Effects of a Mixture of Stabilizers on the Structure and Mechanical Properties of Polyethylene During Reprocessing

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ABSTRACT: The properties of two polyethylenes [a high-density polyethylene (HDPE) and a low-density polyethylene (LDPE)] were studied after several extrusion cycles. To reduce the degradation effects during the reprocessing, a mixture of two stabilizers was added to the formulations. The predominant degradation mechanism was chain scission for the HDPE and chain branching and crosslinking for the LDPE. For both polyethylenes the FTIR spectra exhibited a growth in the number of carbonyl groups as a function of the number of extrusion cycles. Their tensile properties were degraded with the reprocessing but both polyethylenes maintained their nearly constant thermal behavior and crystallinity. The addition of a primary phenolic antioxidant and a secondary phosphite antioxidant preserved the melt behavior of virgin materials after the reprocessing and reduced the degradation effects. From the tensile tests, the efficiency of the antioxidants in the LDPE was very high and, after the reprocessing, the material retained the mechanical properties of virgin LDPE. The efficiency of the antioxidants for the HDPE was not significant. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3910–3916, 2004

Key words: polyethylene (PE); extrusion; mechanical properties; antioxidants; FTIR

INTRODUCTION

During processing, polymer materials can be subject to either one or several steps. Thus, it is necessary to evaluate the effects of reprocessing on their structure and their properties.[1–8]

The chemical reactions induced by high temperatures, oxygen, and shear during the melt polymer processing are uncontrolled, and change the structure of the chains and the properties of the processed material.

Polyolefins are very sensitive to these kinds of reactions, collectively identified as degradation.[9–11] The addition of stabilizers before processing is the most effective way to protect against polymer degradation.[12]

Stabilization during the melt processing should be achieved by the suppression of any kind of radical species formed by thermooxidative and thermomechanical processes, which lead to chain scission and/or chain branching and crosslinking. The main stabilizer formulations for polyolefins include a primary antioxidant such as hindered phenols and hydroperoxide-decomposing antioxidants such as phosphites.

It was demonstrated that the combined action between the hindered phenols and phosphites produces a synergistic effect. Together, they provide greater protection than using either additive alone.[13,14] The cooperative effect of hindered phenols and phosphites occurs through two steps, whereby phenols scavenge alkylperoxyl radicals and phosphites decompose peroxides into nonradicals, which enhanced the melt stability of the polymer. Further interaction between the colored transformation products of phenol and the phosphite antioxidants results in noncolored products, and thus color degradation is reduced.

Drake and coworkers[15] proved that the most efficient ratio for protection of the melt flow of several polyolefins is a 4 : 1 ratio of phosphite to phenol.

The aim of this work was to study the effect of reprocessing on a high-density polyethylene (HDPE) and a low-density polyethylene (LDPE), both of which included a processing stabilizer formulation. The physical properties and chemical structures of polyethylenes were evaluated as a function of the number of extrusion cycles.

EXPERIMENTAL

Materials

In this work, two extrusion grades of polyethylenes, HDPE [Alcudia C-240-UV (Repsol YPF, Spain)] and LDPE [Lupolen 1840 H (Basell, Wilmington, DE)], were used.

TABLE I
Processing Parameters

Material	Extrusion parameters		
	Barrel temperature (°C)	Die temperature (°C)	Screw speed (rpm)
HDPE	225	230	32
LDPE	200	210	60
	Injection parameters		
	Melt temperature (°C)	Injection pressure (bar)	Injection speed ($cm^3 s^{-1}$)
HDPE	250	1400	56
LDPE	200	1200	56

A mixture of two antioxidants was added to the polyethylenes: 0.05% Irganox 1010 [i.e., pentaerythrityl-tetrakis (3′,5′-di-*tert*-butyl-4′hydroxyphenyl)-propionate] and 0.20% Irgafos 168 [i.e., tris-(2,4-di-*tert*-butylphenyl) phosphate], supplied by Ciba Specialty Chemicals (Basel, Switzerland).

The materials, with and without stabilizers, were reprocessed by extrusion five times in a corotating twin-screw extruder (DSE-20; C. W. Brabender Instruments, South Hackensack, NJ). The extrusion parameters for the polyethylenes are summarized in Table I.

The HDPE samples were designated HD-0 to HD-5 (0 for the virgin HDPE and 5 for the material with five extrusion cycles). The samples with antioxidants were designated HD-1a, HD-3a, and HD-5a, where the number indicates the number of extrusion cycles.

In the same way, the LDPE samples were designated LD-0 to LD-5 (samples without stabilizers) and LD-1a, LD-3a, and LD-5a (formulations with stabilizers).

Characterization of the chemical structure

The melt flow indices (MFIs) were measured in a melt flow tester (Ceast S.p.A., Torino, Italy) according to ISO 1133. The test temperature was 190°C and the mass was 21.6 kg for the HDPE samples and 5 kg for the LDPE samples.

The changes in the chemical structure of the samples were studied by FTIR with a Bruker Vector 22 (Bruker Instruments, Billerica, MA). The FTIR spectra were obtained at room temperature, after 16 scans, with a resolution of 2 cm^{-1}.

The FTIR samples were molded by compression at 220°C (HDPE samples) and 150°C (LDPE samples) and 200 bar for 5 min.

Tensile tests

After each extrusion cycle, the extrudate was pelletized and tensile specimens were molded using a Bat-tenfeld Plus 350 injection-molding machine (Battenfeld Extrusionstechnik GmbH, Bad Oeynhausen, Germany) according to ISO 527. Table I shows the injection parameters. Eight specimens were tested for each reported value and the results were averaged to obtain a mean value. Tensile tests were performed at a crosshead speed of 10 mm min^{-1} and at 23°C using an Instron 5566 universal testing machine (Instron, Canton, MA).

Characterization of the physical structure

Differential scanning calorimetry (DSC) analyses were performed with a PE DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) in nitrogen atmosphere, at a temperature range between 30 and 160°C. The samples were held at 160°C for 5 min to erase their thermal history and then they were cooled at a cooling rate of 64°C min^{-1} to the isothermal temperature (T_{iso}). The samples were maintained 1 h at the T_{iso} and then they were heated from 30 to 160°C at a heating rate of 10°C min^{-1}. The isothermal temperatures were 120°C for the HDPE and 105°C for LDPE. The melting temperature (T_m) and the heat of fusion (ΔH_m) were measured in the last scan. The percentage crystallinity was calculated based on the relationship $X = (\Delta H_m/\Delta H_0) \times 100$, assuming a value of ΔH_0 for 100% crystalline PE[14,16] of 293 J g^{-1}.

RESULTS AND DISCUSSION

Characterization of the chemical structure

The MFI measurement is a good method to study the effects of reprocessing because the melt flow index is associated with the melt viscosity of the material and is an indicator of the changes in molecular weight.

Figure 1 shows the MFI behavior of the HDPE and LDPE after five extrusion cycles. In the HDPE samples, the MFI values increased from 15.4 to 20.5 g/10 min as a function of the number of the extrusion
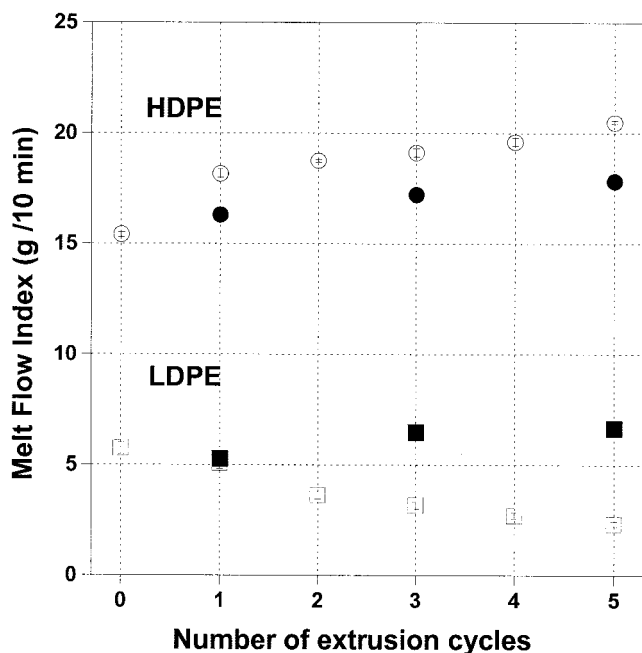
Figure 1 MFI as a function of the number of extrusion cycles: (○) HDPE, (●) HDPE with antioxidants, (□) LDPE, and (■) LDPE with antioxidants.

cycles. This growth was caused by the thermomechanical degradation and thermooxidation of the material and was attributed to a diminution in the molecular weight resulting from chain scission. Although the MFI values of the formulations with antioxidants increased with respect to the HD-0, this increase was less than that for the samples without antioxidants. After five extrusion cycles, the value attained was 17.8 g/10 min for HD-5a.

For the LDPE, the extrusion cycles led to a strong decrease in the MFI data (from 5.7 g/10 min for LD-0 to 2.3 g/min for LD-5). This fact proved that the viscosity of the material increases with reprocessing, caused by the chain branching and crosslinking of the LDPE molecules. The PE crosslinking under thermooxidation conditions has often been attributed to alkyl radical coupling.[9]

The antioxidants produced a slight increase in the MFI with respect to the value of LD-0. The MFI measured for LD-5a was 6.6 g/10 min. This behavior shows that two degradation mechanisms can be in competition, that is, the mechanisms of crosslinking and chain scission. Depending on whether the crosslinking or the chain scission predominates, the viscosity of the material increases or decreases. Processing temperatures have an important role in the competition between the two degradation mechanisms. Several studies have shown that, in general, crosslinking predominates at low temperatures and chain scission prevails at high temperatures. However, other factors must be considered, such as the

concentration of unsaturated groups (mainly vinyls), which principally depends on the PE polymerization conditions. Thus, PE devoid of vinyl groups does not crosslink, whereas other PEs with high vinyl concentration crosslink under the same extrusion conditions.

The MFI data show that for the HDPE, the degradation produces a chain scission in the molecules, which is reduced with the addition of antioxidants before the extrusion processing. For the LDPE, the crosslinking is the predominant mechanism in the degradation. The MFI of the LDPE samples with antioxidants verified that chain scission is also present in the degradation process and that the efficacy of antioxidants is greater for crosslinking than for chain scission.

Reprocessing of polymer materials produced thermooxidative degradation arising from the temperatures and the presence of oxygen in the extrusion. This degradation process is usually associated both with the increasing number of carbonyl groups and with the appearance of new species. These chemical changes, supported by the materials, were studied by IR spectroscopy.

Figure 2(a) shows the spectra of HD-0, HD-5, and HD-5a. The HDPE spectra obtained for the different extrusion cycles were similar to that of HD-0 except for the HD-5. The characteristic band of carbonyl group at 1760 cm^{-1} and distinct peaks around 1120 cm^{-1}, attributed to stretching of the C—O—C bond of the ester group observed for the degraded samples, show the presence of chain scission. IR did not detect the oxidation until the fifth extrusion, although the MFI values indicate that there was degradation in the material since the first extrusion cycle. This degradation is probably attributable to thermomechanical degradation and is not easily measurable by IR. The effectiveness of the stabilizers was confirmed by the decrement in the intensity of the peak at 1760 cm^{-1} for the sample without antioxidants.

The spectra of LD-0, LD-5, and LD-5a are displayed in Figure 2(b). For the LDPE samples without antioxidants, the carbonyl group band was detected from the third extrusion, although it was not very important until the LD-5 sample. The spectra revealed there was also thermal oxidation degradation in the LDPE samples. The stabilizers added to the material reduced the number of carbonyl groups and the corresponding spectrum showed a lower intensity in the band at 1760 cm^{-1} and the peaks around 1120 cm^{-1}.

For the HDPE, the chain scission was associated with a higher intensity of the characteristic bands at 1760 and 1120 cm^{-1} and with the increment in melt flow indices.

For the LDPE, two mechanisms were in competition: the crosslinking mechanism caused a strong increase of the material viscosity (i.e., a decrease in the
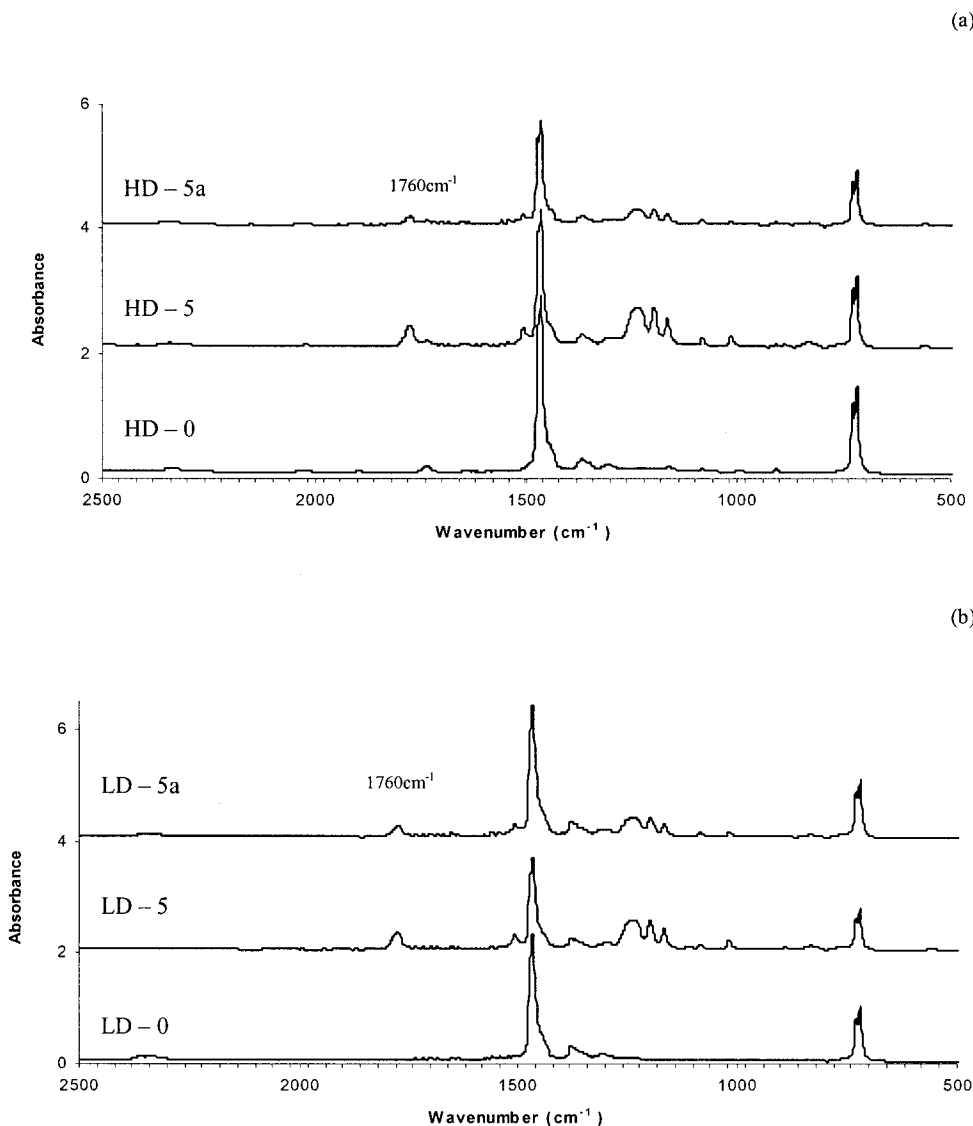
Figure 2 FTIR spectra of (a) HDPE samples and (b) LDPE samples.

MFI data), although the chain scission mechanism was also perceived in the FTIR spectra.

Mechanical properties

Figures 3–5 show the tensile properties of the formulations with and without stabilizers. During the tensile tests, stress whitening, caused by changes in the refractive index (attributed to the presence of microcrazes or/and voids in the material), was observed.[17]

For the HDPE samples without antioxidants, the modulus (E) values display an increase in the HD-1 to HD-5 samples compared to that of the HD-0 sample (Fig. 3), although, the standard deviations did not provide a clear trend in function of the extrusion cycles.

The stress at break (σ_B) also shows small variations after different numbers of extrusion cycles (Fig. 4), although no clear tendency can be seen for the data.

Figure 5 shows the behavior of the strain at break (ε_B) for the different samples. In general, the typical fracture of the ductile materials was observed, although the degradation mechanisms produced a random break in the specimens and the standard deviation in ε_B was higher than expected. The ε_B value of HD-5 was not reported because the deviation obtained in the experiment was excessive. The cause of the high deviation can be the fibrillar fracture observed in these specimens (different from that of the other HDPE samples). The ε_B value seems to decrease after the third extrusion, which is in agreement with reduction of molecular weight shown from the MFI data. The lower the molecular weight, the greater the number of chain ends and the fracture happened at lower strain.

In the LDPE without antioxidants, the modulus (E) improved slightly with the number of extrusion cycles, until the fourth (Fig. 3), and had a clear increase after the fifth cycle. This fact proved that the thermo-
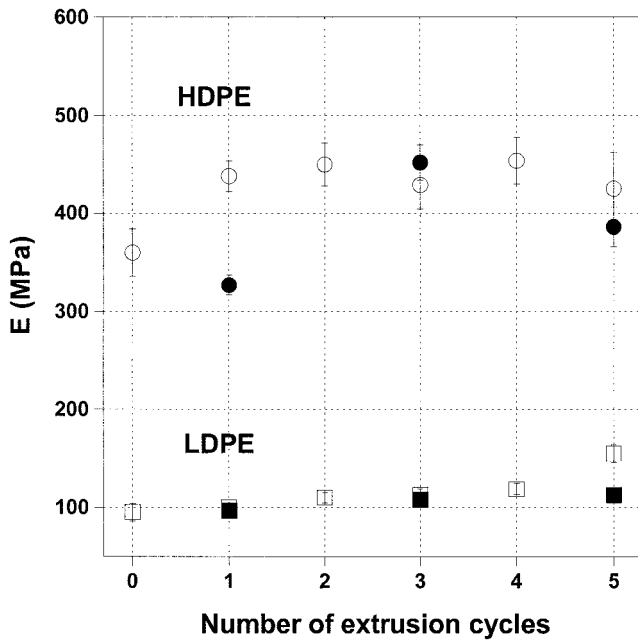
Figure 3 Young's modulus as a function of the number of extrusion cycles: (○) HDPE, (●) HDPE with antioxidants, (□) LDPE, and (■) LDPE with antioxidants.

mechanical degradation enhanced the material stiffness. The stress value at the break point increased as a function of the number of extrusions (Fig. 4) and the graph of Figure 5 proves that the ε_B was slightly diminished from the second extrusion. These results revealed that the degradation weakly deteriorated the
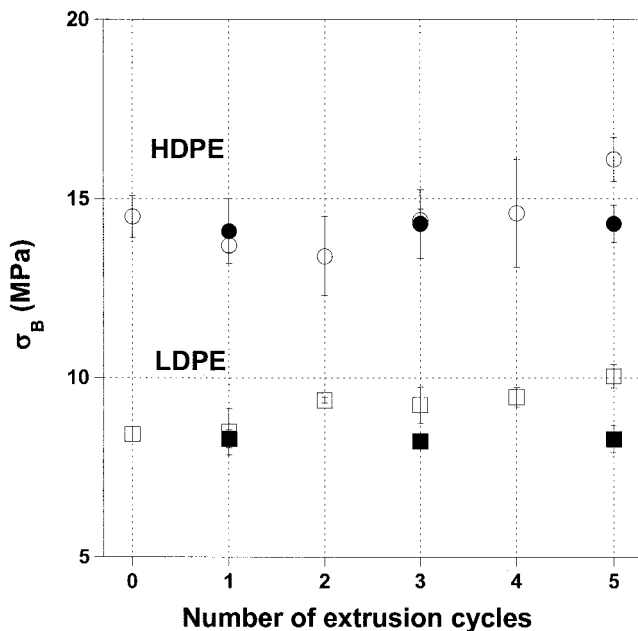

Figure 4 Stress at the break point as a function of the number of extrusion cycles: (○) HDPE, (●) HDPE with antioxidants, (□) LDPE, and (■) LDPE with antioxidants.

Figure 5 Strain at the break point as a function of the number of extrusion cycles: (○) HDPE, (●) HDPE with antioxidants, (□) LDPE, and (■) LDPE with antioxidants.

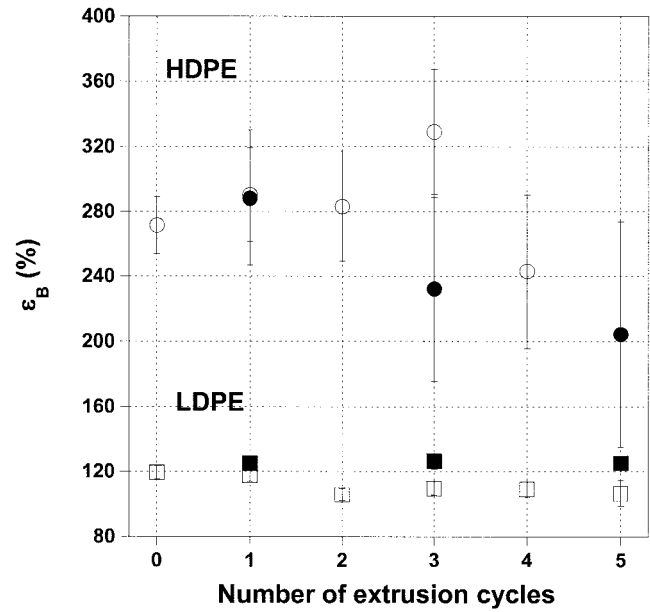tensile properties of LDPE, although the degradation was less than that in HDPE samples. Deviations of the mean value were tolerable in all the mechanical tests of the LDPE.

The efficacy of the antioxidants on the mechanical properties was different in the HDPE samples than that in the LDPE samples.

In the HDPE samples with antioxidants, the modulus underwent small changes and the stress at break was kept constant after the reprocessing. However, the results showed that the antioxidants were less effective in preventing the strain at break from decreasing.

For the LDPE, the effectiveness of the antioxidant was substantial in all the mechanical parameters. By addition of the antioxidants, the modulus, stress, and strain at break point remained constant with the reprocessing, as observed in Figures 3–5.

Characterization of the physical structure

Analysis of the polymer crystallization is important for understanding the structure–properties relationships. After isothermal crystallization, heating DSC curves for HDPE samples showed two exothermic peaks around 123 and 131°C. These temperatures were nearly constant with the number of extrusion cycles. Degrees of crystallinity for HDPE and LDPE, both with and without antioxidants, are shown in Table II. If the deviation of the measurements is kept in mind, the number of extrusion cycles did not affect the crystalline content of the HDPE samples. Some

TABLE II
Crystallinity for the Samples With and Without Stabilizers

Number of extrusion cycles	Crystallinity (%)			
	HDPE	HDPE with antioxidants	LDPE	LDPE with antioxidants
0	48.8 ± 4.5	—	31.5 ± 0.5	—
1	52.1 ± 2.2	49.3 ± 3.7	34.3 ± 2.5	34.1 ± 0.8
2	51.3 ± 2.3	—	30.7 ± 0.3	—
3	50.4 ± 5.0	51.1 ± 2.0	31.4 ± 1.1	32.0 ± 1.7
4	50.5 ± 1.9	—	32.0 ± 0.2	—
5	47.3 ± 5.5	46.0 ± 2.6	31.1 ± 1.3	31.0 ± 1.4

investigators found that a higher crystallinity in the polyolefins degraded. This increase agrees with a molecular weight decrease, which should allow enhanced mobility of the polymer chains.[18] In this work, the decrease of the material viscosity, associated with a small molecular weight estimated during the HDPE reprocessing, was not enough to produce a change in the crystallinity, measurable by DSC. The addition of antioxidants did not alter either the thermal behavior or the crystallinity of the samples (see Table II).

For the LDPE samples, with and without antioxidants, the heating curve after the isothermal crystallization exhibited a single peak around 107°C. The degree of crystallinity of the samples is summarized in Table II. There were no significant changes with the number of extrusion cycles. This fact proved that the thermal properties studied by DSC are not sensitive to the changes in the chemical structure produced by the degradation mechanisms.

For both polyethylenes, the crystallinity degree showed that the changes in the material properties produced by degradation mainly affected the amorphous part of the samples.

CONCLUSIONS

After five extrusion cycles, the changes in the HDPE and LDPE properties were different. Thermomechanical degradation and thermooxidation both produced a decrease in the molecular weight of the HDPE, atributed to the chain scission that supported the material during the reprocessing. Chain branching and crosslinking predominated over the chain scission mechanism for the degradation of LDPE samples. An increase in molecular weight was detected as a function of the number of extrusion cycles. The addition of the mixture of stabilizers reduced the chain scission in the HDPE samples after five extrusion cycles. In the LDPE samples with stabilizers, the MFI values proved there was also chain scission during the reprocessing.

The FTIR spectra showed that the degradation produced an increase in the number of carbonyl groups and the presence of new species in the two polyethyl-

enes. The stabilizers were sufficient to reduce these degradation effects in both materials.

For tensile properties, the behavior was different for HDPE than for LDPE. The Young's modulus increased with the number of extrusion cycles. In the HDPE, the increase was measurable from the first extrusion. In the LDPE, the modulus value remained constant until the fourth cycle, after which the modulus increased. With the stabilizers, the modulus value for the LDPE after reprocessing was similar to that of the virgin LDPE. For the HDPE, the antioxidants generated small changes in the modulus value compared to that of HD-0.

At the break point, the stress increased and the strain decreased with the number of extrusion cycles. Moreover, the degradation produced high deviations in the mechanical tests for the HDPE.

The efficiency of the stabilizers in the HDPE was not as good as expected: passable values for the strain at break were obtained after five extrusion cycles, but addition of a mixture of stabilizers did not improve the strain at break point. However, the addition of stabilizers maintained the mechanical properties of the virgin LDPE at the break point after reprocessing.

The thermal behavior and crystallinity of both polyethylenes were not altered after reprocessing, even with the addition of stabilizers to the formulations.

In summary, the mixture of stabilizers chosen was useful for preserving the physical properties and the chemical structure after reprocessing of both polyethylenes, although it was proved that the efficiency of the stabilizers was higher for the LDPE than for the HDPE.

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