium and then distilled. Catalyst and co-catalyst were handled under a strong nitrogen stream.

The commercial polymers used were high-density polyethylene GF4960 (Petroquímica Ipiranga, Brazil) and low-density polyethylene Trithene JX7300 (Petroquímica Triunfo, Brazil) in pellet form. Synthesized ethylene homopolymer and ethylene-1-hexene and ethylene-1-octadecene metallocene copolymers were obtained as powder at the Laboratorio de Ingeniería de Polímeros, Universidad de Chile.

2.2. Polymerisation

Ethylene homopolymer and ethylene-1-olefin copolymers with different comonomer size (1-hexene and 1-octadecene) and content were synthesized by coordination polymerisation using the metallocene catalyst *rac*-ethylenebis(indenyl)zirconium dichloride (Et(Ind)₂ZrCl₂) and methylaluminoxane (MAO) as co-catalyst.

The polymerisation was carried out in a 1 L Parr reactor previously heated to 150 °C for 2 h to eliminate traces of water. Once in operation, nitrogen purges were made to eliminate air from the reactor. Toluene (500 mL) was added to the reactor in a nitrogen environment and reactor was warmed to 60 °C, adding MAO co-catalyst in an Al/Zr ratio of 6×10^3 under a flow of nitrogen, with constant stirring at 500 rpm. Once the nitrogen flow was stopped, ethylene (2 bar pressure) and comonomer in the case of copolymerization were introduced, adding metallocene catalyst at a concentration of 3.5×10^{-7} mol/L, keeping the reaction 30 min. The polymerisation reactions were terminated by addition of a 2 vol% HCl/CH₃OH solution. The synthesized polymers were precipitated from the reaction medium, washed several times with cold ethanol, and dried for one day at room temperature.

2.3. Polymer characterization

The synthesized and the commercial polymers were characterized by GPC, NMR, FTIR, DSC and tensile tests.

Molar comonomer content (%) in the main copolymer backbone was measured by ¹³C NMR at 120 °C on a Varian Inova XLS 300 spectrometer at 75 MHz. Samples were prepared by dissolving the polymer in *o*-dichlorobenzene and benzene-*d*₆ (20% v/v) in 5 mm tubes. Chromium(III) tris(acetylacetonate) was used as paramagnetic substance to reduce relaxation times. The results are shown in Table 1. The nomenclature used to identify the metallocene homopolymer and copolymers are “mPE”, “mPE-H#” and “mPE-O#”, where mPE refers to linear metallocene ethylene homopolymer, mPE-H refers to metallocene ethylene-1-hexene copolymers, mPE-O to ethylene-1-octadecene copolymers, and # is

Table 1
Properties of commercial and synthesized polymers

Film code	Comonomer (%)	Melting (°C)	$M_w \times 10^{-3}$ (kg/kmol)	$M_n \times 10^{-3}$ (kg/kmol)	M_w/M_n	Crystallinity (%)	D (g/cc)
HDPE	–	136	128	21	6.0	74	0.94
LDPE	–	110	46	13	3.6	45	0.92
mPE	–	136	116	64	1.8	68	0.94
mPE-H7.8	7.8	88	69	41	1.7	6	0.87
mPE-H14.1	14.1	69	67	41	1.7	3	0.84
mPE-O7.1	7.1	92	95	55	1.7	4	0.86
mPE-O9.2	9.2	82	75	45	1.7	2	0.85

the molar comonomer content (%) in the main copolymer backbone.

Molecular weight was measured by gel permeation chromatography (GPC) on a Waters Alliance 2000 apparatus with a differential refractive index detector. The mobile phase was 1,2,4-trichlorobenzene to which 2,6-di-*tert*-butyl-4-methyl phenol (BHT) antioxidant (0.1%) was added. The analytical flow rate was 1 mL/min and the temperature was 140 °C. The values obtained were referenced to a universal curve with the following viscometric parameters $K = 3.95 \times 10^{-4}$ and $\alpha = 0.726$ (polyethylene).

Melting temperature and melting heat were measured by differential scanning calorimetry on a TA Instruments DSC 2920 apparatus connected to a cooling system calibrated with different standards. The heating/cooling ramp rates were 10 °C/min in an inert atmosphere of N₂ flowing at 80 mL/min from ambient temperature to 180 °C. To erase the thermal history of the material, first a heating ramp rate of 20 °C/min was used, followed by a cooling ramp and a consecutive heating ramp of 10 °C/min each. The data gathered are from the second and third ramp. A value of 290 J/g has been taken as the enthalpy of a perfect polyethylene crystal in order to calculate crystallinities from the melting enthalpies.

Chemical structures were determined from the FTIR spectra on a Bruker Vector 22 spectrometer. The spectra were accumulated as four scans between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹.

Polymer densities were measured according to ASTM standard D 792 (Density and Specific Gravity of Plastics by Displacement).

Tensile strength and Young's modulus were obtained on an HP D500 tensile stress dynamometer. Five samples were tested for each material (ca. 0.3 mm thick, 5 mm wide, 80 mm long, and 30 mm grip-to-grip length) at 23 °C, 32% relative humidity, and a displacement rate of 50 mm/min. Young's modulus was obtained from the slope of the stress-strain curve (linear curve zone), and tensile strength was obtained at the yield point where the material suffers permanent strain once the stress is removed. The method of tangents for determining stress, where the tangents to the initial and final parts of the load-elongation curve intersect, was used in those cases in which the yield point could not be distinguished [10].

2.4. Polymer thermal oxidation

Commercial and synthesized polymer films were aged in a forced draft oven (MEMMERT, model ULM400, vol. 53 L) at 60 °C with ca. 3 m/s air velocity near to the fan centre measured by an Airflow anemometer model LCA 6000.

Pellets and powders were placed in a 10 cm × 10 cm × 0.1 mm steel strap frame between two 0.4 mm thick Teflon sheets, and compression moulded for 3 min at 170 °C and 40 bar in a hydraulic press (Industria HP). Two films of each polymer to be aged were placed separately in the oven so that a homogeneous air stream would go through them.

One film was monitored during aging, cutting some pieces for characterization by FTIR and GPC. The other was tested mechanically for tensile strength once the aging was finished.

In the FTIR method the carbonyl group peak was measured between 1715 and 1720 cm⁻¹ [11]. As a qualitative parameter, the carbonyl index was determined as the ratio between the CO stretching band peak intensity at 1715 cm⁻¹ and the peak intensity of a reference band at 718 cm⁻¹, corresponding to methylene rocking vibrations. The oxidation rates of the materials were compared from the slope of the carbonyl index vs. aging time graphs.

For the GPC determination, weight-average molecular weight (M_w) and number-average molecular weight (M_n) were measured to account for size evolution and polymer chain distribution.

Table 2

Mechanical parameters obtained from tensile tests of polymer films without (0 h) and with aging (9136 h) in a forced draft oven at 60 °C (average values)

Film code	0 (h)				9136 (h)			
	E (MPa)	σ_{yield} (MPa)	ϵ_{break} (%)	σ_{break} (MPa)	E (MPa)	σ_{yield} (MPa)	ϵ_{break} (%)	σ_{break} (MPa)
HDPE	1078	32	300	24	971	30	230	22
LDPE	173	8	103	7	203	8	64	7
mPE	648	26	596	27	x	x	x	x
mPE-H7.8	41	3	959	28	38	3	141	5
mPE-H14.1	7	1	1407	14	4	1	432	4
mPE-O7.1	48	3	708	21	44	3	337	10
mPE-O9.2	27	2	686	15	19	2	446	9

x represents no data exist because of material's fragility.

3. Results and discussions

3.1. Metallocene synthesis

Table 1 presents the properties of commercial and synthesized polymers where metallocene polymers exhibit a lower polydispersity of ca. 2, which means they have a narrower molecular weight distribution compared to the commercial polymers. In the literature it is known that comonomer (branch) size and content have an influence on the material's crystallization, melting temperature and crystallinity [12]. This is shown in our results. It is seen that for a given comonomer size, as its content in the linear backbone chain (mol%) increases, the polymer's melting temperature decreases. Branching inserted into the linear polymer's backbone inhibits the sliding movement of the chain to form an ideal folded structure (chain folding), producing a shorter fold length than that with no branches, and therefore decreasing crystal size (lamellar thickness). Melting temperature and lamellar crystal thickness are correlated by the Gibbs–Thomson equation. Due to the decrease in lamellar crystal thickness, there is an increase of the amorphous content in the polymer.

3.2. Mechanical tensile parameters

According to Li Pi Shan et al. [13,14], tensile strength at yield (σ_{yield}) increases when the material's percentage crystallinity increases. In Table 2 it is seen that the tensile strength at yield values of the two most crystalline polymers (HDPE and mPE) is higher than that of the more amorphous polymers (LDPE, mPE-H and mPE-O). Furthermore, and according to the authors, the increase in tensile strength at yield carries with it an increase in the material's rigidity. This would explain the trend observed with Young's modulus, with the more crystalline polymers (HDPE and mPE) having higher elastic modulus than the amorphous ones (LDPE, mPE-H and mPE-O). In general, tensile strength at break follows the same trend. Therefore, a material with low crystallinity

Table 3

Weight-average molecular weight (M_w) of commercial and synthesized films aged in a forced draft oven at 60 °C

Aged (h)	$M_w \times 10^{-3}$ (kg/kmol)						
	HDPE	LDPE	mPE	mPE-H7.8	mPE-H14.1	mPE-O7.1	mPE-O9.2
0	128	46	116	69	67	95	75
756	122	45	57	69	60	82	75
1432	126	49	54	69	60	74	65
1649	130	48	53	68	59	82	73
1839	126	46	39	67	59	83	72
2435	124	47	42	62	58	83	71
4888	141	47	26	62	48	79	60
9136	132	24	22	21	10	42	26

Table 4

Number-average molecular weight (M_n) of commercial and synthesized films aged in a forced draft oven at 60 °C

Aged (h)	$M_n \times 10^{-3}$ (kg/kmol)						
	HDPE	LDPE	mPE	mPE-H7.8	mPE-H14.1	mPE-O7.1	mPE-O9.2
0	21	13	64	41	41	55	45
756	22	13	34	41	33	42	47
1432	23	16	28	42	36	43	39
1649	25	15	26	40	35	46	43
1839	22	13	23	40	36	49	44
2435	19	15	21	37	35	47	42
4888	26	12	13	35	27	48	35
9136	20	8	11	11	5	22	12

requires a low stress to become irreversibly strained. With respect to elongation, it is known that slippage and disentanglement would allow amorphous polymers to be deformed [13]. It is seen that when the amorphous proportion in the polymer increases, the percentage of elongation also increases. However, lower molecular weights cannot handle large strain deformation properties. This is the case when elongation at break value of LDPE is examined. Also in Table 2, the decreased elongation observed after the polymers have been aged occurs because degradation takes place mostly in the amorphous phase [14], scissioning polymer chains which then lack the capacity to elongate when the polymers undergo mechanical deformation. It is also noticed that copolymers of higher comonomer content aged 9136 h have higher elongation at break than the lower ones. It can be explained from the standpoint of tie molecules (TMs). These TMs in alpha olefin copolymers are co-unit exclusion that disturbs the mechanism of regular chain folding which allow the crystallization process to occur, and so when the comonomer content increase the amorphous fraction increase allowing longer deformation. In molecular topology of semicrystalline polymers the TMs are molecular interconnections which are active elements for the stress transfer [15] because they allow the sample to carry large stresses to prevent higher strains [16]. The same author establishes that as comonomer content increase the concentration of TMs increase and then their tertiary hydrogen concentration in the amorphous phase. Due to the fact that tertiary hydrogen atom possess lower dissociation energy than other hydrogen atoms thus making it easier to convert to free radicals [17], any molecular scission produced by the effect of

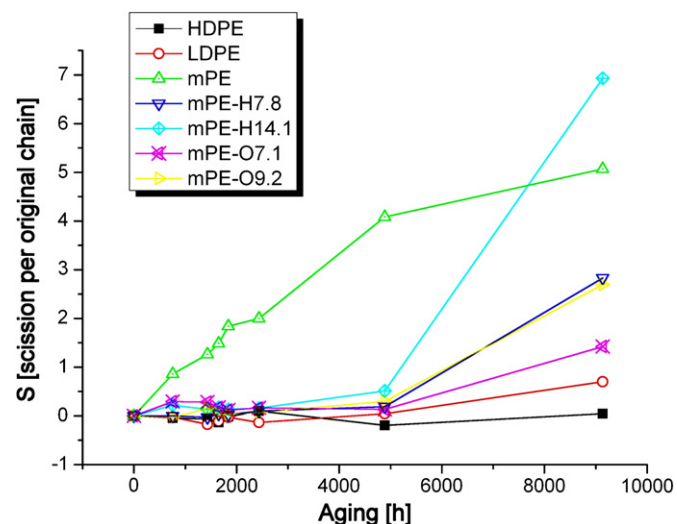


Fig. 1. Scission factor for commercial and synthesized polymers aged in a forced draft oven at 60 °C.

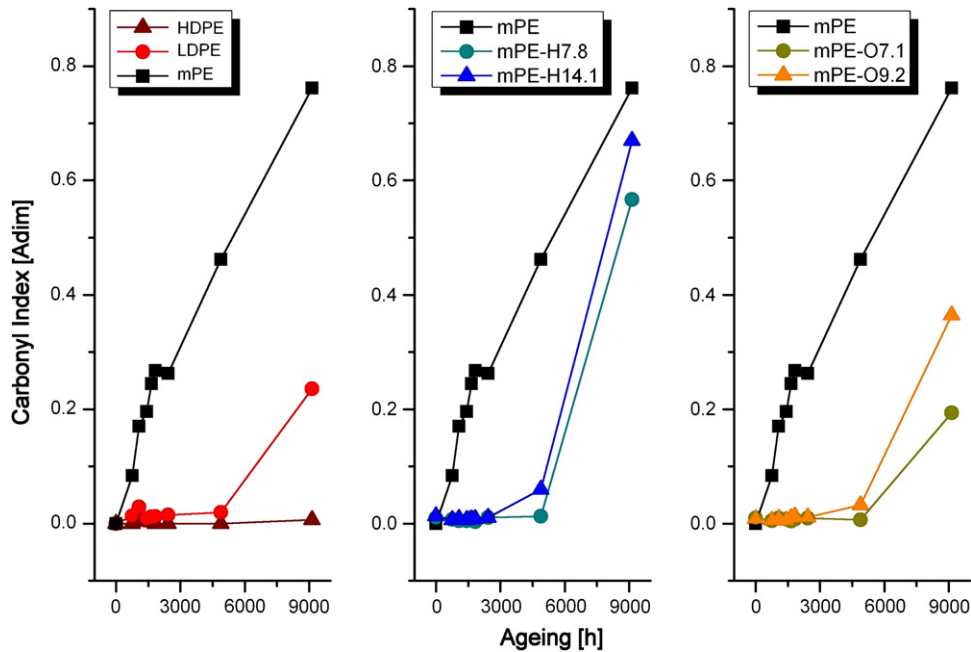


Fig. 2. Carbonyl index graph for commercial and synthesized polymers aged in a forced draft oven at 60 °C.

thermal aging will happen preferentially in this zone of the amorphous phase responsible of the stress transfer allowing the polymers with higher tertiary atom concentrations to undergo higher strains which will produce longer elongations.

As Young's modulus, tensile strength at yield, and tensile stress at break depend mostly on the material's crystallinity, they are not affected when their magnitudes for the polymers with and without aging are compared.

3.3. Molecular weight and infrared spectroscopy

It is seen in Tables 3 and 4 that metallocene polymer films and commercial low-density polyethylene films undergo changes in their molecular weight after one year of accelerated aging. Commercial polymers (high-density and low-density polyethylenes) do not undergo changes due to stabilizers added previously in the extrusion process by which HDPE and LDPE

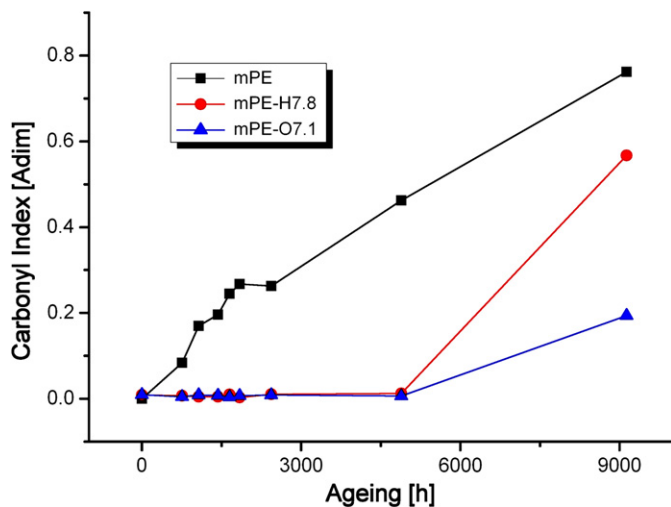


Fig. 3. Carbonyl index graph for metallocene ethylene homopolymer and ethylene-1-olefin copolymers in a forced draft oven at 60 °C.

pellets are formed. After approximately one year of aging of commercial and synthesized polymer films it is found that metallocene polyethylene (mPE) as well as metallocene ethylene-1-hexene copolymers with 14.1% hexene content undergo a maximum degradation of ca. 80% compared to the other materials. However, metallocene polyethylene degrades earlier in greater proportion than the metallocene ethylene-1-hexene copolymer with 14.1% hexene. The degradation occurs by random chain scission, reducing chain length and thereby shifting the molecular weight distribution to lower values [18]. Then those scission reactions have a clear influence on the number-average molecular weight.

One way to visualize the influence of scission reactions over number-average molecular weight (M_n) is by means of the scission factor (S), which is defined as the apparent number of chain scissions per molecule.

$$S = (M_{n,0}/M_{n,t}) - 1 \quad (1)$$

where $M_{n,0}$ and $M_{n,t}$ are the number-average molecular weights at time zero and time t , respectively, whose data are obtained from Table 4.

In Fig. 1 it is seen that metallocene polyethylene degrades earlier than the other polymers. In general, linear chain polymers such as metallocene polyethylene are more prone to rupture than coiled chain polymers represented by metallocene ethylene-1-olefin copolymers and commercial low-density polyethylene. An increase in branch length induces a mainly globular polymer conformation. If this really happens, a degradation rate delay should be expected during polymer aging. In fact, this can be deduced from Figs. 1 and 3. In Fig. 1 the scission graph shows that the degradation rate of the copolymers starts increasing after 4880 h of aging, representing an increase in autocatalytic degradation [15], close to the trend shown by the carbonyl index graphs of Fig. 2, with respect to the growth of carbonyl. This confirms the idea of degradation rate delay. On the other hand, from Figs. 1 and 2 it is possible to deduce that when the molar content of comonomer (branch) increases, regardless of its size, degradation rate increases. One possible explanation would be that when comonomer content increases in the main chain, the

terminal hydrogens of tertiary carbons, whose bonds are more labile than those of secondary hydrogens, would also increase. When the polymer undergoes an external thermal action, radical concentration could increase by an intramolecular scission mechanism; then, radicals could catalyse the chain degradation by means of an intermolecular scission mechanism. This step determines the degradation rate.

4. Conclusions

Metallocene synthesis of homoethylene and ethylene-1-olefin copolymers allows narrower molecular weight distributions to be obtained. This fact makes possible the study of the influence of structure on degradation rate and final physical properties. It is clearly seen that branching in the main chain affects stability, with comonomer size and content as two parameters to be studied. It is observed that lowering comonomer size as well as increasing comonomer content leads to an increase in autocatalytic oxidation rate when subjected to external thermal degradation. Tensile mechanical assays of copolymers showed the influence of comonomer content over percentage amorphous phase and then on their elongation properties. It is suggested that co-units of tie molecules have twofold importance, i.e. increasing amorphous phase and prevents higher strain which would explain that when copolymers of higher comonomer content are subjected to thermal aging they show longer elongation values.

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