

Dielectric Relaxations of High and Low Density Irradiated Polyethylenes

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Synopsis

A systematic study of dielectric spectrum on a series of high and low density commercial polyethylenes has been performed. Every polyethylene was characterized by determination of molecular weight distribution, the number of functional groups: ketone, aldehyde, vinyl, vinylidene, *trans*-vinylene, the fraction crystalline, and the degree of branching. We have observed that both γ and α dielectric relaxations zones are formed by two overlap relaxations which have been labeled γ_{II} , γ_I , α' , and α , respectively, in order of increasing temperatures. The intensity of the dielectric spectrum of all polyethylenes depends over and above other parameters on the number of the carbonyl groups formed as a result of irradiation. This number is different for every polyethylene even when they receive the same dose of irradiation (20 Mrad). However, the participation of carbonyl groups in the γ_I and α' dielectric relaxations decreases with the total crystalline content of each polyethylene. The α dielectric relaxation position in the temperature axis is governed by the most probable crystallite thickness.

INTRODUCTION

The dielectric and mechanical spectrum of high and low density polyethylenes displays three characteristic relaxation zones; these have conventionally been designated as the α , β , and γ relaxation in order of decreasing temperature.

Most authors¹⁻¹⁷ accept a complex mechanical spectrum in the γ and α zones, but, in general, only admit a single γ and α dielectric relaxation in the γ and α dielectric zones.^{1,13}

The molecular origin and the morphological assignment of each dielectric zone are still subject to debate due to the large number of experiments carried out by different authors and the variety of both the experimental results and the interpretation of them, as seen from the reviews of Boyd.^{4,5} This is a consequence of the many factors that may influence the experimental results. These factors may be inherent in the chemical structure, characteristic of each polyethylene (molecular weight distribution, functional groups, etc.), and could also be due to the morphology of the samples, which depends on the chemical structure, crystallization conditions of samples, and the annealing process each sample was subjected to.

We have studied the dielectric spectrum on a series of commercial irradiated polyethylenes. Due to the great number of factors which influence the relaxation process, we have characterized all the studied polyethylenes and have fixed the morphological and chemical parameters which define each polyethylene.

The alternative dielectrical measurements provide in general a useful tool in the study of the dielectrical spectrum, but these polymers present low dielectric activity due to their particular chemical structure. In order to increase this activity, the polyethylenes must be subjected to some external action, which increases dielectric activity. In this case, the samples are subjected to the γ radiation. This modifies the chemical structure of the polyethylenes, and produces an increase in the number of *trans*-vinylene and carbonyl functional groups in the samples.⁶ Therefore, the intensity of the dielectric relaxation spectrum of these polyethylenes depends on the number of carbonyl groups that have been formed largely as a result of the irradiation process.

We have studied every one of the dielectric relaxations and have fixed their position on the temperature axis, their intensity, their apparent activation energy values, and the percentage of carbonyl group participation, and also which morphological (crystalline content, melt temperature) or chemical parameters (carbonyl, transvinylene, vinyl, vinylidene functional groups, degree of branching, molecular weight distribution) govern the dielectric parameters which characterize the dielectric relaxation process.

EXPERIMENTAL

The polyethylenes used were from Dow Chemical Iberica, S.A. (Tarragona). The commercial labels of high density polyethylenes are 10062, 25057, 25055, 8067, 6067, 16050, and the low density polyethylenes are 710, 980, 519, and 549. We use the same label in this paper.

Samples of all polyethylenes were irradiated in air at constant temperature of 20°C with γ radiation from a Co⁶⁰ source. The irradiation rate was 1.4×10^{-4} Mrad/s. The total dose was 20 Mrad. The thicknesses of samples were about 1 cm.

All the irradiated samples were characterized by determination of the functional groups vinyl, vinylidene, transvinylene, aldehyde, ketone, and the degree of branching. The spectrophotometer used is a Perkin-Elmer 781.

To determine the number of methyl groups in alkyl group larger than ethyl groups in 100 carbon atoms (degree of branching), we followed the ASTM D 2238-69-79 norm. The number of functional groups were determined by the analysis of the absorption peak at 1730 cm^{-1} (aldehyde), 1713 cm^{-1} (ketone), 965 cm^{-1} (*trans*-vinylene), 909 cm^{-1} (vinyl), and 888 cm^{-1} (vinylidene). The equations⁷ used are

$$\text{aldehyde:} \quad \text{CHO}/1000 \text{ C} = 0.076K_{1730} \quad (1)$$

$$\text{ketone:} \quad \text{CO}/1000 \text{ C} = 0.056K_{1713} \quad (2)$$

$$\text{trans-vinylene:} \quad \text{RHC} = \text{CHR}/1000 \text{ C} = 0.118K_{965} \quad (3)$$

$$\text{vinyl:} \quad \text{RCH} = \text{CH}_2/1000 \text{ C} = 0.100K_{909} \quad (4)$$

$$\text{vinylidene:} \quad (\text{RRC} = \text{CH}_2)/1000 \text{ C} = 0.090K_{888} \quad (5)$$

where K is the absorptivity, i.e., the absorbance of the corresponding band divided by the density and thickness of the sample.

The crystalline morphology of the samples was studied by scanning differential calorimetry in a Mettler TA 3000 thermoanalyzer, with a 10°C/min scan velocity. The total crystalline content of each sample was determined¹⁷ by $X = (H_a - H_c)/H_m$, where H_a and H_c are the enthalpy in the melt state and the crystalline state, respectively, and H_m is the change in melting enthalpy of a perfect crystal of infinite size.

The dielectric measurements have been done with a capacitor bridge (General Radio 1615A) which allowed us to obtain the values of capacity and $\tan \delta$ in the range from 20 to 20⁵ Hz. The real and imaginary parts of the complex dielectric permittivity $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are calculated from ($\epsilon' = C_x/C_0$, where C_x and C_0 are the capacity of the sample and the air respectively) and ($\epsilon'' = \epsilon' \tan \delta$).

RESULTS AND DISCUSSION

The degree of branching and the number of functional groups aldehyde, ketone, *trans*-vinylene, vinyl, and vinylidene have been calculated with the eqs. (1)–(5), and the results are given in Table I.

Figures 1–5 show the values of ϵ'' calculated for each polyethylene in the temperature range of –140–120°C and for frequencies between 5×10^2 and 10^4 Hz. It must be emphasized that we could not obtain values of $\tan \delta$ and capacity of the samples for higher and lower frequencies than the above-mentioned because of the low dielectric permittivity of polyethylenes. In all the Figures 1–5 the three relaxation zones α , β , and γ of the polyethylenes can be clearly seen.

In order to analyze in detail these relaxation zones, each relaxation time distribution has been adjusted to the empirical Fuoss–Kirkwood model:

$$\epsilon'' = \epsilon''_{\max} \operatorname{sech} m \ln \omega \tau_0 \quad (6)$$

where the Fuoss–Kirkwood parameter m is related to the width of the relaxation time distribution.

The dependence of m on the temperature at the frequency of 1 kHz for the α , β , and γ relaxation is shown in Figure 6.

Furthermore, the relationship between the relaxation time and the temperature has been adjusted to an Arrhenius equation:

$$f = f_0 \exp(-E_a/RT) \quad (7)$$

which allows the apparent activation energy E_a for the relaxation process to be calculated. Figure 7 shows an Arrhenius diagram for all the relaxations.

In Figures 6 and 7, the results for some polyethylenes have been omitted for reasons of clarity. The discussion of more important results obtained for each relaxation zone are analyzed separately.

TABLE I
 Characterization of Polyethylenes

Sample	Aldehyde	Ketone	<i>Trans</i> -vinylene	Vinyl	Vinylidene	Fraction crystalline	Degree branching
10062	1.3	2.3	0.2	0.05	0.02	74	0.2
25055	1.0	1.9	0.3	0.04	0.02	69	0.9
25057	1.0	1.9	0.2	0.03	0.02	73	0.5
6067	0.6	1.2	0.3	0.04	0.03	76	0.9
8067	0.9	1.6	0.3	0.05	0.03	77	0.6
16050	0.9	1.8	0.3	0.07	0.03	68	1.8
519	0.3	0.4	0.3	0.03	0.06	45	2.5
549	0.2	0.3	0.4	0.02	0.05	45	2.4
710	0.4	0.4	0.3	0.02	0.03	48	2.0
980	0.3	0.2	0.3	0.02	0.06	44	2.5

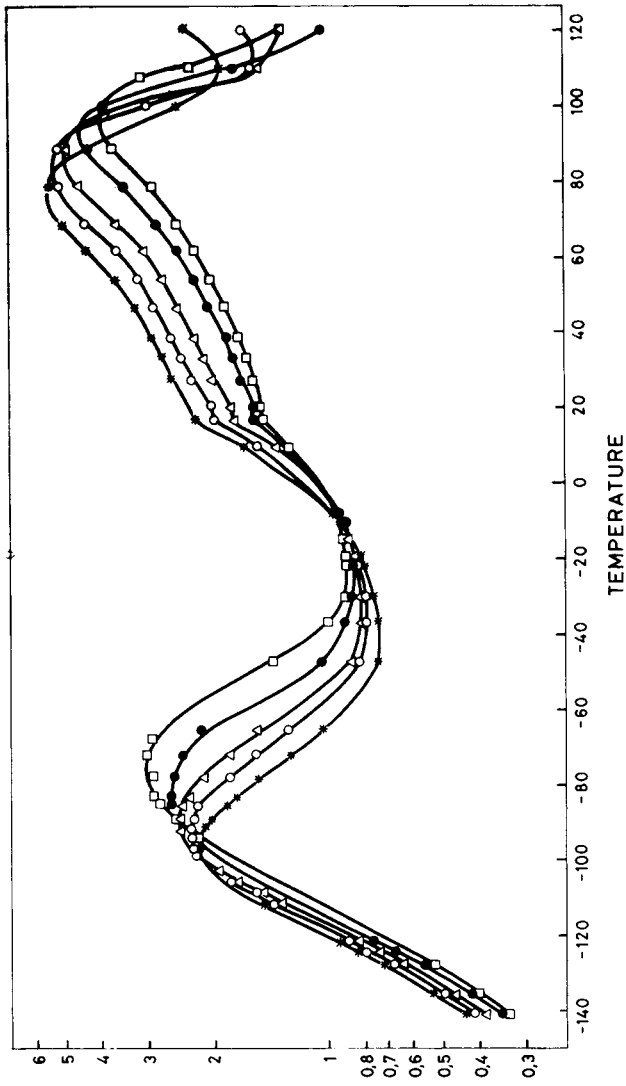


Fig. 1. Values of ϵ'' vs. T for the polyethylene 10062 at different frequencies (Hz): (\bullet) 5×10^2 ; (\circ) 10^3 ; (Δ) 2×10^3 ; (\bullet) 5×10^3 ; (\square) 10^4 .

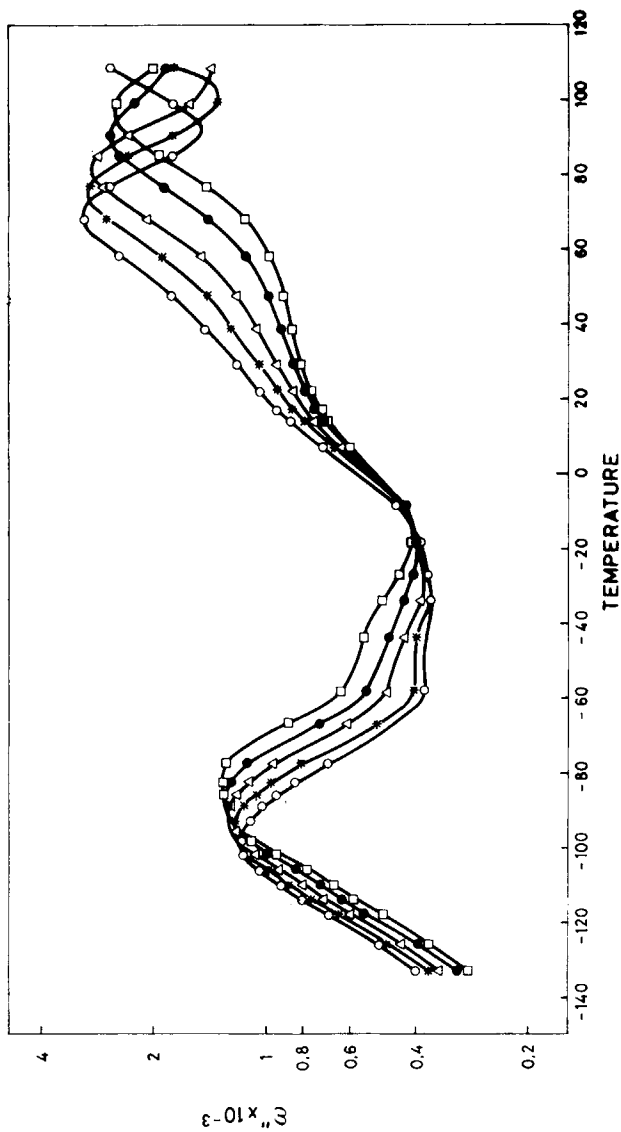


Fig. 2. Values of ϵ'' vs. T for the polyethylene 8067 at different frequencies (Hz): (○) 5×10^2 ; (*) 10^3 ; (△) 2×10^3 ; (●) 5×10^3 ; (□) 10^4 .

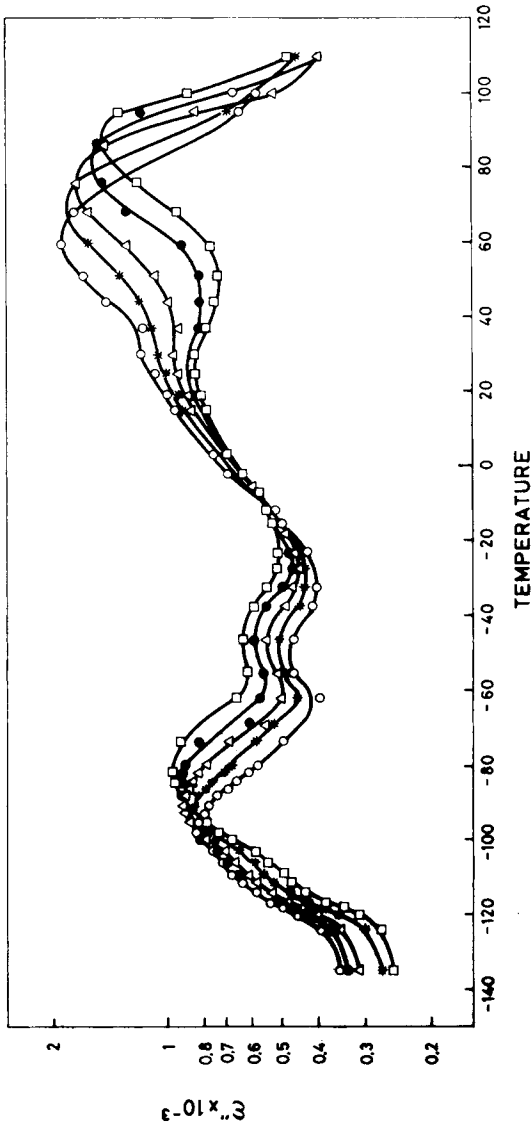


Fig. 3. Values of ϵ'' vs. T for the polyethylene 16050 at different frequencies (Hz): (○) 5×10^2 ; (●) 5×10^3 ; (□) 10^4 ; (△) 2×10^3 ; (*) 10^3 .

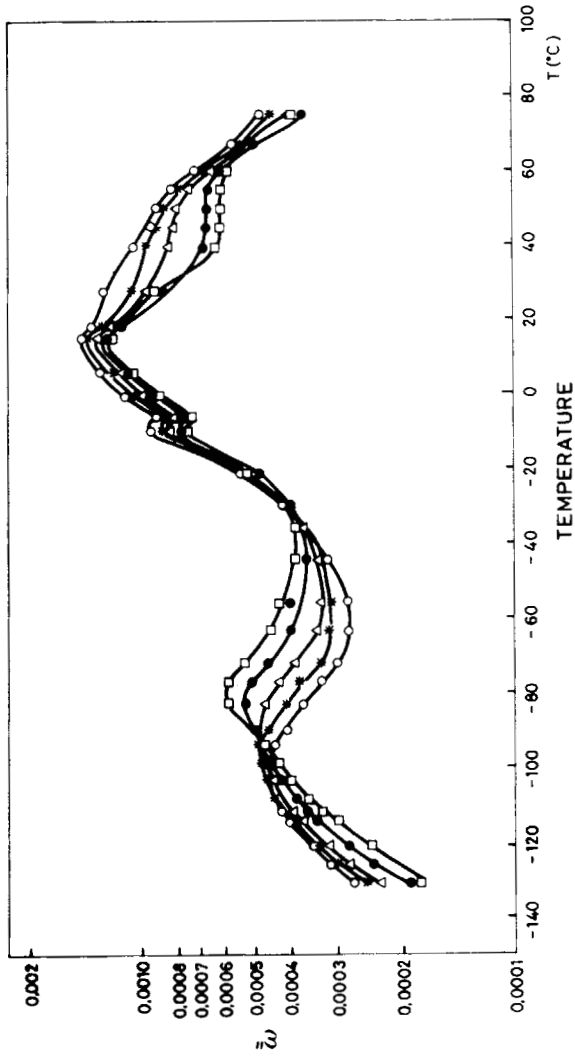


Fig. 4. Values of ϵ'' vs. T for the polyethylene 519 at different frequencies (Hz): (○) 5×10^2 ; (●) 10^3 ; (△) 2×10^3 ; (◐) 5×10^3 ; (◑) 10^4 .

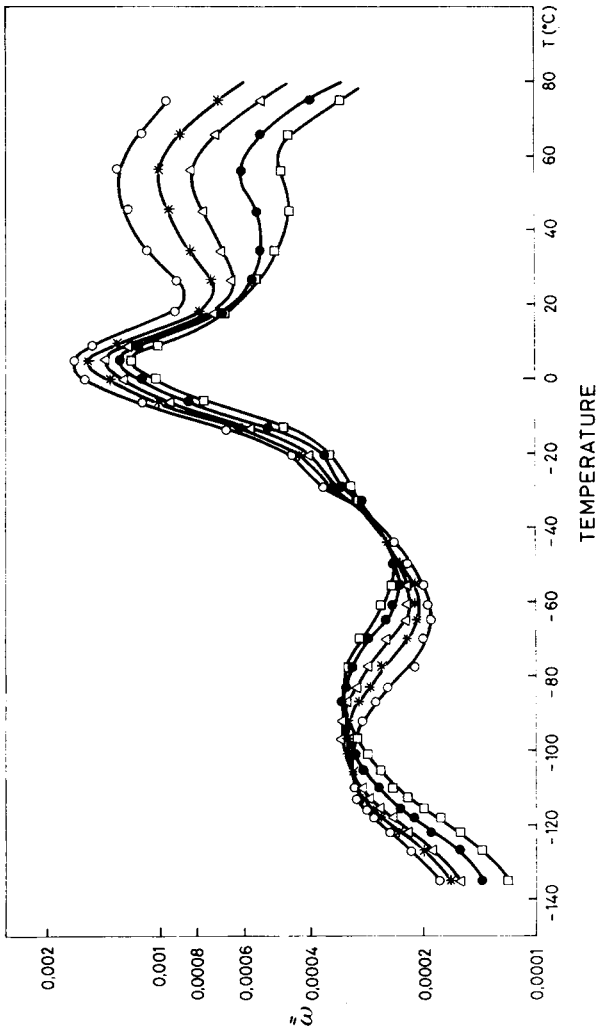


Fig. 5. Values of ϵ'' vs. T for the polyethylene 980 at different frequencies (Hz): (○) 5×10^2 ; (*) 10^3 ; (Δ) 2×10^3 ; (●) 5×10^3 ; (□) 10^4 .

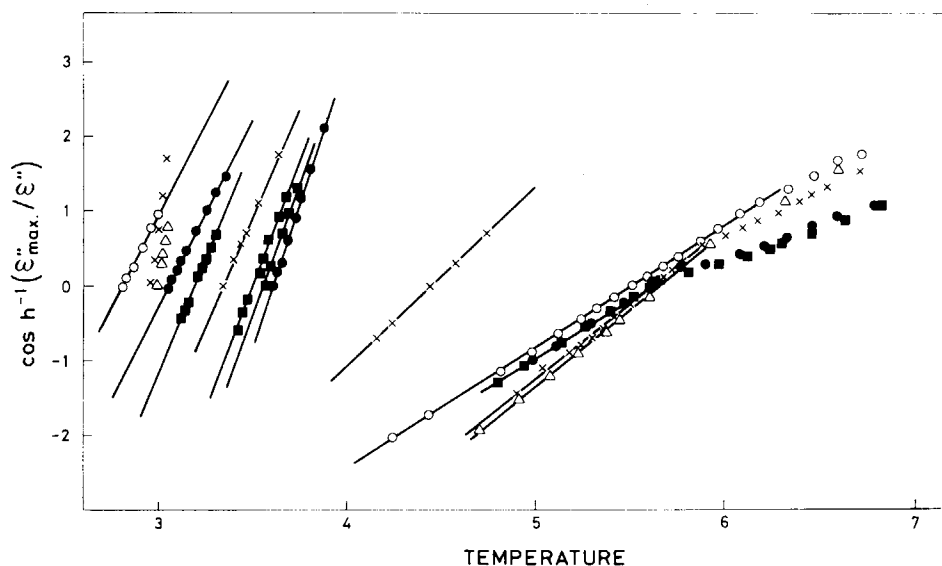


Fig. 6. Relationship between the parameter m of Fuoss-Kirkwood and the temperature for α , α' , β , and γ_1 relaxations at 1 kHz frequency for the polyethylenes 519 (\square), 980 (∇), 10062 (\circ), 16050 (\times), and 25055 (Δ).

γ Dielectric Relaxation Zone

The first issue is to determine how many relaxations or subrelaxations constitute this relaxation zone. When Boyd³ represents the values of $\epsilon''/\epsilon''_{\max}$ vs. temperature, he interprets the peak symmetry as an indication of the existence of a single relaxation.

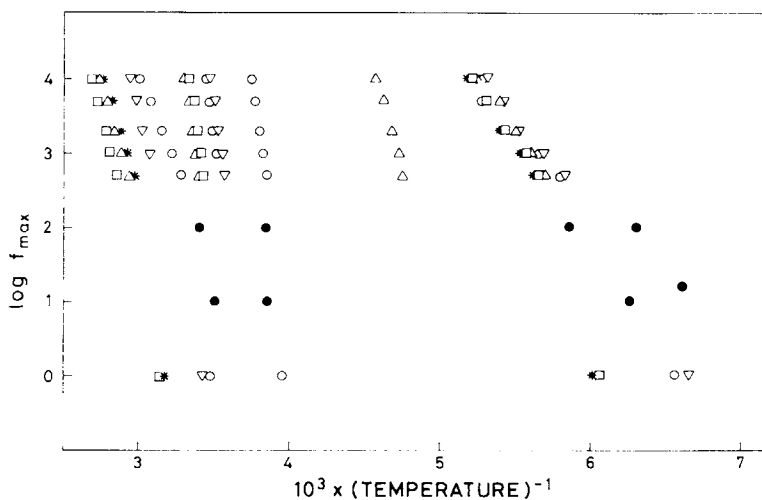


Fig. 7. Arrhenius diagram of α , α' , β , γ_1 relaxations for the polyethylenes 16050 (Δ), 10062 ($*$), 25055 (\square), 710 (∇), and 519 (\circ). In this diagram are included the dielectric results of Boyd³ (\bullet) and our dynamic mechanical results on same samples at 1 Hz.

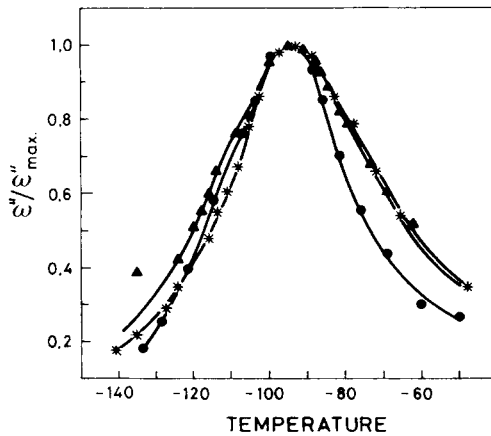


Fig. 8. Values of $\epsilon''/\epsilon''_{\max}$ vs. temperature for γ_I dielectric relaxation for the polyethylenes 16050 (\blacktriangle), 10062 (*), and 25057 (\bullet).

We have represented the values of $\epsilon''/\epsilon''_{\max}$ vs. temperature for the high density polyethylenes (10062, 25057, 16050) and low density polyethylenes (549, 519, 980) in Figures 8 and 9, respectively. We omitted the other polyethylenes for the sake of clarity in the figures.

These figures show the presence of a shoulder at lower temperatures, which is more evident in the low density polyethylenes. These results and other reasons discussed below, along with other results obtained by thermostimulated currents⁸ for the 710 and 10062 polyethylenes lead us to affirm that these relaxation zones are formed at least by two overlapped relaxations γ_I and γ_{II} in decreasing temperature.

The γ_I dielectric relaxation is more predominant than the γ_{II} ones. We could analyze it, but the γ_{II} dielectric relaxation is completely overlapped by the γ_I dielectric relaxation and, therefore, we were not able to.

The mean Fuoss-Kirkwood parameter of γ_I dielectrical relaxation is obtained from the slope of the curve of $\cosh^{-1}(\epsilon''/\epsilon'')$ vs. $10^3/T$. The results are

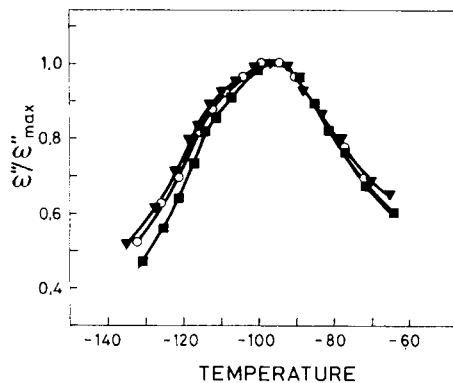


Fig. 9. Values of $\epsilon''/\epsilon''_{\max}$ vs. temperature for γ_I dielectric relaxation for the polyethylenes 549 (\blacksquare), 519 (\circ), and 980 (∇).

TABLE II
Dielectric Analysis of γ , β , α' , and α Relaxations

Sample	Relaxation γ_1		Relaxation β		Relaxation α'		Relaxation α		
	E_a	m	A	E_a	\bar{m}	\bar{E}_a	A'	\bar{E}_a	\bar{m}
10062	13	0.27	4.9			44	9.7	36	0.30
25055	12	0.26	5.0			51	12.7	25	0.45
25057	13	0.28	4.6			46	9.3	28	0.48
6067	14	0.24	5.0			49	7.2	27	0.47
8067	14	0.24	4.2			41	7.2	25	0.48
16050	14	0.20	3.2	31	0.15	67	7.0	31	0.61
519	9	0.25	6.2	51	0.84	93	42	25	0.52
549	11	0.23	12.3			92	40	24	0.56
710	11	0.25	7.0			88	43	46	0.26
980	9	0.24	5.5			79	38	51	0.19

shown in Table II. These values are similar to those obtained by Boyd³ from other polyethylenes (0.23–0.31).

In Figure 6 it can be seen that the slope of the curve $\cosh^{-1}(\epsilon''_{\max}/\epsilon')$ vs. $10^3/T$ changes abruptly at lower temperatures, which confirms the presence of the relaxation γ_{II} with a different distribution of relaxation times.

The values obtained for the apparent activation energy of the γ_I dielectric relaxation process are given in the same Table (II). These values are also comparable with the values obtained by Boyd³ and Sato^{9,10} for the apparent activation energy of the γ_I dielectric process in other polyethylenes, and seems to increase when the total crystalline content of the sample increases. This result suggests that the crystalline matrix contributes with an intermolecular component to the potential barrier that causes the γ_I dielectric relaxation process. Therefore, this intermolecular component is lower in the low density polyethylenes than in the high density ones.

Figure 10 shows that the imaginary part of the complex dielectric permittivity is greater in the high density polyethylenes than in the low ones. At first sight, the results appear to be contradictory to the results obtained by other authors in dielectric³ or mechanical^{2,11,12} measurements, since the values of $\epsilon'' \cdot \tan \delta$ would be greater in the low density polyethylene if it is supposed that the γ_I dielectric relaxation is due to molecular movements in the chains forming the amorphous phase of polyethylenes.

The beginning of this contradiction we believe is due to the irradiation because the number of polar groups formed by irradiation is different for every one of the polyethylenes in spite of their being submitted to the same irradiated dose, as shown in Table I. The dielectric activity of polyethylenes is due largely to the movement of molecular chains which have the polar groups.

This indicates the different concentration of the polar groups in each polyethylene may mask the relationship between the values of $\tan \delta_{\max}$, ϵ''_{\max} , the intensity of γ_I dielectric relaxation, and the morphological and structural parameters such as crystalline content, degree of branching, etc.

Therefore, starting from the Onsager equation,

$$(\epsilon_0 - \epsilon_\infty) = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \frac{(\epsilon_\infty + 2)^2}{3} \frac{4\pi}{3KT} \frac{dNa}{14 \times 10^3} n\mu^2$$

assuming that

$$\tan \delta_{\max} = (\epsilon/\epsilon') = (\epsilon''/\epsilon_0) = (\epsilon''/\epsilon_\infty)$$

as is assumed by other authors.^{9,10}

And supposing that the relaxation time distribution of γ_I dielectric relaxation could be adjusted to the Fuoss–Kirkwood equation, we obtain

$$\tan \delta_{\max} = \frac{2\pi}{KT} \frac{1}{3} \frac{1}{\epsilon'} \frac{(\epsilon' + 2)^2}{3} \frac{dNa}{14 \times 10^3} n \cdot \mu^2 \cdot m \quad (8)$$

Equation (8) allows us to calculate the value of $\tan \delta_{\max}$ related to the polar groups by 1000 carbon atoms of the main chain.

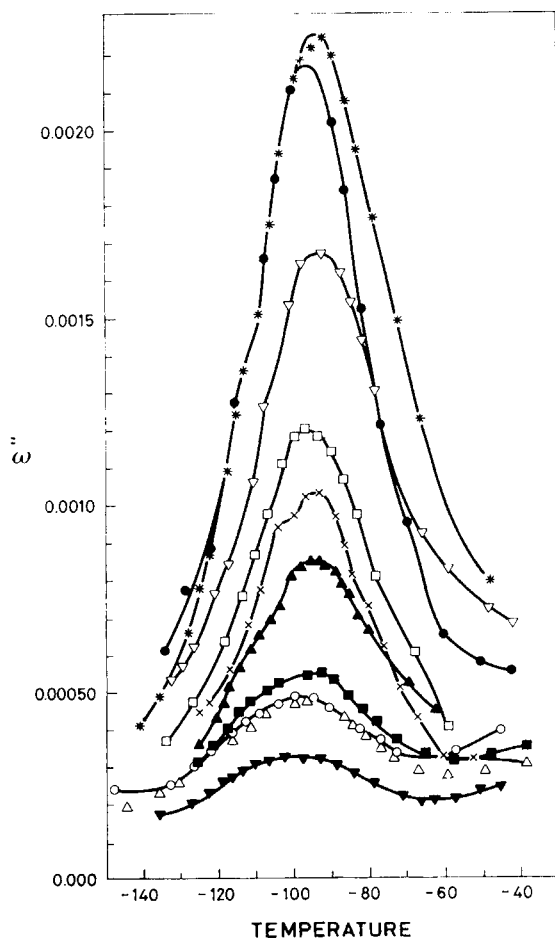


Fig. 10. Plot of ϵ'' vs. temperature in the dielectrical relaxation zone at 1 kHz frequency for the polyethylenes 10062 (*), 25057 (●), 25055 (○), 8067 (□), 16050 (Δ), 710 (□), 519 (○), 549 (■), and 980 (▽).

We considered in this calculus only the carbonyl groups as polar groups because the dipolar moment values of the vinyl, vinylidene, and *trans*-vinylene groups are lower than the values for the carbonyl groups, and this hypothesis introduces in the calculus an error less than 1.6% in the $\tan \delta_{\max}$ value.

Therefore, if all the carbonyl groups were to take part in the γ_1 dielectric relaxation, the $\tan \delta_{\max}$ values calculated from eq. (8) would coincide with the $\tan \delta_{\max}$ values observed experimentally, but this does not happen. So we can calculate the percentage of carbonyl groups that take part in the γ_1 dielectric relaxation process as

$$\text{participation percentage } A = (\tan \delta_{\max} \text{ exptl} / \tan \delta_{\max} \text{ calcd}) \times 100$$

The participation percentage values obtained for each polyethylene are shown in Table II. We emphasize that the participation percentage is greater

in the low density polyethylenes than in the high ones. This result confirms that the γ_1 dielectric relaxation is due to molecular movements of the molecular chains which form the amorphous phase, and that the possibility of the carbonyl groups moving is greater in the low density polyethylenes, than in the high ones.

β Dielectric Relaxation Zone

The information that these measurements provide about the β dielectric relaxation is limited because this relaxation is overlapped by the γ relaxation in the high density polyethylenes and by the α relaxation in the low density ones. Thus it is only possible to separate and analyze the dielectric relaxation in the 16050 and 519 polyethylenes. In this case, the values obtained for the mean Fuoss-Kirkwood parameter and the apparent activation energy of the β dielectric process are shown in Table II.

In spite of the lack of results for this relaxation, it is important to point out that the β dielectric relaxation is present in all the polyethylenes and its form and position on the temperature axis apparently depends more on the amorphous content than the degree of branching.

α Dielectric Relaxation Zone

Aschcraft and Boyd³ and Kakizaki and Hideshima¹³ assumed that the α dielectric relaxation zone is formed by a single relaxation, but we have observed that the α dielectric relaxation zone is formed by two relaxations in both the high and low density polyethylenes. We labeled these relaxation α' and α in order of increasing temperature.

The relaxations α' and α were separated considering the contribution of the two relaxations as additive and supposing that the α dielectric relaxation was assumed to be symmetrical in the high density polyethylenes and the α' dielectric relaxation was calculated by the difference between the two overlapped peaks and the α dielectric relaxation. The α' dielectric relaxation was assumed to be symmetrical in the low density polyethylenes and the α dielectric relaxation was calculated by the difference between the two overlapped peaks and the α' dielectric relaxation.

Thus the α and α' were analyzed determining the mean Fuoss-Kirkwood parameters and the apparent activation energy of both processes. The values obtained are shown in Table II.

The values obtained for the apparent activation energy may seem uncertain because these were calculated from the α' and α peaks, the separation of which may be approximated; however, the apparent activation energy values of the α relaxation process are similar to the values obtained by other authors.³

The most recent studies by other authors^{2,14,16} and our own studies¹⁷ on α relaxation is governed by the mean thickness of the crystallites which form the crystalline phase in polyethylene.

One way of calculating the mean thickness of the crystallite is from calorimetric measurements, because this mean thickness governs in turn the position of the fusion peaks too.¹⁷

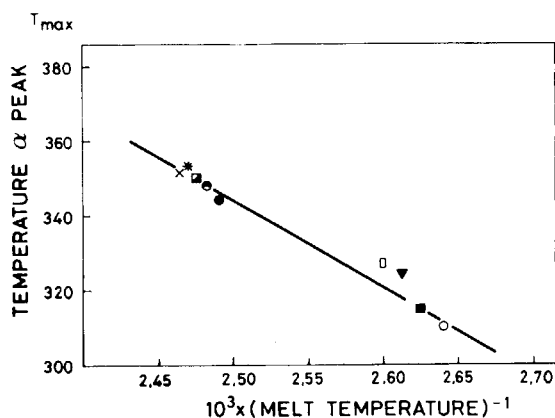


Fig. 11. Relationship between temperature of α peak, at 1 kHz frequency, and melting temperature for the polyethylenes 10062 (*), 25057 (●), 25055 (○), 8067 (□), 16050 (△), 710 (◻), 519 (○), 549 (■), and 980 (▽).

Thus we have related the position of the α' peak on the temperature axis with the melt temperatures of each polyethylene, in order to check if α' and α relaxation had the same molecular origin. We observed that the temperature of the α' peak has no relation to the melt temperature, however, the temperature for the α peak increases when the melt temperature of polyethylene T increases (Fig. 11).

In order to analyze in greater detail the α' dielectric relaxation, we calculated the participation percentage of carbonyl groups in this relaxation, in the same way as we calculated the participation percentage in the γ_1 relaxation. The values obtained are in Table II. It can be seen that the participation percentage of the carbonyl groups is greater in the low density polyethylenes than in the high density ones.

These results suggest that the α relaxation is related to molecular movements of the main chains which form the crystalline phase and the α' relaxation would be assigned to the molecular movements of the main chains that formed the amorphous phase.

CONCLUSIONS

The intensity or the height of relaxations measured in $\tan \delta_{\max} \cdot \epsilon''_{\max}$ values of α , β , and γ dielectric relaxation depend largely on the polar groups, mainly carbonyl, which were formed by irradiation.

The γ dielectric relaxation zone is composed of two relaxations γ_1 and γ_{II} . The γ_1 relaxation is due to molecular movements of the main chains, which form the amorphous phase. A small number of carbon groups take part in these movements. The apparent activation energy of the γ_1 dielectric process increases with the crystalline content; this suggests that the potential barrier that causes the γ_1 dielectric relaxation may be formed by an intermolecular component.

The α dielectric relaxation zone is composed of two relaxations α' and α . The position on the temperature axis of α' relaxation does not depend on the mean thickness of the crystallites and the participation percentage of car-

bonyl groups in this relaxation increases with the amorphous content; thus the α' dielectric relaxation may be associated with molecular movements of main chains in the amorphous phase.

The position on the temperature axis of α relaxation seems to be governed by the mean thickness of the crystallites, and this relaxation may be assigned to molecular movements of main chains in the crystalline phase.

Seen as a whole, the dielectric relaxation spectrum of high and low density polyethylenes is more complex than predicted by other authors.

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