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ORIGINAL PAPER

Effect of ultrasonic irradiation on low-density polyethylene molecular structure

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Abstract

The effect of ultrasonic (US) irradiation on solutions of low-density polyethylene (LDPE) was studied. Different irradiation times and intensities were examined. It was found that gel content increased very little as a result of US irradiation. However, this increase showed no variation with either the US irradiation time or intensity. The IR spectra of irradiated LDPE showed new absorption bands, indicating the presence of C–O groups, assumed to be the result of the US irradiation. GPC showed that the LDPE average molecular weight (Mw) decreases with an increase in either the US irradiation time or intensity. But these MWD curves, however, do not say if the "observed" modifications in Mw are due to chain scission or chain branching, which was inferred from the chain scission distribution function (CSDF) curves. From the GPC curves, it appears that chain scission is the dominant reaction at all US irradiation times and intensities. On the contrary, using the CSDF methodology, it appears that chain scission is the dominant reaction up to the intermediate irradiation times and intensities, but chain branching becomes dominant at the US higher times and intensities. On the contrary, using the proposed methodology, it appears that chain scission is the dominant reaction up to the intermediate irradiation times and power intensities, but chain branching becomes dominant at higher times and power intensities.

Keywords Polyethylene · Ultrasonic irradiation · CSDF · Molecular weight

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Introduction

Polyethylene is among the most widely used polymers because of its low cost, low weight, low temperature toughness, low density, low moisture absorption, good optical properties, and ease of processing and recycling. In recent years [1–13], interest in using high-intensity ultrasonic radiation, as an alternative method for the generation of free radicals in polymers, has arisen. Some studies [12–25] have reported on the effect of ultrasonic energy on polymer degradation in which temperature has a significant effect. The time and intensity of incidence of the ultrasonic energy play an important role in the formation and rate of formation of free radicals, which ultimately will be related to the degree of chain degradation and/or cross-linking and therefore will have a direct influence on the performance and properties of the polymer [26].

Knowledge of the effect of different operating parameters of ultrasonic energy, such as time and intensity of irradiation, on the polymer properties is very important in order to recommend the most suitable operating conditions for large-scale operation [14, 17].

The chemical effects on the polymers caused by the ultrasonic irradiation (sonochemistry) are commonly related to the phenomena of acoustic cavitations which are the formation of bubbles with the negative pressure. These bubbles grow to a certain size, become unstable, and collapse [6, 7]. These implosions produced during the bubble's collapse generate high temperatures (>5000 K), high pressures (>20 MPa: >200 kg/cm^2), and high rates of cooling (>107 K/s) which are large enough to break chemical bonds [4, 23, 26]. Polymer chains sufficiently close to the collapsing bubble will experience very high stresses along the chain that can cause various levels of uncoiling, bond deformation, or scission [2]. Bond scission tends to occur more readily in high molecular weight polymers, as has been reported by Wu et al. [7] and Kaan and Isayev [27], and this scission is more probable near the middle point of the chain [2, 6, 21, 25, 28–57].

Considering the above-mentioned facts, it is evident that if a polymer macromolecule is subjected to ultrasonic irradiation, its degradation is inevitable. Shifting of the GPC curves to lower molecular weights is commonly observed during studies of polymer degradation due to the action of ultrasonic irradiation [7, 11, 21, 39, 40]. However, it is still difficult to discriminate which is the governing mechanism between chain scission or chain branching, or both. In addition, it is difficult to establish the effect of the polymer initial molecular weight on the preferred occurrence of each mechanism.

In order to differentiate these subtle changes due to the different initial molecular weights (when subjecting a polymer molecule to ultrasonic irradiation), David et al. [26] proposed the use of the "chain scission average number" (ChSc), which can quantify the magnitude of the degradation process. This is obtained from the ratio of the "number average molecular weight" of the non-degraded sample (Mn_0) to that of the degraded sample (Mn_f). This ChSc parameter, however, represents just one point in the GPC curve, does not cover the entire MWD curve.

In this sense, a study by Canevarolo [44], of the degradation during multiple extrusion of PP, proposed a method that estimates the average number of chains that participate in the degradation processes, both, by chain scission and chain branching, as a function of the initial Mw. This is known as the chain scission distribution function (CSDF), and this does considers the entire MWD curve. This methodology has been used by Martini et al. [45] to study the degradation process of PP, in solution, when subjected to high temperature and high pressure. Otaguro et al. [46] studied the effect of gamma radiation on the PP chain scission and branching. Penheiro et al. [47] studied the HDPE degradation during processing in an internal mixer and observed that Phillips-type HDPE produces a higher level of chain branching than the Zieglere Natta's type at the same processing conditions. Cáceresa et al. [48] studied the thermomechanical degradation of PP with and without thermal and UV stabilizers in a twin-screw extruder using the CSDF methodology, finding a predominant chain scission at low molecular weights and a preferential chain scission at higher molecular weights. When the stabilizers were incorporated the cPP Mw is kept constant, even after four extrusions, independently of the stabilizers concentration used. Its chain scission is greatly reduced, only being noteworthy at high values of molecular weight, presenting in this case a preferential chain scission process. Cosate et al. [49] studied the PLA degradation during the extrusion in a single-screw extruder. During the PLA recycling in a single-screw extruder using a chain extender and applying the CSDF methodology, they found that the chain extender was able to recover the molecular weight although it caused an increase in the polydispersity, showing a change in the chain structure. In all these cases, the form of the CSDF curve is clearly related to the type of degradation process chain scission or chain branching. The interesting thing about this methodology is that it provides information on what type of long or short chains the type of polymer degradation process is carried out.

The goal of his work is to study the effect of high-energy and time ultrasonic radiation on molecular structure and molecular weight of polyethylene in solution, using the methodology proposed by Canevarolo [44], as well as a modification to this methodology, proposed in this study. These results will help to understand the structural changes and degradation processes of polyethylene when subjected to high-energy and time ultrasonic irradiation.

Experimental

Materials

The polyethylene used in this study was: low-density polyethylene (LDPE) of Mw = 194,500, Mn = 16,200, Mw/Mn = 12, and MFI = 25 g/10 min, from Sigma-Aldrich (USA). Xylene and acetone were from JT Baker (USA).

Methods

Ultrasonic irradiation of polyethylene solution

LDPE solutions in xylene were subjected to different times and amplitudes of ultrasonic irradiation, as shown in Table 1. The ultrasonic irradiation was produced using a 12.5-mm-diameter disruptor horn probe at amplitudes of 21, 76, and 146 μm, which correspond to power intensities of 50, 100, and 150 W, respectively. The instrument was a Model 250, from Branson Ultrasonics, Danbury, USA, with a maximum power output of 250 W at 20 kHz. All ultrasonic irradiations were carried out in a Branson reactor (Fig. 1), at 60 °C.

The polymer solutions were prepared by dissolving 1 g of polymer in 60 ml of xylene at about 120 °C and magnetically stirring it until completely dissolved. The solution was cooled down to about 60 °C, at which temperature the polymer still remained in solution. In this reactor, the solutions were sonicated in the presence of air, for different periods of time, at different intensities, as shown in Table 1. After the ultrasonic treatment, the polymer was precipitated with acetone at room temperature and separated by vacuum filtration. The polymer was then washed with acetone ten times to remove the xylene. The product was dried overnight in a vacuum oven at 40 °C.

Characterization

Gel content of samples was measured according to ASTM D2765, putting ca. 0.5 g samples under xylene reflux, at 120 °C for 12 h. Gel content was determined by differences in weight. Films of samples for FTIR were prepared by compression molding at 180 °C, under a pressure of 130 kg/cm^2, for 5 min. The carbonyl and C–O index of the different samples were conducted using an FTIR spectrometer (Nicolet Mod 710) with 32 scans. A high-temperature Waters GPC was used

Table 1 Designation of samples subjected to different times and intensities of ultrasonic irradiation

Sample	Ultrasonic irradiation intensity (W)	Ultrasonic irradiation time (min)
0	0	0
1	50	10
2	50	15
3	50	20
4	100	10
5	100	15
6	100	20
7	150	10
8	150	15
9	150	20

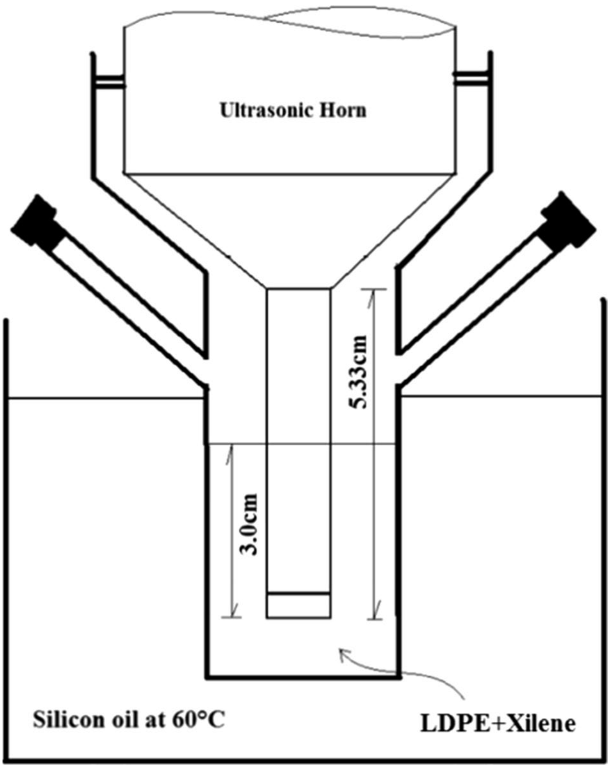


Fig. 1 Ultrasonic reactor

to determine the molecular weight distribution (MWD) of all polymer samples, using 1,2,4-trichlorobenzene (TCB), at 140 °C. In this case, each CSDF curve was obtained, using a proprietary Excel software, by comparing the MWD curve at a given time and intensity of irradiation, with the MWD curve of the original untreated LDPE. The chain scission distribution function (CSDF) curves were calculated using an Excel running software, called CSDF4.1, that is, comparing the sample treated for 15 min at 50 W, with the untreated one, and the sample treated for 20 min at 50 W, with the untreated one.

In the other case, each CSDF curve is obtained, using the same proprietary excel software, but comparing now the MWD curve at a given time and intensity of irradiation, with the MWD curve of the sample treated for the previous shorter period of time and the same intensity, that is, comparing the sample treated for 15 min at 50 W with that treated for 10 min at 50 W, and the sample treated for 20 min at 50 W with that treated for 15 min at 50 W.

According to Canevarolo et al. [44–47], the type of the CSDF curve indicates the type of reaction that occurs in the polymer being subjected to a degradation/modification process. CSDF values above zero (positive values) indicate that chain scission is happening, whereas CSDF values below zero (negative values) indicate that chain branching is happening. CSDF values above zero and constant (horizontal in a CSDF vs Log(Mw) graph) indicate random chain scission, irrespective of molecular weight, whereas CSDF values above zero with positive slope indicate random and preferential chain scission (preferential with respect to molecular weight, i.e., preferential degradation of the longest chains). CSDF values below zero and constant (horizontal in a CSDF vs Log(Mw) graph) indicate random chain branching, irrespective of molecular weight, whereas CSDF values below zero with positive slope indicate random and preferential chain branching (preferential degradation of the longest chains). CSDF curves with a slope ≠ zero (usually positive slope) indicate preferential chain branching (preferential degradation of the longest chains). If both processes (random and preferential chain scission) happen at the same time the curve will start with a constant positive value (slope equal to zero) that increases continuously (slope continuously increasing). The effect of ultrasonic irradiation on the crystallization and fusion behavior of the polyethylene samples was studied using a TA Instruments differential scanning calorimetry (DSC). The samples were first heated to 160 °C, at 5 °C/min, and let there for 3 min to eliminate any thermal history. Thereafter, the samples were cooled down at − 5 °C/min down to 25 °C to obtain the crystallization temperatures Tc and finally heated to 160 °C at 5 °C/min to obtain the fusion temperature.

Results and discussion

Gel content

Gel content increased very little as a result of ultrasonic irradiation. However, this increase showed no variation with either irradiation time or intensity. All ultrasonic irradiation-treated samples presented a gel content of 0.0050 ± 0.0006%. These results are presented in Table 2; however, this represents an increase of ca. 35% over the gel content of the untreated LDPE (0.0037% ± 0.0003). These results indicate that the cross-linking produced in the LDPE by this ultrasonic irradiation treatment is still negligible.

Table 2 Effect of ultrasonic irradiation time and intensity on gel content of LDPE, (%)

Ultrasonic irradiation time (min)	Gel content to different ultrasonic intensity (%)		
	50 (W)	100 (W)	150 (W)
10	0.0046 ± 0.0002	0.0058 ± 0.0001	0.0053 ± 0.0003
15	0.0056 ± 0.0001	0.0049 ± 0.0003	0.0048 ± 0.0003
20	0.0044 ± 0.0001	0.0050 ± 0.0006	0.0049 ± 0.0004

Infrared analysis

Figure 2 shows the FTIR spectra of samples 0, 1, 5, and 9 at increasing ultrasonic irradiation energies, as shown in Table 1. The spectra of irradiated LDPE showed new absorption bands (narrow) at 1250 and 1020 cm^{-1}. The significant increase in these bands indicates the presence of C–O groups. The C–O index, determined from the 1250 cm^{-1} band, for ultrasonic-treated LDPE sample 9 (time and power intensity of irradiation equal to: 20 min and 150 W), had a value of 0.074, while the LDPE without treatment did not show any peak at this wave number. These C–O groups are evidence of the occurrence of polymer oxidation due to ultrasonic irradiation. In addition, when polyethylene is degraded under ambient air and ultrasonic irradiation, oxidized structures like alcohols, aldehydes, ketones, esters are produced [42, 43], most of them showing the carbonyl group.

In our case, this carbonyl band around 1720 cm^{-1} was present in all cases, in the untreated as well as in the ultrasonic-treated samples, maintaining always a very similar weak intensity. That is, the ultrasonic treatment does not show any apparent effect on the carbonyl signal at 1720 cm^{-1}. This indicates that the oxidation mechanism of polyethylene is different. With high-energy ultrasonic irradiation and long exposure times, as in this study, the oxidative degradation process of polyethylene results in the formation of C–O groups only. Nonetheless, these results are different from those reported by Li et al. [15]. They found both C = O and C–O groups when subjecting HDPE to high-power intensity ultrasonic irradiation for 10 min.

According to these results, we suggest that the macro-radicals produced by ultrasonic irradiation are formed by chain scission. Then, the oxygen reacts with other macro-radicals to form the COOH groups. According to this, ultrasonic

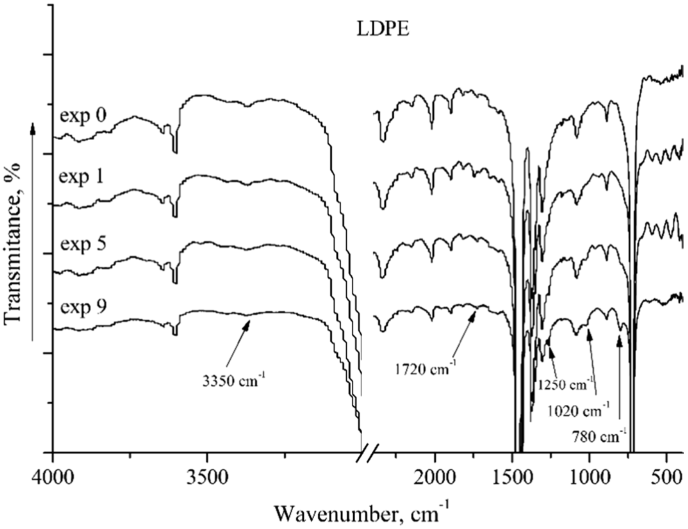
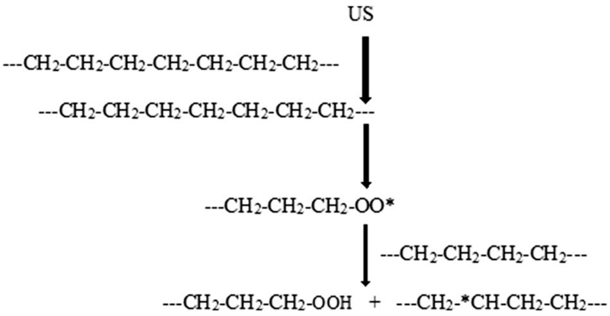
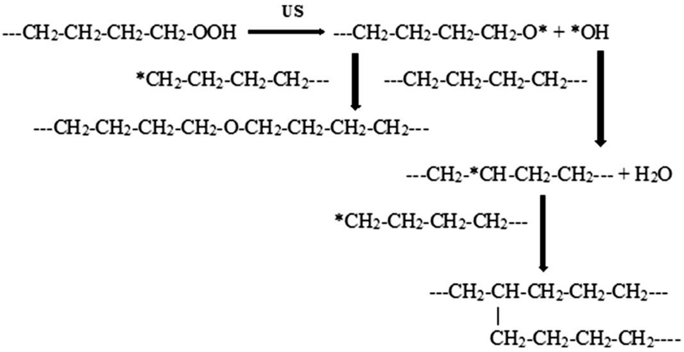


Fig. 2 FTIR of LDPE samples 0, 1, 5, and 9 of Table 1, which, respectively, correspond to samples treated with irradiation times and intensities of: 0–0; 10–50; 15–100; 20–150



Scheme 1. Suggested branching reactions of polyethylene under ultrasonic irradiation



Scheme 2. Suggested crosslinking reactions of polyethylene under ultrasonic irradiation

degradation of LDPE in solution can be symbolized as shown in Scheme 1. Hydroperoxides formed by the oxygen in the air can be decomposed to produce hydroxyl macro-radical that can attack other chains, forming –C–O–C– bonds and promote chain cross-linking by oxygen linkage. The –*CH–CH_2– macro-radical may lead to chains scission and/or chain cross-linking by oxygen linkage (Scheme 2).

Comparing the obtained results in US degradation mechanism with other reported degradation mechanisms of polymers applied high energy, an important difference in the LDPE oxidation can be identified. For instance, in weathering degradation, the UV irradiation can interact with the polymer to induce the formation of macro-radicals along the polymer chain and subsequently introduce oxygen O_2 [50]. This same process is observed in thermal [51] and gamma radiation [52] degradation. However, in US degradation, the macro-radical is generally formed during chain scission with the subsequent introduction of oxygen O_2 at the end of the chain. On the other hand, the amount of US energy considered in this study varies from low to high energy, which increases the oxidation magnitude to a certain extent. This simple difference in the polymer degradation by US radiation, which induces the formation of macro-radicals during the chain

Table 3 Effect of ultrasonic irradiation time on molecular weight and intrinsic viscosity of LDPE (constant ultrasonic power intensity of 150 W)

Ultrasonic irradiation time (min)	Mw ($\times10^4$)	Mn ($\times10^4$)	Mw/Mn	(η)
0	19.45	1.62	12.01	1.075
10	13.24	1.16	11.41	0.893
15	12.90	1.25	10.33	0.797
20	12.41	1.59	7.81	0.742

$(\eta) = \lim\{\phi\ 0\}\ (\eta - \eta_0)/(\phi\cdot\eta_0)$

Table 4 Effect of ultrasonic intensity on molecular weight and intrinsic viscosity of LDPE (constant irradiation time of 15 min)

Ultrasonic intensity (watts)	Mw ($\times10^4$)	Mn ($\times10^4$)	Mw/Mn	(η)
0	19.45	1.62	12.01	1.075
50	16.88	1.37	12.32	0.854
100	14.71	1.35	10.90	0.942
150	12.91	1.25	10.33	0.797

$(\eta) = \lim\{\phi \rightarrow 0\}\ (\eta - \eta_0)/(\phi\cdot\eta_0)$

scission, could be considered as a great scientific and technological advantage over the other types of degradation by the application of high energy. The specific knowledge of defining where hydroperoxide groups (COOH) will be formed in the chain, opens up the possibilities to control and/or modify the polymer functionalization. This is because this type of oxidized groups (COOH) is highly reactive according to previous studies of LDPE [53].

The effect of time and power intensity of ultrasonic irradiation on LDPE, in solution, was also determined by changes in molecular weight, molecular weight distribution, and intrinsic viscosity. The results are listed in Tables 3 and 4.

The average molecular weight (Mw) of LDPE decreases with an increase in either the time or the power intensity of ultrasonic irradiation. The GPC curves in Fig. 3 show a bimodal distribution for both, the untreated and the ultrasonic irradiated samples. Coinciding with Tables 3 and 4, the GPC curves in Fig. 3 shift to lower molecular weight as the time and/or power intensity of irradiation increases. Additionally, the intrinsic viscosity showed a significant change with the application of ultrasonic irradiation, decreasing with either power intensity and/or time of ultrasonic treatment, and this effect was also observed by Desai et al. [19, 20]. These changes clearly indicate a decrease in the molecular weight of LDPE due to ultrasonic radiation.

The thing here is that with these curves, it is difficult to establish if the “observed” modifications in molecular weight are due to chain scission or chain branching, or if these two different reactions occur at random or preferentially. Additionally, the GPC curves do not say if the initial polymer molecular weight has an influence on the reaction route or in the extent of the reaction.

In order to elucidate the questions presented in the last paragraph, the molecular weight distribution curves obtained from the GPC studies were used to obtain the “chain scission distribution function” (CSDF).

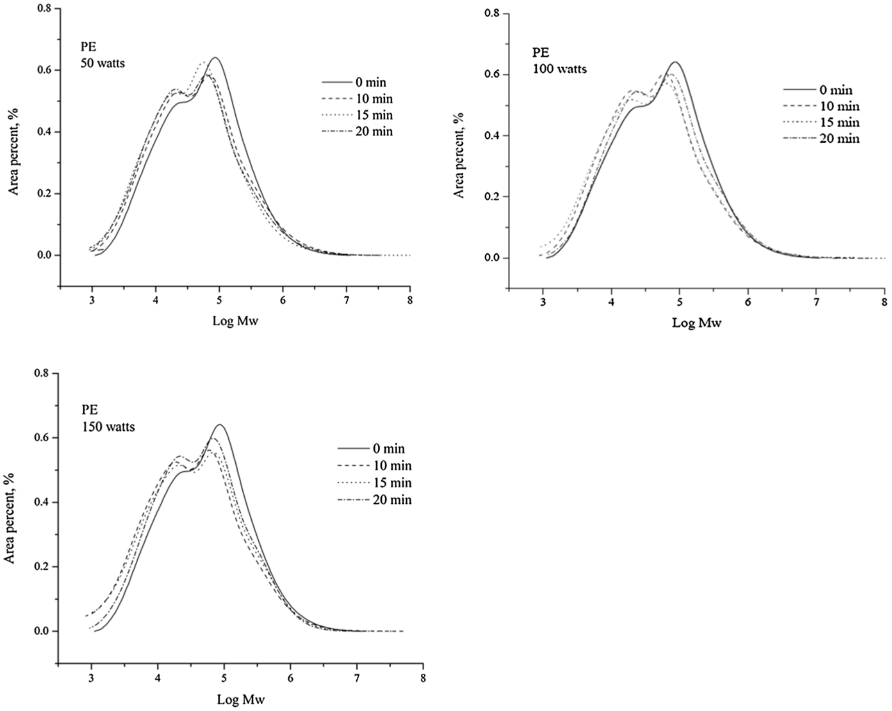


Fig. 3 Effect of ultrasonic irradiation time and intensity on the MWD curves of LDPE as obtained by GPC

CSDF curves

In the Canevarolo methodology, each CSDF curve is obtained, using a proprietary Excel software, by comparing the MWD curve at a given time and intensity of irradiation, with the MWD curve of the original untreated LDPE, that is, comparing the sample treated for 15 min at 50 W with the untreated one, and the sample treated for 20 min at 50 W with the untreated one. In this case, the CSDF curves are presented in Figs. 4a, 5a, and 6a, as a function of time and intensity of ultrasonic irradiation.

In the proposed modified methodology, each CSDF curve is obtained, using a proprietary Excel software, but comparing now the MWD curve at a given time and intensity of irradiation, with the MWD curve of the sample treated for the previous shorter period of time and the same intensity, that is, comparing the sample treated for 15 min at 50 W with that treated for 10 min at 50 W, and the sample treated for 20 min at 50 W with that treated for 15 min at 50 W. In this case, the CSDF curves are presented in Figs. 4b, 5b, and 6b, as a function of time and intensity of irradiation.

For an irradiation intensity of 50 W, Fig. 4a shows that, along the three irradiation intervals, between 0 and 10 min, 0 and 15 min, and 0 and 20 min, the CSDF

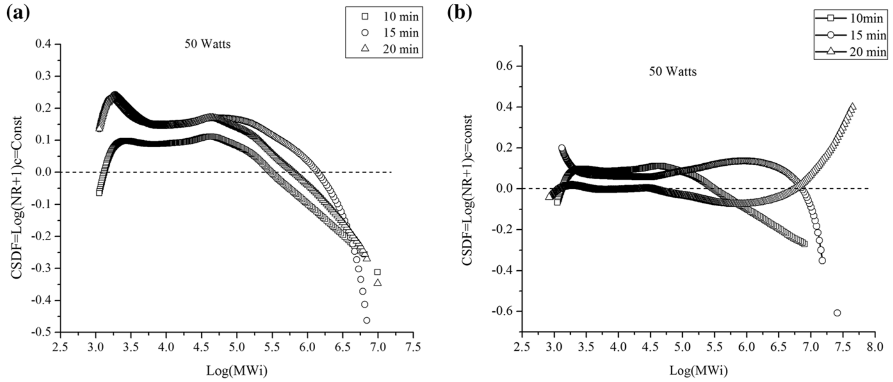


Fig. 4 Chain scission distribution function (CSDF) of LDPE, according to the methodology by Canevarolo (**a**) and according to the methodology proposed in this study (**b**), when subjected to different times to an ultrasonic irradiation intensity of 50 W

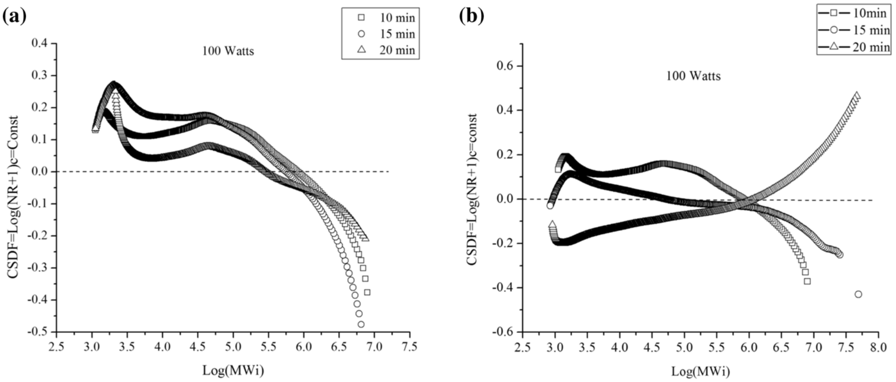


Fig. 5 Chain scission distribution function (CSDF) of LDPE, according to the methodology by Canevarolo (**a**) and according to the methodology proposed in this study (**b**), when subjected to different times to an ultrasonic irradiation intensity of 100 W

curves indicate that the ultrasonic irradiation produces mostly random chain scission, independently of the Mw. Figure 4b, on the other hand, shows that, along the two irradiation intervals, between 0 and 10 min, and 10 and 15 min, the CSDF curves indicate that the ultrasonic irradiation produces mostly random chain scission, independently of the Mw, whereas the third irradiation interval, between 15 and 20 min, indicates chain scission as well as chain branching.

For an irradiation intensity of 100 W, Fig. 5a shows that, along the three irradiation intervals, between 0 and 10 min, 0 and 15 min, and 0 and 20 min, the CSDF curves indicate that the ultrasonic irradiation produces mostly random chain scission, independently of the Mw. Figure 5b, on the other hand, shows that, along the first irradiation interval, between 0 and 10 min, the CSDF curve indicates that the ultrasonic irradiation produces mostly random chain scission, independently

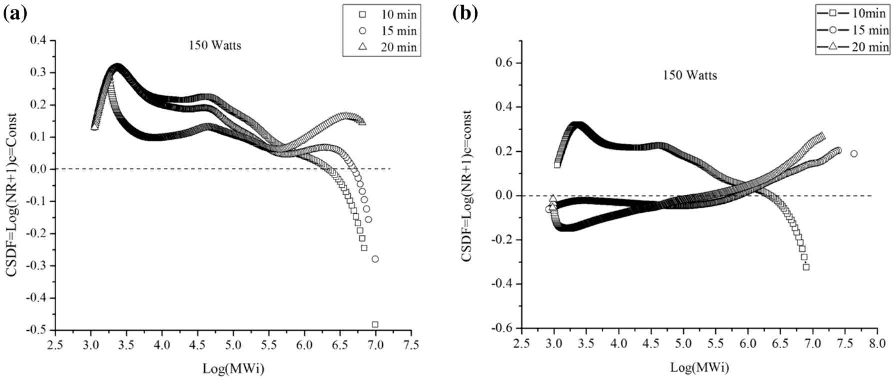


Fig. 6 Chain scission distribution function (CSDF) of LDPE, according to the methodology by Canevarolo (**a**) and according to the methodology proposed in this study (**b**), when subjected to different times to an ultrasonic irradiation intensity of 150 W

of the Mw, whereas the second irradiation interval, between 10 and 15 min, indicates chain scission in the low Mw part, as well as chain branching in the high Mw part, but finally, the third irradiation interval, between 15 and 20 min, produces apparently, only chain branching.

For an irradiation intensity of 150 W, Fig. 6a shows that, along the three irradiation intervals, between 0 and 10 min, 0 and 15 min, and 0 and 20 min, the CSDF curves indicate that the ultrasonic irradiation produces mostly random chain scission, independently of the Mw. Figure 6b, on the other hand, shows that, along the first irradiation interval, between 0 and 10 min, the CSDF curve indicates that the ultrasonic irradiation produces mostly random chain scission, independently of the Mw, whereas along the following two irradiation intervals, between 10 and 15 min and between 15 and 20 min, the CSDF curves indicate mostly chain branching, along the molecular weights being examined.

The occurrence of scattered data at very low and very high molecular weights (below 2000 and above 500,000 in our case) should be taken with care because the low concentration of chains in these regions greatly increases the uncertainty of the calculus. The discussion that follows, therefore, considers only the molecular weight data between 2000 and 500,000.

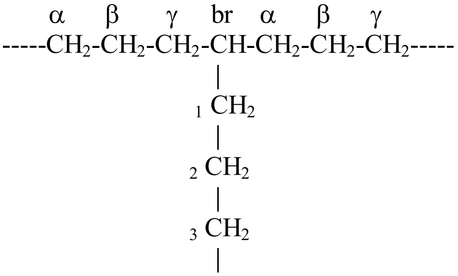
That is, if the complete interval is considered as a whole (the Canevarolo methodology), the CSDF curves tend to show the “average” or the “most dominant reactions”, as the ones that occur during the induced polymer modification/degradation. If this interval is sectioned (the proposed methodology), the CSDF curves will tend to show, again, the “average” or the “most dominant reactions”, but, of that section, as the ones that occur during the induced polymer modification/degradation. And the differences clearly stand out. According to the first methodology, all combinations of time and intensity of ultrasonic irradiation (Figs. 4a, 5a, 6a) indicate random chain scission reactions. But, according to the proposed modified methodology (Figs. 4b, 5b, and 6b), it seems that as the time and/or intensity of ultrasonic irradiation increases, the chain scission reactions give way to the chain branching reactions.

It appears then that, in general, at low ultrasonic irradiation intensities and/or times, polymer chain scission is the dominant reaction, but as intensity and/or time of irradiation increases, polymer chain branching tends to occur. These results show that through the use of ultrasonic irradiation, it is possible to mechanically activate the polymer chains, in order to produce chain alterations. Also, these results show that, depending on the time and intensity of irradiation, these chain alterations can be either chain scission or chain branching. This knowledge is very useful in the sense that, by selecting the intensity and/or time of ultrasonic irradiation, it is possible to produce certain desired alterations in the polymer chain.

Además comparando los resultados de los espectros FTIR de la Fig. 2 y los mecanismos de degradación propuestos en los esquemas 1 y 2 con las curvas de CSDF obtenidas, se puede destacar que con esta última técnica de análisis del peso molecular proporciona una perspectiva más clara de la degradación del LDPE a baja y alta energía ultrasonica, sobre todo proporciona el conocimiento de en qué tipo de cadenas (bajo, mediano o alto peso molecular) se está llevando a cabo la reacción de sciccion de cadenas y por lo tanto la oxidación del polímero con grupos hidroperóxidos (COOH) los cuales son altamente reactivos [53]. Este precedente abre la posibilidad de controlar con radiación US que tipo de cadenas se desean fracturar, oxidar y/o funcionalizar, con lo cual se pueden generar diferentes tipos de LDPE con MWD modificadas y estructuras ramificadas, así como la funcionalización de tipos de cadenas.

^{13}C RMN spectroscopy

Figure 7 shows the ^{13}C NMR spectra of untreated as well as ultrasonic irradiation-treated LDPE at increasing ultrasonic irradiation energies, as shown in Table 1. New bands around 29.9 ppm, indicating the presence of $(CH_2)n$, can be observed, which in time suggest the appearance of additional chain branches in the ultrasonic-treated LDPE [54–57]. A slight increase in the intensity of band at 33.8 ppm (which would correspond to CH; br), with respect to that at 29.9 ppm, corresponds to α of the treated LDPE. The branching scheme below represents localization of the C atoms in the branching of the LDPE structure [54, 55].



$$\begin{array}{cccccccccc} & \alpha & \beta & \gamma & \text{br} & \alpha & \beta & \gamma & \\ \text{-----} & CH_2- & CH_2- & CH_2- & CH- & CH_2- & CH_2- & CH_2 & \text{-----} \\ & & & & | & & & & \\ & & & & {}_1\,CH_2 & & & & \\ & & & & | & & & & \\ & & & & {}_2\,CH_2 & & & & \\ & & & & | & & & & \\ & & & & {}_3\,CH_2 & & & & \\ & & & & | & & & & \end{array}$$

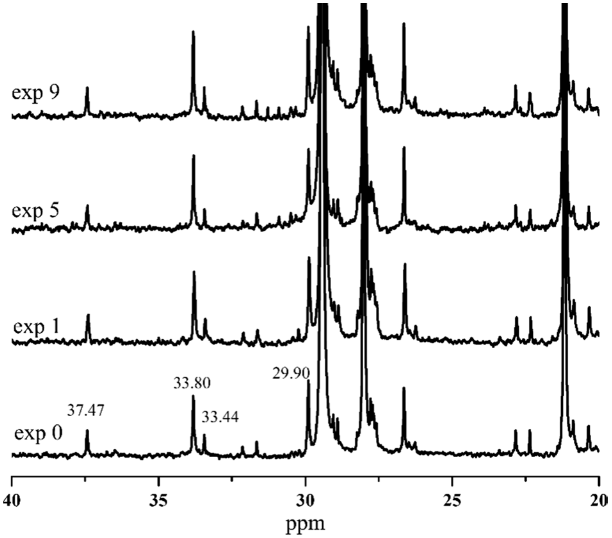


Fig. 7 13C NMR spectra of polyethylene with and without ultrasonic treatment

Figure 2 shows that, as time and power intensity of ultrasonic irradiation increased, the magnitude of the band at 780 cm^{-1} of the FTIR spectra also increased. This can be related to ethylene branches, as reported by Blitz and McFaddin [58] These FTIR results, in conjunction with those of the ^{13}C NMR, strongly indicate an increase in the number of branches in the LDPE molecule, as a result of the ultrasonic treatment.

Differential scattering calorimetry

Crystallization and melting results are presented in Table 5. The crystallization temperature (*T*c) increased with the ultrasonic irradiation, from 98.4 for the untreated LDPE to 100.4 ± 0.6 °C for all the treated LDPE samples, irrespective of the time and intensity of irradiation. That is, the effect of ultrasonic irradiation on *T*c is very little.

The melting temperature (*T*m), as well, increased with the ultrasonic irradiation, from 111.3 for the untreated LDPE to 111.9 ± 0.3 °C for all the treated LDPE samples, also, irrespective of the time and intensity of irradiation. That is, the effect of ultrasonic irradiation on *T*m is negligible.

The heat of fusion and the corresponding crystallinity percent, on the other hand, do change with an increase in time and intensity of irradiation. First, they decrease to the lowest values at 10 min and 50 W of ultrasonic irradiation, but then, they increase, though a little, with an increase in time and intensity of ultrasonic irradiation, up to 120.6 (J/g) and 41.4 (%), respectively, at 20 min and 150 W.

Table 5 Crystallization and melting behavior of untreated and ultrasonic-treated LDPE

Ultrasonic intensity (W)	Ultrasonic time (s)	*T*c (°C)	*T*m (°C)	ΔH_f (*J/g*)	Crystallinity (%)
0	0	98.4	111.3	115.6	39.7
50	10	99.8	111.9	112.7	38.7
50	15	100.1	112.3	113.2	38.9
50	20	100.4	111.6	114.3	39.2
100	10	100.7	111.9	114.5	39.3
100	15	100.1	111.8	115.4	39.6
100	20	100.5	111.7	116.4	39.9
150	10	100.2	112.0	115.1	39.5
150	15	101.0	111.9	120.3	41.3
150	20	100.7	112.2	120.6	41.4

Flexural modulus

Table 6 shows the flexural modulus results. It is noticeable a continuous reduction in modulus for all the ultrasonic-treated samples, indicating an eminent LDPE degradation by the ultrasonic radiation. This has relation with the reduction in Mw and viscosity results discussed before in Tables 3 and 4. At a power intensity of 100 and 150 w and 20 min of irradiation, the reduction in modulus is less drastic, which can be related to the prevalence of branching (longer and medium Mw chains) over chain scission reactions (higher Mw chains) that are occurring at these conditions. This is in accordance with the methodology proposed as discussed in Figs. 5b and 6b in which these branching reactions prevent the Mw to be reduced. The chain scission reactions (lower Mw chains) observed in the treated samples at lower irradiation times and power intensities (Figs. 4, 5, and 6) promoted a significant reduction,

Table 6 Flexural modulus of untreated and ultrasonic-treated LDPE

Sample	Ultrasonic irradiation power intensity (W)	Ultrasonic irradiation time (min)	Ultrasonic irradiation energy (KJ)[a]	Flexural modulus (MPa)[a]
0	0	0	0	315 ± 13
1	50	10	30	295 ± 9
2	50	15	45	297 ± 11
3	50	20	60	294 ± 17
4	100	10	60	281 ± 8
5	100	15	90	284 ± 12
6	100	20	120	292 ± 9
7	150	10	90	279 ± 15
8	150	15	135	275 ± 10
9	150	20	180	288 ± 11

[a] 1 Joule of energy = (1 Watt of power) × (1 s of time)

near 12%, on modulus. This indicates that the stiffness of LDPE strongly depends on the longer Mw chains. As was observed in Fig. 2, the LDPE oxidation was very low and had no significant effect in flexural modulus as is observed in Table 6 (samples 1, 5, and 9). The observed chain branching at high US energy and sonication times is directly proportional to the decrease in the chain ends which results in a less drastic reduction in flexural modulus, which can be seen in the results presented in Table 6 (samples 6 and 9). These results show that the LDPE mechanical properties can also be modified and controlled based on the US intensity and sonication time. This type of ultrasonic treatment can be an alternative for the control and modification of polyethylene properties.

Conclusion

Gel content increased very little as a result of ultrasonic irradiation. However, this increase showed no variation with either time or intensity of irradiation. All ultrasonic irradiation-treated samples presented a gel content of 0.0050 ± 0.0006%. These results indicate that the cross-linking produced in the LDPE by this ultrasonic irradiation treatment is still negligible. The IR spectra of irradiated LDPE showed new absorption bands (narrow) at 1250, 1020, and 780 cm^{-1}. The significant increase in these bands indicates the presence of C–O groups. We concluded that the radicals produced by ultrasonic irradiation are formed by scission at or near the middle of the chain. GPC showed that the average molecular weight (Mw) of LDPE decreases with an increase in either the time or the intensity of ultrasonic irradiation. But these curves do not say if the "observed" modifications in molecular weight are due to chain scission or chain branching, or if these two occur at random or preferentially. According to chain scission distribution function (CSDF) curves obtained via the proposed modified methodology, at low ultrasonic irradiation times and/or intensities, polymer chain scission is the dominant reaction, but as time and/or intensity of irradiation increase, polymer chain branching tends to occur. In addition, the amplitude of each interval or "section" of the whole degradation/modification process can be taken as smaller as desired. These results show that through the use of ultrasonic irradiation (sonochemistry), it is possible to mechanically activate macromolecular structures like polymer chains, in order to produce desired chemical modifications in different types of chains of higher or lower molecular weight. The structural changes induced on the LDPE by the ultrasonic irradiation have no significant effect on *T*c, Tm, and crystallinity, but these changes promoted a reduction in flexural modulus. On the other hand, it also provides the possibility of not only fracturing certain chain sizes, but of activating those chains by the selective grafting of COOH groups in the PE modification and functionalization in the new chain ends created by the action of US radiation. This also would allow to control and modify the PE mechanical properties.

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