Degradation and biodegradation of polyethylene with pro-oxidant aditives under compost conditions establishing relationships between physicochemical and rheological parameters

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ABSTRACT: In the present work, an analysis is carried out to provide a relationship between the Molecular Weight (M_w) of degraded LDPE films (containing Mn stearate as pro oxidant (MnSt-LDPE) and changes in viscosity, elongation at break (EB %) and carbonyl index (CI) occurring during thermal degradation in the thermophilic phase of the compost process. The thermal treatment comprised various temperatures (50°C, 60°C, and 70°C) and exposure times, and was characterized through a so-called Energy-Time Factor (the product of thermal energy and exposure time). Changes in viscosity, EB %, and CI were correlated to this factor. A modified Mark-Houwink equation was used to relate the zero shear-rate viscosity and M_w of the degraded LDPE films. Results indicate that the EB %, M_w and viscosity decrease simultaneously with an increase in the CI as the Energy-Time Factor augments, allowing the assessment of the variation of these properties with M_w. Calculations of the percentage abiotic degradation (%D) of LDPE films indicate that a M_w of 6 kg mol^{-1} corresponds to a maximum abiotic degradation degree of 91.85%, which is henceforth susceptible to biodegradation. The film treated with Energy-Time Factor of 2.79E+09 J s mol^{-1} reached a 74% of biodegradation in 90 days (average time of the composting process). Results exhibit clearly the correlation between abiotic and biotic degradation. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42721.

INTRODUCTION

The amount of plastic wastes is growing every year and consequently the fraction of plastics in Municipal Solid Wastes (MSW) is increasing. Industry has extensively used low-density polyethylene (LDPE) Films in packaging and distribution of foodstuffs. Usually, LDPE-Films are disposed in landfills and compost plants.[1]

Compost plants are a good alternative to manage organic waste and produce quality compost, however, it is known that in several countries some polyethylene materials are disposed with organic waste in compost plants, producing pollution and requiring expensive separation processes from the organic waste in the compost production.

These products go through the three compost stages: mesophilic, thermophilic, and maturation. The compost thermophilic phase has the highest and longest temperatures (40°C, 50°C, 60°C, and 70°C; time varies depending on temperature: from 2 hrs to 48 days) (ASTM D 5510-94, 2001). Studies indicated that the highest temperatures achieved during the thermophilic phase of the compost process, depend on the environmental temperature. For example, it is reported that in the winter season the thermophilic compost phase has reached 50°C as the maximum temperature.[2]

The photo-thermal degradation and biodegradation of LDPE films with pro-oxidant additives has been the subject of numerous studies. These analyses have pointed out that molecular weight (M_w) is one of the most important parameters to determine the feasibility of polyolefin bio-degradation.

PE has been used as a synthetic industrial polymer because of its exceptional properties against degradation, resistance to peroxidation, and possesses biologically inert properties, good optical and mechanical properties, low weight, and manufacture cost.[3] On the other hand, molecular weight of commercial LDPE films has values of M_w between 100,000 and 500,000 g mol^{-1}, making biodegradation difficult.[4]

To achieve biodegradable LDPE-films, pro-oxidant additives have been utilized to create oxo-biodegradable materials. Pro-oxidant additives are made of transition metals complexes, such as manganese stearate (MnSt) and cobalt stearate (CoSt).[5,6]

Oxo-biodegradable LDPE mineralization comprises two steps: abiotic and biotic degradation. Abiotic degradation occurs when the inclusion of pro-oxidant additives in LDPE films accelerate the degradation process under photo and thermal conditions.[7,8] This degradation is observed by the M_w reduction. Other parameters as humidity, mechanical stress, air temperatures, solar radiation, and critical combinations of the above factors have been reported to increase the rate of abiotic degradation.[9,10]

Biodegradation or mineralization of polymers consists in the degradation involving microorganisms, and occurs when the reduction of M_w is enough that microorganisms and/or catalytic enzymes[11] convert polymer into carbon dioxide, water, minerals, and biomass (aerobic biodegradation) in compost and soil environments; or carbon dioxide, methane, and humic material (anaerobic biodegradation) in landfills.[12] Elsewhere, reports reveal that LDPE-Films can be subjected to biodegradation if the M_w of such films is lower than 6000 g mol^{-1} as feasible to biodegradation.[13,14] However, the time required for biodegradation is difficult to predict.

LDPE-Films degradation has been analyzed through changes in the mechanical, physical, thermal, morphological, spectroscopic, and chemical properties, but these changes are scarcely linked properly with the photolytic and thermal variables.

Mechanical testing is usually made by elongation at break (EB %) and tensile strength measurements. Physical testing involves measurements of melt flow index, density, and apparent viscosity.[15] Thermal analysis includes the thermo-gravimetric analysis (TG) and Differential-Scanning Calorimetry (DSC). Morphological studies include Scanning Electron Microscopy (SEM); structural studies are Gel Permeation Chromatography (GPC) and spectroscopic analysis by Fourier Transform Infrared Spectroscopy (FTIR), and chemiluminescence.[16] Biodegradation analysis by CO_2 evolution studies have also been considered.[17]

M_w is normally determined by GPC (Size-exclusion) requiring 0.5–2 h per sample and only a few milligrams of soluble material. GPC gives important information concerning polydisperse polymers, such as weight-average and number-average molecular weights (M_w and M_n, respectively), average molecular weight (M_z), and polidispersity (M_w/M_n).[18] Problems with PE arising in this technique are the requirement of high temperatures to obtain soluble material, shear degradation, high cost, and the use of toxic solvents.[19]

To avoid these problems it is necesary to consider alternative methods to evaluate M_w, namely shear viscosity, elongation at break, and carbonyl index. The M_w is related to the intrinsic viscosity [η_o] by the Mark-Houwink relationship equation:[20–22]

$$\eta_o = \kappa M_w^{\alpha} \qquad (1)$$

A modification of eq. (1) for polydisperse polymers with $M_w/M_n > 1.5$ [LLDPE-Films (Linear LDPE films)],[23] has been made according to the following expression:

$$\eta_o = 0.51 \kappa M_w^{\alpha} \frac{M_z^{0.8}}{M_w} \qquad (2)$$

The Flory-Schulz distribution function is used to calculate the coupling constant κ, eq. (3), defined as the number of independently growing chains required to form one dead chain.[21] The viscosity average molecular weight can also be estimated by eq. (4):

$$\frac{M_n}{\kappa} = \frac{M_w}{\kappa + 1} = \frac{M_z}{\kappa + 2} \qquad (3)$$

$$\eta_o = 016.5 \times 10^{-3} M_w^{0.83} \qquad (4)$$

The polymer critical molecular weight (Mwc) is related to the onset for entanglement formation among molecules. Experimental Mwc values for LDPE-Films are reported between 35,000 and 85,000 gmol^{-1}.[24]

Established methodologies provide methods to evaluate the abiotic and biotic polymer degradation. In particular, the ASTM D 6954-04 norm provides methods to characterize biodegradation in LDPE films, which occurs at M_w of the order of 6000 g mol^{-1} or lower. Abiotic degradation includes thermal-induced processes; in this context, the ASTM D 5510-94 (2001) norm suggests a series of temperatures and exposure times depending upon the environment: soils (20–30°C), waste disposal (20–35°C), and composting (30–70°C). Methodologies for abiotic degradation of polymers include strain at break (5%) [ASTM D 3826-98(2002)] and CI [ASTM D 5576-00(2006)]. It was found that when M_w is lower than 10,000 g mol^{-1}, CI is larger than seven,[25,26] and when M_w of LDPE is lower than 6000 gmol^{-1} is susceptible to biodegradation.[13,14] In this work the correlation between M_w and viscosity changes during thermal degradation of MnSt-LDPE films under compost conditions is obtained by using the modified Mark-Houwink equation, which was experimentally confirmed.

In this work, the relationship between abiotic and biotic degradation was investigated through the analysis of the physical, chemical, and rheological properties of MnSt-LDPE films. With this information we found that it is possible to estimate the biodegradation potential of films with pro-oxidant additives through inexpensive and environmentally feasible techniques.

MATERIALS AND METHODS

Abiotic Degradation

Extruded films[27] were thermo-oxidized at 70°C, 60°C, 50°C, in an air oven (FELISA), for extended periods indicated in Table I, in accordance with the ASTM D 5510-01 standard. Thermo-oxidation of samples follow the methodology established in ASTM D 5510-01 "Heat Aging of Oxidatively Degradable Plastics".

Energy-Time Factor. The thermal treatment was carried out at different temperatures and exposure times. To rationalize and compare the results of each treatment, the Energy-Time Factor (ETF) was calculated according to eq. (5) and results are presented in Table II. T is the temperature (°K), t is time (s), and R is the gas constant (8.3143 Jmol^{-1}K^{-1}).

Table I. Thermal Treatment of LDPE Films. Temperatures and Exposure Times Under Compost Conditions.

Temperature °C	Exposure time (h)					
	t_1	t_2	t_3	t_4	t_5	t_6
70	2	4	8	16	24	32
60	8	16	32	64	96	128
50	24	48	96	192	288	384

$$ETF = (T[°K])(t[s])\left(R\left\lfloor\frac{J}{mol°K}\right\rfloor\right) \qquad (5)$$

Molecular Weight (M_w). MnSt-LDPE-Films were analyzed by GPC to obtain M_w, M_n, M_z, and polydispersity values. An Agilent PL-GPC220 equipment with three columns connected in series and a refractive index detector was used. Samples (0.15 mg) were dissolved in 10 mL of 1,2,4 trichlorobenzene at 170°C during one hour. The solution was filtered in a 0.5 u membrane to eliminate insoluble material. M_w was measured using an universal calibration curve with polystyrene standards. Molecular weight was carried out following the D 6474-99 method.

Shear Viscosity. The shear viscosity was measured in an AR-2000 TA-Instruments controlled-stress rheometer with the cone-and-plate fixture equipped with a thermally controlled oven. Films were melted before testing. Tests include the continuous simple-shear in the low-shear rate range and oscillatory tests to accurately evaluate the zero shear-rate viscosity.

Carbonyl Index. The Carbonyl Index (CI) determines the degree of thermal-oxidation of LDPE-Films containing pro-oxidant additive and was calculated according to the ASTM D 5576-06 method. Infrared spectra were recorded in a Perkin Elmer spectrophotometer. Films were mounted on cardboard frames with a 1 cm x 1.5 cm space. Data obtained from 12 scans recorded at a resolution of 2 cm^{-1} were averaged and background-corrected using air. The CI was calculated by taking the ratio of the absorbance of the carbonyl band between 1700 and 1750 cm^{-1} and the reference band at 720 cm^{-1}.

The interval between 1700 and 1750 cm^{-1} cover the bands corresponding to sub-products of LDPE degradation, such as carboxylic acids (1700 cm^{-1}), ketones (1714 cm^{-1}), and aldehydes (1733 cm^{-1}). The reference value corresponds to the CH groups. Five samples were analyzed for each ETF in duplicate. Accordingly, the CI was calculated by the following equation:

$$CI = \frac{A1720cm^{-1}}{A720cm^{-1}} \qquad (6)$$

Elongation at Break Percentage (EB %). The EB % was measured using a Materials-Testing-Machine Instron LF plus Lloyd Instruments. Samples with a gauge length of 80 mm and width of 10 mm were cut from the films. The speed of testing was 100 mm min^{-1}. The tests were undertaken in an environment chamber at 22°C and relative humidity of 45%. Ten samples were tested for each experiment and the average value is reported. Elongation at break was calculated using eq. (7),

where EB % = Elongation at break percentage, L_F = Final length, L_I = Initial length:

$$EB(\%) = \frac{L_F - L_I}{L_I} \times 100 \qquad (7)$$

In addition, tensile tests were carried out in a servo-hydraulic loading device (MTS 858 MiniBionix axial) according to ASTM D882-02 standard. The tensile tests were done at 24°C using a strain rate of 10 mm/min and a gage length of 30 mm. Five rectangular strips of each material were tested under uniaxial tensile test (60 × 10 × 0.025 mm –length, width and thickness– respectively).

To control the MiniBionixMTS a 407 MTS controller was used while data were supported by National Instruments PXI-1002 and PXI-boards (6281, 8331, and 4220) and a PC. A virtual instrument was programmed in LabVIEW in order to save the data. With the displacement and force data, the stress vs. strain curves were obtained.

Calculation of Percentage Abiotic Degradation (%D). Since the CI is proportional to carbonyl concentration and the %D is equal to the ratio of carbonyl concentration to total carbon concentration, it is possible to calculate the %D as the ratio of the CI of the thermo-oxidized film sample ($CI_{C=O}$) and the maximum of the carbonyl index (CI_{max}) as in eq. (8). CI_{max} is obtained by extrapolation of the plot of $CI_{C=O}$ versus molecular weight as Mw→0. As observed, the limits of %D are zero, namely, the no-thermo-degradation limit, and 100%, as the concentration of C-H groups tends to zero (total degradation limit). The extrapolated value amounts to $CI_{max} = 9.14$:

$$\%D = 100\frac{CI_{C=O}}{CI_{C=O} + CI_{C-H}} = 100\frac{CI_{C=O}}{CI_{max}} \qquad (8)$$

Abiotic Degradation Results. Seven plots were made, but three of them correspond to direct experimental data. These primary plots were related to the thermal treatment by calculating the ETF for every experimental value of EB %, CI, and viscosity. The fourth plot relates viscosity and M_w, using the modified Mark-Houwink equation corroborated by experimental data. From this plot, it is then possible to construct the variation of M_w with ETF, from which the plots for EB % and CI can be made as functions of M_w.

Table II. Energy-Time Factor (ETF) Calculations

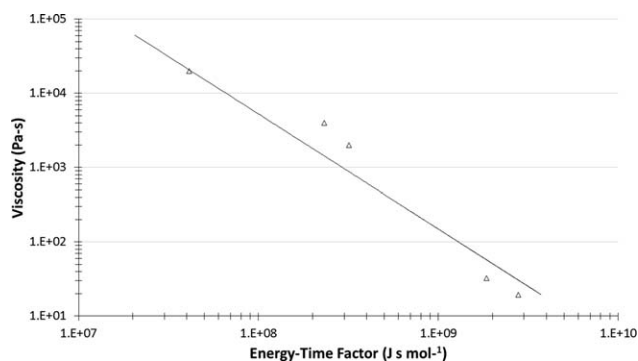| Treatment (°C, h)	ETF (J s mol^{-1})	Treatment (°C, h)	ETF (J s mol^{-1})
70°C 2 h	2.05E+07	50°C 48 h	4.64E+08
70°C 4 h	4.11E+07	60°C 64 h	6.38E+08
70°C 8 h	8.22E+07	50°C 96 h	9.29E+08
70°C 16 h	1.64E+08	60°C 96 h	9.57E+08
50°C 24 h	2.32E+08	60°C 128 h	1.28E+09
70°C 24 h	2.46E+08	50°C 192 h	1.86E+09
60°C 32 h	3.19E+08	50°C 288 h	2.79E+09
70°C 32 h	3.29E+08	50°C 384 h	3.71E+09

Figure 1. Viscosity versus energy-time factor of MnSt-LDPE-Films with MnSt. Experimental data (Δ) comprised several temperatures and exposure times.

Biotic Degradation Results

Compost Inoculum Characterization. The inoculum compost was collected from the composting plant (Bordo Poniente) in Mexico City. To obtain a representative and homogeneous sample the quartering method was applied. Before starting the biodegradation experiment (day 0), the compost was characterized via pH, moisture, organic matter, nitrogen, carbon, and ash, in order to evaluate the homogeneity of the composting reactors, to decrease the differences in the production of CO_2 between reactors at the end of the experiment. During biodegradability test, each reactor with compost and sample was analyzed at 45 and 90 days.

The oxidized organic matter content was determined through dichromate oxidation (K2Cr207 + H2SO4 mixture); the humidity was analyzed quantifying the loss of water-mass by the dry method at 105°C; total nitrogen was measured through the Kjeldahl method; the pH was determined by the potentiometric method mixing a 1/9 ratio of compost/water. The humidity content of the compost was maintained constant adding water (keeping the limits within 40% and 60%, as recommended).

Aerobic Biodegradability System. Reactors of 1.8 L were provided with 300 g dry matter of mature compost plus 4 g dry matter of tested material. MnSt-LDPE films were subjected to abiotic degradation at 50°C during 12 days, with an ETF larger than 2.79E+09 J s mol^{-1} and M_w lower than 6000 g mol^{-1}. White bond paper was used as positive control. Materials tested were cut into squares of 2×2 cm^2. Three pairs of reactors were utilized, two reactors containing MnSt-LDPE films, two with cellulose and two blanks.

To evaluate the aerobic biodegradability under control compost conditions, the ASTM procedure D 5338–03 (Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions) was carried out.

Calculation of Percentage Biodegradation. The total carbon content of the test material was calculated from the chemical composition and M_w of the MnSt-LDPE films. This carbon percentage in the material was used to estimate the carbon content in the dry mass of films used in the reactors [eq. (9)]. This step

allows calculating the maximum theoretical CO_2 production obtained in the biodegradability test:

$$ThC_{CO2M} = \frac{(DM)(\%C)}{12} \tag{9}$$

ThC_{CO2M} = Maximum theoretical moles of CO_2 that DM (g) can produce DM = Dry mass of test material added to reactors. %C = Percentage of carbon calculated from the chemical composition of the test material.

Biodegradation of the test material was determined by following the ASTM D 5338-03 methodology. The percentage of biodegraded material was calculated as the ratio of the average CO_2 production of the MnSt-LDPE films and the ThC_{CO2M} (the following equation):

$$\%BioDeg = \frac{(C_g)_{Rtest} - (C_g)_{Rblank}}{ThC_{CO2M}} = \frac{(C_g)_{TestMat}}{(ThC_{CO2M})} \tag{10}$$

where %BioDeg = percentage of biodegraded test material. (C_g) = amount of carbon converted to CO_2 (g). Rtest = Test material reactor. Rblank = Compost control reactor. TestMat = Test material (MnSt-LDPE films or cellulose) ThC_{CO2M} = Maximum theoretical amount of CO_2 production (g).

Statistical Analysis. Because the six reactors were treated under the same conditions, the ANOVA measuring design was applied in this experiment. Two reactors of each material were evaluated (cellulose, MnST-LDPE films and compost). Biodegraded MnST-LDPE films were analyzed to reveal possible effects on the quality of the compost, by characterizing organic matter, nitrogen, and CO_2 production during 90 days of experimentation.

RESULTS AND DISCUSSION

Abiotic Degradation

Abiotic degradation of LDPE with oxidant additives occurs in the presence of UV light (photodegradation) or heat (thermodegradation).[28] MnSt-LDPE-Films as pro-oxidant additives were characterized by measuring EB %, CI, and M_w, as functions of the ETF after the thermal treatments (Table II). Data are plotted in Figures 1–3. Observation of these plots reveals that EB % and viscosity diminish as a power- law with
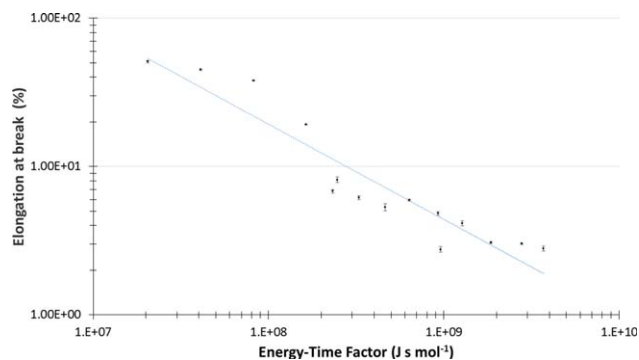

Figure 2. Elongation at break % as a function of the Energy-Time Factor for MnST-LDPE-films. The films were thermally degraded at different temperatures (50°C, 60°C, and 70°C), with different exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
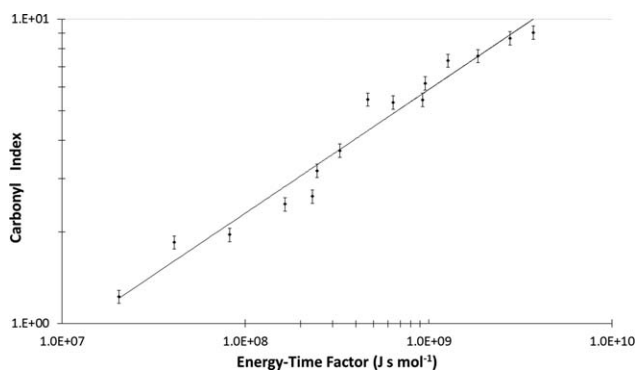
Figure 3. Carbonyl Index as a function of the Energy-Time Factor for MnST-LDPE films. Films were thermally degraded at 50°C, 60°C, and 70°C with different exposure times.

increasing ETF, and CI augments with ETF, also as a power-law. These plots, or primary plots, relate directly experimental data with exposure time and thermal energy.

Previous studies that relate M_w with shear viscosity in degraded films have not considered the correlation of the change in viscosity with an Energy-Time Factor as is analyzed here.[22] In Figure 1, experimental data of the variation of viscosity with ETF is illustrated.

Previous studies on the photo and thermal degradation of PE films with added oxidant additives indicate that the EB % is reduced with exposure time keeping the temperature constant, and also a reduction is measured for increasing temperature keeping the exposure time constant.[6,8,12, 25] Here, both effects are simultaneously plotted with the ETF. In Figure 2, it is shown that for ETF values larger than 9.29 E+8 J s mol^{-1}, the EB % renders values lower than 5%. The norm ASTM D 3826-98 (2002) points out a limit of 5% in the EB % to start the biodegradation stage tests.

CI data versus ETF is shown in Figure 3, thereby increasing as a power-law. The increment in the CI indicates degradation as the carbonyl group (C=O) concentration increases with both temperature and exposure time.[29] The mechanisms of thermal degradation using oxidant additives make LDPE susceptible to hydro-peroxidation by Norrish reactions.[30] The general mechanism of oxidation reactions includes three stages: initiation, propagation, and termination. In the first stage free radicals have generated because of C-H bond breakage forming peroxides and unstable hydro-peroxides; the C-C bond breakage also contributes to molecular weight loss. Along the propagation and termination reactions, the peroxides react to form stable compounds such as alcohols, aldehydes, ketones, and carboxylic acids.[31] Carbonyl compounds have been identified by the measurements of the CI (see Figure 4).[32] Data in Figure 8 reveal that for ETF larger than 9.29E+8 J s mol^{-1} (value at which the EB % is 5%) CI is larger than 5.45. This value is lower than that reported for LDPE-Films with molecular weights around 6000 g mol^{-1} (conditions reported as susceptibility of biodegradation).[20,24]

Previous studies on the thermo-oxidation of blown LDPE-Films with oxidant additives considered a range of temperatures of 55°C, 70°C y 100°C, with exposure times of 0, 100, 200, 300, 400, 500 y 600 h (which gives higher values of ETF than those considered here). Such conditions are not suitable in the compost process. There are, however, similarities with this work in analyses reported elsewhere where values of EB % of 5%, 2% y 1% with CI values of 4, 8 y 14, are disclosed, respectively.[2] In addition, in thermo-oxidized films treated with MnSt y CoSt at 70°C during 75 h, EB % presented values of 10% and 5%, with CI values of 12 and 14, respectively.[6] Similar tendency was obtained in this work, with a range of 2.7%-5% (EB %) with CI values of 5.45-9.45. These data validate experiments and calculations.

By appropriate calibration, the viscosity of dilute polymer solutions may be associated to the M_w of the polymer. Usually M_w distribution fractions are related to the intrinsic viscosity $[\eta]$ by the Mark-Houwink relationship [eq. (1)], where η_o, is shear viscosity; M_w, is weight average Molecular Weight; α, a power-law exponent, and k is a constant that depends on temperature. The power-law exponent α depends on fluid properties, were $\alpha < 1$ if the fluid is shear thinning, $\alpha > 1$ if the fluid is shear thickening, and $\alpha = 1$ if the fluid is Newtonian.
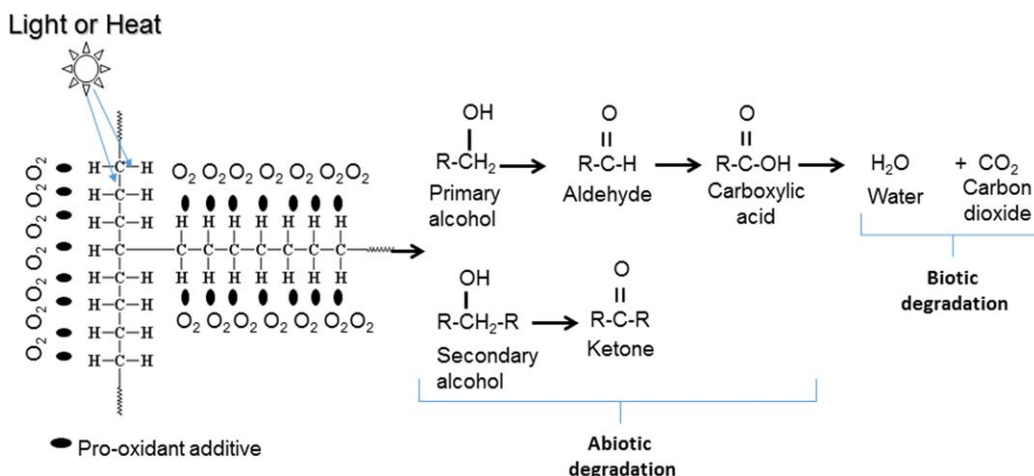

Figure 4. Subproducts of polyethylene abiotic and biotic degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. M_z/M_w Ratio, k and M_w and Expressions to Calculate the Viscosity

Molecular weight (M_w) g mol^{-1}	M_z/M_w	k	α	Equation
$M_w > $ Mwc	1.8	0.0027	3.4	$\eta = 0.51(0.0027)M_w^{3.4}(1.8)^{0.8}$
$M_{wc} = 35{,}000$				
20,000–34,000	27	0.0027	1	$\eta = 0.51(0.0027)M_w^1(27)^{0.8}$
<19,000	20	0.0065	1	$\eta = 0.51(0.0065)M_w^1(20)^{0.8}$

The dependence of viscosity on M_w is more pronounced in entangled systems, and for this reason, polymers which have $M_w > $ Mwc the power-law exponent is $\alpha = 3.4$, and for $M_w < $ Mwc, $\alpha = 1$. This relationship is observed for many linear entangled polymers.[22,23] An improved relationship for polydisperse polymers with $M_w/M_n > 1.5$ is given in eq. (2). This equation allows calculating the viscosity from molecular weight data of M_w and M_z.

To establish the relationship between the molecular weight and viscosity, eq. (2) was used, so it was necessary to calculate and define the values of k, M_z/M_w, and α. The value for k was calculated with the Flory-Schulz Distribution function eq. (3). Here k is the coupling constant, defined as the number of independently growing chains required to form one dead chain.[20] Because the M_z/M_w ratio and k increase with M_w, it was necessary to fix them for various ranges of M_w (Table III) to calculate the viscosity.

The Mwc of LDPE is reported to range between 35,000 and 85,000 gmol^{-1}, so an average value of Mwc = 35,000 gmol^{-1} was given. For M_w values larger than Mwc, $\alpha = 3.4$, and for values lower than Mwc, $\alpha = 1$ (see Table III). To calculate the relationship of viscosity with M_w (see Figure 5), three equations were proposed in Table III, with the previously established parameters of the modified Mark-Houwik equation.

Experimental data (Δ) of this study were complemented by reported data ($\square$).[34] GPC data analysis of thermally degraded LDPE-Films with MnSt ($\blacktriangle$) and CoSt ($\blacklozenge$) are shown together

with viscosity calculations using the modified Mark-Houwink equation. These results are in agreement with data from several authors and they are strongly supported by the values obtained with the Mark-Houwink equation.[20–22,24]

In Figure 1, the viscosity was plotted against the ETF. Considering the variation of viscosity with M_w depicted in Figure 5, it is possible to express the variation of ETF with M_w and this is shown in Figure 6.

The relationship between ETF and M_w shown in Figure 6 reveals within a single semi-log correlation, in a direct manner, how the exposure time and temperature affects the M_w of LDPE-Films under the thermal treatment with pro-oxidant additives. It is shown that for an ETF of 2.79E+9 J s mol^{-1}, the M_w reduces down to 6000 g mol^{-1}, which is the observed condition for the possibility of biodegradation.

In Figure 7, the EB % is plotted against M_w. This plot has been built from data of Figure 2 (EB % versus ETF) and with the correlation shown in Figure 6 (ETF versus M_w). Despite the power-law variation of the EB % versus ETF, a linear three-staged variation of EB % with M_w is revealed. The slope changes are observed to occur at M_w of 84,000 and 60,000 g mol^{-1}, for EB % of 8% and 38%, respectively. Below $M_w = 60{,}000$ g mol^{-1}, EB % is not affected by entanglements, and above 84,000 g mol^{-1}, entanglements dominate the onset for EB %. The transition region in the range 60,000–84,000 g mol^{-1} is ascribed to the beginning and end of the entanglement formation process as the M_w increases above the onset of the Mwc as reported between 35,000 and 85,000 g mol^{-1} for LDPE.[24] For required conditions for biodegradation, it is observed that the thermo-oxidized films have M_w around 6000 g mol^{-1} with EB % of 3% approximately.

In Figure 8, data from Figure 4 (CI versus ETF) and the correlation shown in Figure 6 (ETF versus M_w) produce the semi-log
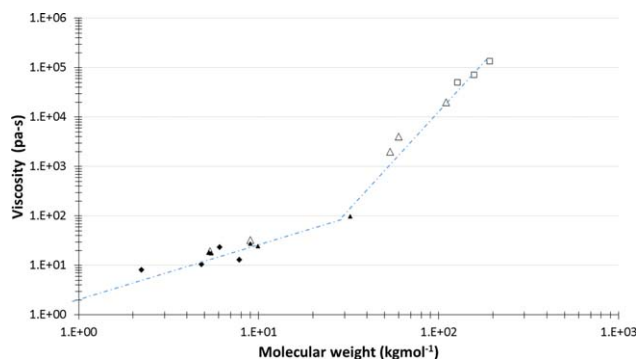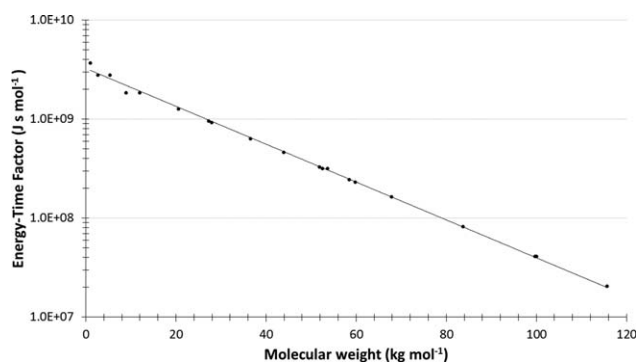
Figure 5. Viscosity versus M_w of LDPE-Films exposed at different conditions of experimental abiotic degradation. M_w and viscosity values were reported by Michael, 1994 ($\square$). Experimental data of this work (Δ) with MnSt as oxidant. Viscosity calculated by the modified Mark-Houwink equation with ($\blacktriangle$) MnSt pro-oxidant additive and with ($\blacklozenge$) CoSt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

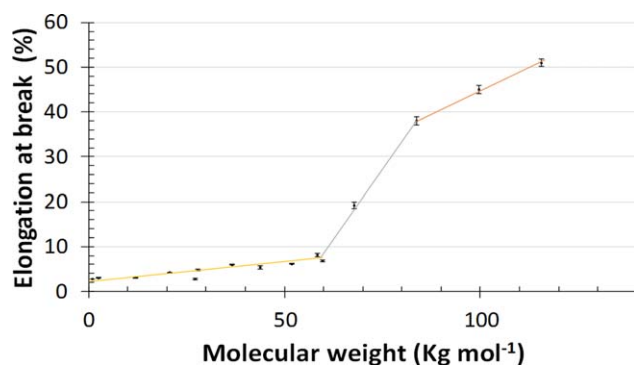**Figure 6.** ETF versus M_w during the thermal treatment.

Figure 7. EB % variation with M_w of thermally-degraded MnSt-LDPE-Films as pro-oxidant additive. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Abiotic Degradation

M_w (gmol^{-1})	CI after thermal treatment (ICC=O)	Abiotic degradation percentage (%D) (ICC=O/ICmax)
115,660	1.23	13.46
99,710	1.85	20.25
100,000	1.85	20.25
58,460	3.18	34.80
51,840	3.71	40.61
27,940	5.45	59.65
11,980	7.58	82.96
8990	7.80	85.37
5360	8.67	94.89

Relationship between M_w, CI, and %D.

variation of the CI with M_w. The CI value at 118,000 g mol^{-1} indicates the degradation involved in the thermo-mechanical work made in the film-making process, and the CI value obtained by extrapolation at $M_w = 0$ indicates complete degradation of the polymeric material into carbonyl groups.[36] Elsewhere, a correlation of CI with M_w was reported (calculated from the bands at 1640–1840 and 1463 cm^{-1}). Although values are slightly different, same trend of data is reported (CI of 0.25 is measured with a M_w of 160,000 g mol^{-1}; for a $M_w = 4400$ g mol^{-1}, the CI increased to 4.4).

Figure 8 shows that for a M_w smaller than 6000 g mol^{-1}, a CI value larger than 8.5 is measured. In previous studies, similar values were reported by Ref. 29 in thermally oxidized films at 60°C and 100°C during 14 days. Results show M_w values of 190,000 and 9000 g mol^{-1} with CI of 1.2 and 8, respectively.

To reach conditions by which LDPE is susceptible to biodegradation, as International Standards establish, it is required a value of ETF larger than 2.79E+09, allowing M_w lower than 6000 g mol^{-1}, EB % lower than 3%, CI larger than 8.67 and viscosity values lower than 17 Pas. A 3% EB % value may be reached when the M_w is 9000 g mol^{-1} and with a CI of 7.58 and with an ETF of 1.86E+09.

The degradation percentage is disclosed in Table IV, with initial conditions after the extrusion of the films of $M_w = 118,000$ g mol^{-1} and CI = 1.22. M_w of order of 6000 g mol^{-1} reported as
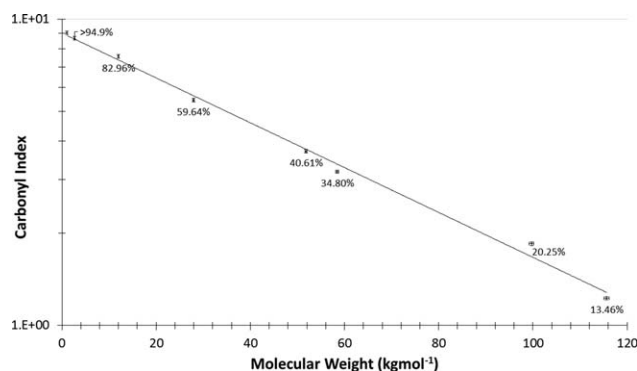

Figure 8. Carbonyl Index against molecular weight during the thermal treatment and percentage abiotic degradation.

susceptible to biodegradation have a 95% abiotic degradation degree, with a CI of 8.4. With the lowest ETF used (2.05E+0 7 J s mol^{-1}) the degradation degree of the MnST-LDPE-Film is 1.98%, corresponding to a M_w of 115,000 g mol^{-1} and CI of 1.28. These figures are consistent with results reported elsewhere,[37] namely, for a M_w of 6720 g mol^{-1}, LDPE-Films degrade between 45% and 60% in soil and compost, respectively, after 600 days (1.7 years). A report presented results of film degradation at 60°C during 4 weeks and reached M_w around 3000 g mol^{-1} with 60% degradation during 200 days of exposure.[31]

These results of abiotic degradation may be contrasted with those reported elsewhere[3] which point out that LDPE without additives degrades less than 0.5% during 100 years, and with sun exposure, this amount is increased to 1% the percentage of biodegradation.

Biotic Degradation

As explained in abiotic degradation section, for biodegradation of the MnSt-LDPE films, abiotic degradation was required with an ETF higher than 2.79E+09 J s mol^{-1} to obtain M_w lower than 6000 g mol^{-1}. After the abiotic degradation stage, the molecular weight of the MnSt-LDPE films changed from 118,000 to 5285 g mol^{-1}. The percentage of degradation was 91.8%, and it is known that for molecular weights lower than 6000 g mol^{-1}, the films can be biodegradable and compostable. To ascertain this possibility, the films biodegradation is analyzed in this section.

Elsewhere, Suresh et al., worked with MnSt-LDPE films which were thermally degraded with an ETF higher (8 days at 50°C, 60°C, and 70°C) than those used in this work, with reported M_w values of 30,000, 13,000, and 4000 g mol^{-1}, respectively. However, with those values, these samples of LDPE films are not susceptible to biodegradation, since values of molecular weights sought should be lower than 4000 g mol^{-1}, otherwise they are not suitable for the composting process.[8]

ASTM D 5338 establishes initial requirements to inoculum into biodegradability tests, which comply with these experiments according to the following conditions. Production of CO_2
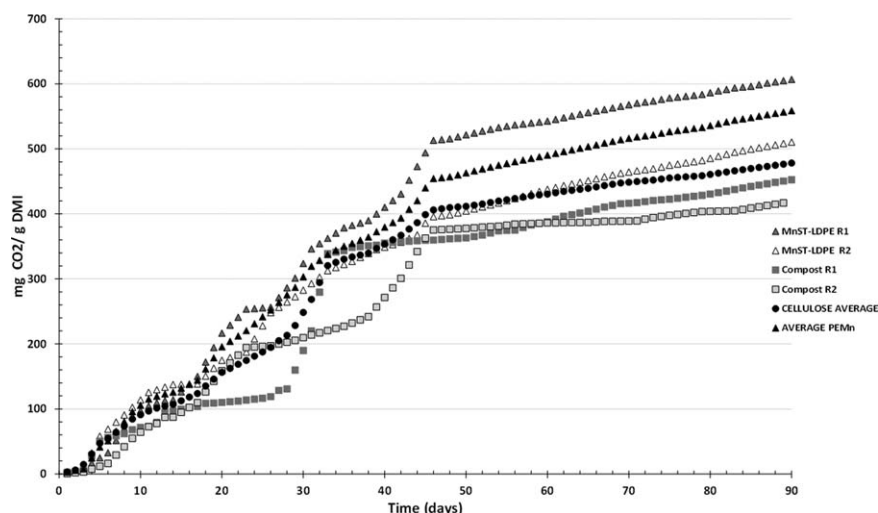
Figure 9. Cumulative CO_2 production of test material and blank reactors, during 90 days of compost process. Where (Δ) is MnST-LDPE-Films, ($\bigcirc$) cellulose and ($\square$) blank reactor. CO_2 production is reported in mg CO_2 by g of Dry Matter Initial (DMI).

during the first 10 days was measured between 64 and 149 mg CO_2/gDMI-1; an initial pH was between 7 and 7.3, the ratio of C/N was around 10 and the ash content was 54.2%, 61.6%, and 70% for MnSt-LDPE films, cellulose, and compost respectively.

Cumulative CO_2 production was quantified to evaluate the biodegradation of films and oxygen consumption for a specific period. MnSt-LDPE film reactors produced an average of 514 mg CO_2/g Initial Dry Matter (DMl) during the 90 days period. These values are equivalent to an average respiration rate of 0.17 mg O_2 g DMI-1 h-1. Reactors with the positive control (cellulose) showed an average 478.15 mg CO_2/gDMI and respiration rate of 0.16 mg O_2.gDMI^{-1}h^{-1} (Figure 9).[37] Control compost reactors produced 449.7 mg CO_2/g DMI and had a respiration rate of 0.15 mg O_2 g DMI-1 h-1). Important observations reveal that the MnSt-LDPE films produced more CO_2 than under compost control.

Barrena et al., 2011, reported a biodegradability classification of organic materials, via respiration activity measurements.[37] They suggest that biodegradability of organic waste could be classified into three categories: highly biodegradable wastes (respiration activity higher than 5 mg O_2 g Organic Matter^{-1}h^{-1}), moderately biodegradable wastes (2 to 5 mg O_2 g Organic Matter^{-1}h^{-1}), and low biodegradable waste (lower than 2 mg O_2 g Organic Matter^{-1}h^{-1}). Considering that in this research the respiration rate was measured between 0.17 and 0.15 mg O_2.gDMI^{-1}h^{-1}, the MnSt-LDPE films can be classified as a low- biodegradable waste. However, it is observed that respiration rate obtained in all reactors is larger than that reported elsewhere,[38] where 1500 mg CO_2/gDMI were measured in a period of 600 days, equivalent to a respiration rate of 0.075 O_2.gDMI^{-1}h^{-1}.[37]

The carbon content changes obtained in each reactor were estimated from the organic matter composition during the biodegradation test (0, 45, and 90 days). The carbon content diminishes during time because of CO_2 production, for this reason is important to compare carbon content losses with carbon converted in CO_2. Losses were detected between 34.4 and 39.6 g

of carbon with respect to 304 g (Initial Dry Matter [DMI]) of initial compost plus the test material. These data are consistent with carbon mass measured by quantification of CO_2 by titration during 90 days. Compost produced 36.3 g C, cellulose 38.6 g C, and the MnSt-LDPE films 41.8 g C (Table V).

For shorter times, same trend was observed in the CO_2 production, in contrast to results reported elsewhere.[38] A difference in CO_2 production between PE films and controlled-reactor compost after 150 days was reported. Here, repeated measurement analysis indicated that after 30 days there are significant differences in CO_2 production between MnSt-LDPE films, cellulose, and compost, with a 95% confidence and a ($P = 0.000$).

In the MnSt-LDPE films, 91.4% of previous abiotic degradation achieved with an ETF of 2.79E+09 J s mol^{-1} produced 74% of biodegradation along 90 days (average time of the composting process). These results allow verifying the correlation between abiotic and biotic degradation. On the other hand, Chiellini et al., 2003, achieved 45% and 60% biodegradation in 600 days (Figure 10).[38] The above information shows that in this research, biodegradation obtained was 14% larger and with 1/7 of the time required by Chiellini et al., 2003. In other cases, LDPE-Films with pro-oxidant additives and M_w near 7000 g mol^{-1}, were subjected at the same compost conditions and obtained only 30% of biodegradation in 425 days.[36]

Here, it was confirmed that if the LDPE-films have molecular weights smaller than 6000 g mol^{-1}, the conditions of susceptibility to biodegradation are fulfilled. Thermal oxidized MnSt-LDPE films with M_w lower than 6000 g mol^{-1} increased 24, 8, and 4 times the rate of biodegradation. This contrasts with M_w of 183,000 and 28,000 g mol^{-1} which have 1% of biodegradation in 90 days, treated under same conditions, as reported elsewhere.[39]

In addition, material-disintegration requirements were reached in 45 days during the composting process (ASTM D 6400-04), because the MnSt-LDPE films are not visible for more than 45

Table V. Biotic Degradation

Day 0	Dry Matter Initial (g)	MO (%)	MO g	% C	C(g)	C (g) produced in CO_2	%N	C/N
MnSt-LDPE-Films	304	36.96+-0.55	112.36	21.44+-0.55	65.17	0	2.82+-0.41	10.55+-1.77
Cellulose	304	36.17+-2.58	109.96	20.98+-2.38	63.77	0	3.10+-0.32	6.78+-0.57
Compost	304	34.99+-2.43	106.37	20.29+-2.33	61.69	0	3.39+-0.23	10.68+-1.90
Day 45	Dry Matter 45 day (g)	% MO	MO g	% C	C(g)	C (g) produced in CO_2	%N	C/N
MnSt-LDPE-Films	272.48	34.62+-1.63	94.33	20.08+-0.87	54.71	10.46	2.20+-0.05	9.11+- 0.56
Cellulose	265.18	33.44+-3.29	88.68	19.40+-0.77	51.43	12.34	1.40+-0.02	13.88+- 2.43
Compost	275.99	32.33+-2.55	89.23	18.75+-0.48	51.75	9.94	1.77+-0.12	10.57+- 0.52
Day 90	Dry Matter 90 day (g)	% MO	MO g	% C	C(g)	C (g) produced in CO_2	%N	C/N
MnSt-LDPE-Films	262.99	16.78+-0.70	44.13	9.73+-0.49	25.60	39.57	1.82+-0.39	5.35+- 1.56
Cellulose	255.08	17.48+-1.08	44.59	10.14+-0.83	25.86	37.91	2.83+-0.07	3.58+- 0.30
Compost	267.24	17.59+-0.90	47.01	10.20+-0.66	27.26	34.43	3.04+-0.08	3.35+- 0.27

Reactor characterization during biodegradability test.

days in the Organic Fraction Solid Waste (OFSW) compost process (Figure 11).

CONCLUDING REMARKS

In this work, a relationship between the relevant variables, which determine the abiotic and thermal degradation of LDPE-Films with pro-oxidant additive (MnSt), was found. For temperatures of 50°C, 60°C y 70°C and exposure times between 2 h and 384 h, data of viscosity, EB %, and CI could be univocally related to an ETF during the thermophilic stage of the compost process. Through the existing relationship of viscosity with M_w, as measured by GPC and corroborated with the Mark-Houwink equation, the variation of viscosity with M_w was calculated, and subsequently, a unique relationship of the

variation of the ETF and M_w was found. On this basis, the EB % and CI functionality with M_w provided the sufficient information to assess the suitability of the degradation methodology, using manganese stearate and other pro-oxidant additives with PE.

This research offers the possibility of determine the susceptibility for biodegradation within compost conditions. Hence, the insight on the relevant variables affecting the biodegradation process of LDPE-Films to find suitable materials for compost remains open. Indeed, in spite of the presence of reports on materials biodegrading 60%, this amount does not occur during the times and thermal treatments feasible in the compost process, considering an average time of 90 days.
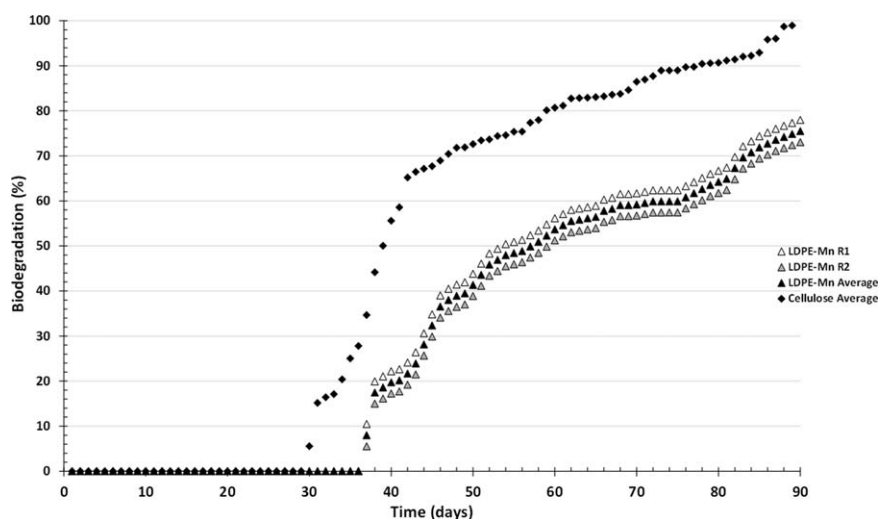

Figure 10. Biodegradation percentage of MnSt-LDPE-Films and cellulose, during 90 days under controlled compost conditions process.

Figure 11. (a) Reactor with MnST-LDPE-Films after15 days. (b) Reactor with MnST-LDPE-Films after 30 days. (c) Reactor with MnST-LDPE-Films after 45 days. (d) Reactor with cellulose after 7 days. (e) Reactor with cellulose after 45 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To better establish the conditions for film production respect to the times for biotic and abiotic degradations, it is required to precisely set additive concentrations and production-control variables to assure a complete biodegradation, bearing in mind the ambient and environmental consequences. In this context, films are required to have a M_w of the order of 6000 g mol^{-1} to be susceptible to biodegradation.

Taking into account the ASTM D 6400 procedure, the MnSt-LDPE films with a molecular weight less than 6000 g mol^{-1}, are classified as degradable, biodegradable and compostable.

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