Dynamic-Mechanical Relaxations in High and Low Density Polyethylenes. Effects of Irradiation and Annealing

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Synopsis

A study of the dynamic-mechanical relaxation spectrum in a series of commercial high and low density polyethylenes (Dow Chemical), irradiated as well as unirradiated, and subjected to different annealing process, has been performed. The effect of 20-Mrad dose of irradiation on the chemical structure has been analyzed and an increase in the number of aldehyde, ketone, and transvinylene groups and a decrease in the number of vinyl and vinylidene groups has been observed. The dynamic-mechanical spectrum of irradiated and unirradiated high and low density polyethylenes contains the γ_{II}-, γ_I-, β-, α_I-, α_{II}-, and α_{III}- relaxations, in order of increasing temperature. It has been observed that γ-irradiation followed by annealing modifies the intensity and the position of relaxations in these polyethylenes.

INTRODUCTION

The mechanical spectrum of high and low density polyethylenes displays three characteristic relaxations. These have conventionally been designated as the α-, β-, and γ-relaxations, in order of decreasing temperature. The molecular origin and the morphological assignment of each mechanical relaxation are still subject to debate due to the variety of interpretations proposed by the different authors, as seen from the reviews of McCrum,[1] Boyd,[2,3] and Popli et al.[4] Therefore, we will not bring up all the previous reported data. In recent literature Popli et al.[4] discussed the α- and β-relaxations in polyethylenes, and Khanna has studied the γ-, β-, and α-relaxations[5] in commercial polyethylenes. In this paper, we have performed a comparative study of dynamic-mechanical relaxation spectra of high and low density polyethylenes, irradiated and unirradiated, in order to analyze the effect of the irradiation on each on the γ-, β-, and α-relaxation zones, which form this dynamic mechanical relaxation spectrum.

When the irradiated samples are subjected to several annealing process, the crystallite morphology (total crystalline content and most probable crystallite thickness) is different from the unirradiated samples subjected to the same annealing process. Thus we have analyzed how the total crystalline content and the most probable crystallite thickness affect the intensity and the temperature of each mechanical relaxation. This has provided us with new results on the controversial topic of the molecular origin and morphological assignment of the γ-, β-, and α-relaxations.

EXPERIMENTAL

The polyethylenes were supplied by Dow Chemical Iberica S.A. (Tarragona). The commercial labels of the high density polyethylenes are 10062, 6068, 25055, XZ86658, 25057, and the low density ones are 710, 980, 519, 549, and XP-5204II.

The distribution of molecular weight, the average molecular weights, M_w, M_n and the polydispersity index were determined through steric exclusion chromatrography (SEC).

All the experimental work was carried out on molded samples, which were subjected to different, annealing processes in order to modify the crystalline morphology. All the samples were molded and then quickly cooled in the mold and subsequently annealed in a oven at different temperatures and for annealing times.

The annealing processes were: A $(T = 75°C, \; t = 46 \; h)$; B $(T = 82°C, \; t = 48h)$; C $(T = 90°C, \; t = 6 \; h)$; D $(T = 100°C, \; t = 41 \; h)$; E $(T = 102°C, \; t = 48 \; h)$; F $(T = 107°C, \; t = 24 \; h)$; G $(T = 85°C, \; t = 48 \; h)$; H $(T = 121°C, \; t = 6 \; h)$.

The changes in crystalline content and melting temperature caused by the annealing processes were studied by differential scanning calorimetry in a METTLER TA 3000 thermoanalyzer, with a heating rate of 10°C/min. The total crystalline content of each sample was determined through ($X = (H_o - H_c)/\Delta H_m$).[6]

Samples of all polyethylenes were irradiated in air at constant temperature of 20°C with γ-radiation from a Co^{60} source. The irradiation rate was 1.4×10^{-4} Mrad/s. The total dose was 20 Mrad. The thicknesses of samples were about 1–1.5 cm.

The chemical structure of polyethylenes, irradiated as well as unirradiated, was studied by infrared spectroscopy. The ketone, aldehyde, vinyl, vinylidene, transvinylene functional groups and the index of branching were determined. The spectrophotometer used is a Perkin-Elmer 781.

The mechanical spectra were obtained in a dynamic mechanical thermal analyzer (DMTA) of Polymer-Laboratory Ltd. All the samples were analyzed at a constant frequency of 1 Hz and from -140 to 120°C with a heating rate of 1°C/min.

RESULTS AND DISCUSSION

The values of average molecular weight M_w, M_n, and polydispersity index are shown in Table I. The number of ketone, aldehyde, vinyl, vinylidene, transvinylene functional groups of irradiated and unirradiated polyethylenes are in Table II.

The crystalline content of all the samples is shown in Table III. It decreases as a result of irradiation followed by remelting, recrystallization, and annealing. The irradiation increases the number of imperfections in the molecular chains (internal unsaturation, carbonyl groups, etc.), which inhibit the process of recrystallization from the melt and the thickening of the crystallites during the annealing process.

The dynamic-mechanical spectra has been represented as the value of E', E'', and tan δ vs. temperature. Figures 1–2 show, for instance, the values

TABLE I
Molecular Characteristics of Polyethylenes

Sample	$M_N \times 10^3$	$M_w \times 10^3$	M_w/M_N
10062	18.80	62.7	3.48
25055	15.30	42.9	2.81
25057	7.68	134.0	17.46
XZ-86658	20.30	61.4	3.03
6067	6.68	67.5	10.10
980	6.22	46.8	7.52
710	7.53	47.6	6.26
519	7.62	53.2	6.98
549	11.20	82.2	7.37
XP5204	13.00	103.0	7.93

obtained for the polyethylene XZ-86658 unirradiates subjected to the D (100°C, 41 h), G (85°C, 48 h), and H (121°C, 6 h) annealing processes. The most important results obtained for each relaxation zone are analyzed separately.

γ Mechanical Relaxation Zone

The γ mechanical relaxation zone is observed between −140 and −90°C at 1 Hz. In order to confirm that this relaxation zone is formed at least by two relaxations, as other authors[7-9] have assumed, we present the values of E''/E''_{max} vs. temperature. For instance, these values are shown in Figures 3 and 4 for the H annealing (121°C, 6 h) in high density polyethylenes and for the C annealing (90°C, 6 h) process in low density polyethylenes, respectively. The values of E''/E''_{max} vs. temperature display a shoulder at low temperatures, which can be assumed to be due to two overlapped relaxations, labeled γ_I and γ_{II} in order of increasing temperature. The γ_I mechanical relaxation is more predominant than the γ_{II}; moreover, the γ_{II}-relaxation is completely overlapped by the γ_I mechanical relaxation, and therefore we were not able to analyze it.

We have compared the position on the temperature axis and the height of the γ_I mechanical relaxation in irradiated and unirradiated samples. We observed that the temperature of the values $\tan \delta_{max}$ o E''_{max} is higher in irradiated low and high density polyethylenes than in unirradiated ones. This result suggests that the molecular defects (internal saturations) resulting from irradiation impede the motion of the molecular chains and increase the potential barrier which causes the γ_I mechanical process.

The height of the γ_I mechanical relaxation determined through E''_{max} or $\tan \delta_{max}$ is greater in all irradiated polyethylenes than in unirradiated ones. These results are similar to those of Woodward and Sauer[10-12] and Peneri[13] and may be due to decreasing crystalline content, as a result of irradiation followed by annealing, as mentioned above and as can be seen in Table III. On the other hand, the position in the temperature axis of the γ_I mechanical peak is lower in low density polyethylenes (−120°C) than in high density ones (−109°C). These results have been shown before by McCrum,[7] Salla et al.,[14]

TABLE II
Structural Characterization of Polyethylenes (Functional Groups/1000 CH_2)[a]

Sample	Ketone		Aldehyde		Vinyl		Vinylidene		Transvinylene	
	N	I	N	I	N	I	N	I	N	I
10062	—	2.3	—	1.28	0.38	0.05	—	0.02	—	0.22
25055	0.03	1.89	0.08	0.98	0.39	0.04	—	0.02	—	0.32
XZ-86658	0.04	0.09	0.04	0.18	0.34	0.03	0.03	0.02	—	0.38
25057	0.09	1.90	0.02	1.03	0.18	0.03	0.03	0.02	—	0.23
6067	0.08	1.19	0.02	0.61	0.33	0.04	0.04	0.03	—	0.28
XP5024 II	0.04	0.5	0.04	0.28	0.03	0.03	0.18	0.04	0.03	0.31
549	0.04	0.25	0.03	0.16	0.09	0.02	0.16	0.05	0.03	0.36
519	—	0.40	—	0.30	0.02	0.03	0.22	0.06	0.03	0.34
980	0.05	0.20	—	0.32	0.03	0.02	0.24	0.06	0.03	0.33
710	0.02	0.36	0.02	0.36	0.05	0.07	0.18	0.03	0.02	0.27

[a] N = samples nonirradiated; I = samples irradiated.

TABLE III
Physical Characterization of Polyethylenes: Crystallinity Index[a]

Sample	A		B		C		D		E		F		G		H	
	N	I	N	I	N	I	N	I	N	I	N	I	N	I	N	I
10062	—	—	—	—	—	—	84	70	—	—			83	72	81	74
25055	—	—	—	—	—	—	78	—	—	—			79	65	82	69
25057	—	—	—	—	—	—	81	75	—	—			79	68	77	73
6067	—	—	—	—	—	—	82	76	—	—			83	72	82	76
XZ86658	—	—	—	—	—	—	86	—	—	—			74	66	71	70
XP-5204 II	47	44	49	—	47	46	48	45	48	—	47	45	—	—	—	—
519	46	44	49	—	45	45	47	45	48	—	48	45	—	—	—	—
549	49	48	46	—	46	45	50	46	50	—	50	45	—	—	—	—
710	50	47	48	—	49	48	49	48	49	—	51	49	—	—	—	—
980	46	44	46	—	44	44	—	—	—	—	47	44	—	—	—	—

[a]Annealing processes: (A) 75°C, 46 h; (B) 82°C, 48 h; (C) 90°C, 6 h; (D) 100°C, 41 h;(E) 102°C, 48 h; (F) 107°C, 48 h; (G) 85°C, 48 h; (H) 121°C, 6 h. N = samples nonirradiated; I = samples irradiated.
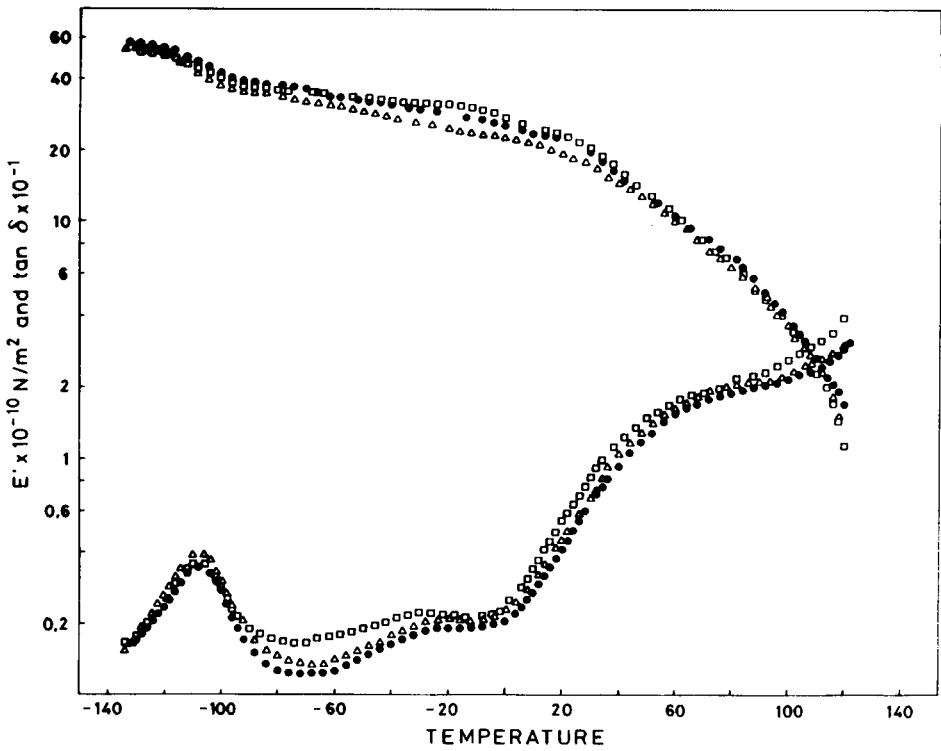
Fig. 1.   Dynamic storage modulus (E') and damping factor (tan δ) vs. temperature of the irradiated (20 Mrad) polyethylene XZ-86658 subjected to annealing processes: ($\triangle$) G; ($\square$) D; ($\bullet$) H. G: 85°C, 48 h; D: 100°C, 41 h; H: 121°C, 6 h.
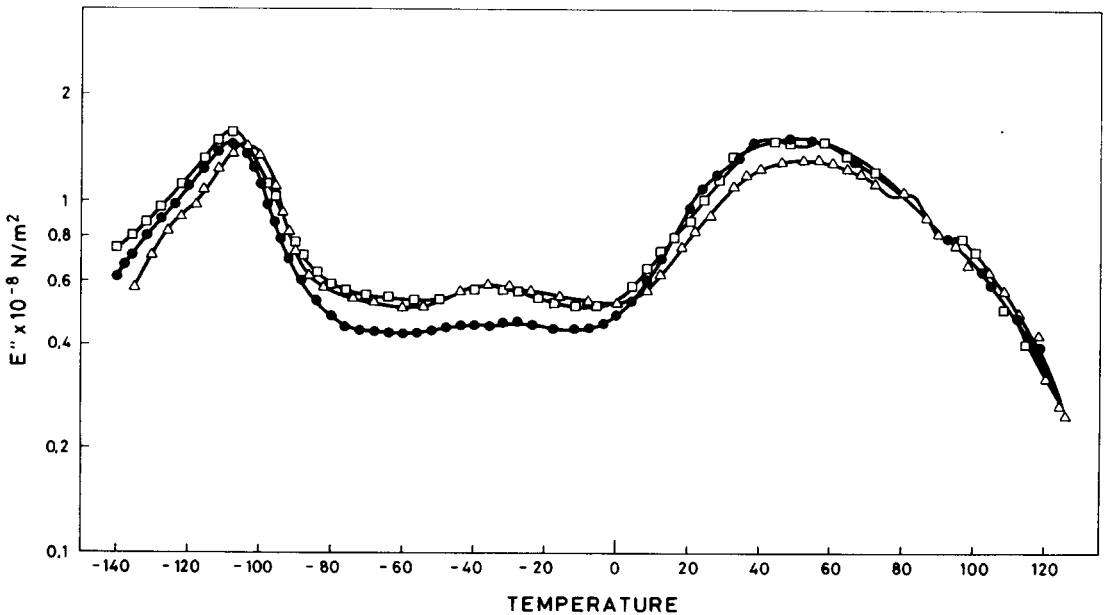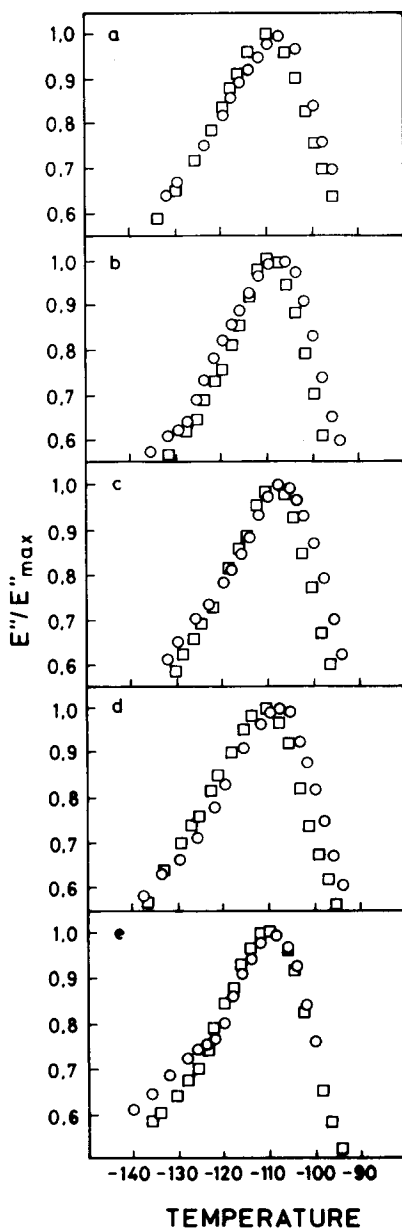

Fig. 2.   Dynamic loss modulus (E'') vs. temperature of the irradiated (20 Mrad) polyethylene XZ-86658 subjected to annealing processes: ($\triangle$) G; ($\square$) D; ($\bullet$) H. G, D, H as in Figure 1.
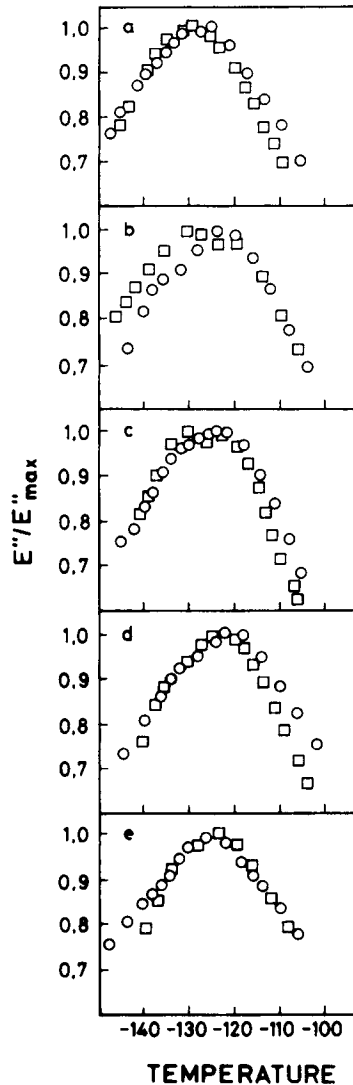
Fig. 3. E''/E''_{max} vs. temperature of irradiated polyethylenes (○) and unirradiated ones (□), subjected to the H annealing process (90°C, 6 h): (a) the 25057 polyethylene; (b) the XZ-86658 polyethylene; (c) the 10062 polyethylene; (d) the 25055 polyethylene.

and Khanna.[5] This last author carried out the measurements in the same dynamic-mechanical thermal analyzer apparatus as we did, and found that the temperature of the γ_I peak in low density polyethylenes is about $-113°C$ and in high density ones $-100°C$. This difference in the position of the γ_I mechanical peaks between the results of Khanna and ours, is due to the different rates: Khanna carried out his measurements at 3°C/min, and we

Fig. 4. E''/E''_{max} vs. temperature of irradiated polyethylenes (○) and unirradiated ones (□), subjected to the C annealing process: (a) the 519 polyethylene; (b) the XP-5204 II polyethylene; (c) the 710 polyethylene; (d) the 549 polyethylene; (e) the 980 polyethylene.

performed ours at 1°C/min and verified that the peaks shift to higher temperatures when the heating velocity is 3°C/min.

In order to study the parameters that govern the height of the γ_I mechanical peak, we plotted the values of tan δ maximum vs. the crystalline content in Figure 5. We observed that this value increases with decreasing crystalline content in the same polyethylene. This result suggests the hypothesis that the mechanical relaxation γ_I is produced by motions of the molecular chains which form the amorphous phase in polyethylene, and the height of the γ_I mechanical peak would be affected by irradiation and annealing as both increase the amorphous content.
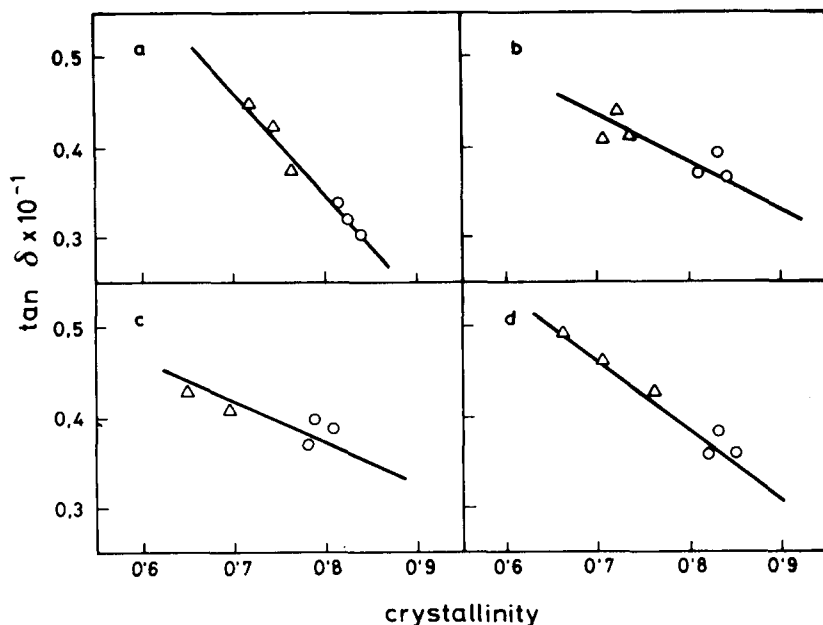
Fig. 5. Maximum values of damping triangle factor vs. crystalline content for irradiated polythylenes (△) and unirradiated ones (○), subjected to the D, G, and H annealing processes. D: 100°C, 41 h; G: 85°C, 48 h; H: 121°C, 6 h. (a) The 6067 polyethylene; (b) the 10062 polyethylene; (c) the 25055 polyethylene; (d) the XZ-86658 polyethylene.

β-Relaxation

The β-relaxation was observed between −45 and −10°C at 1 Hz in all the polyethylenes studied. In order to analyze the parameters which control the temperature of the relaxation, we plotted the temperature of the β peak vs. the crystallinity for all the samples studied, specified above in Table III (Figs. 6 and 7). We observed that the temperature or the β peak measured in tan δ,
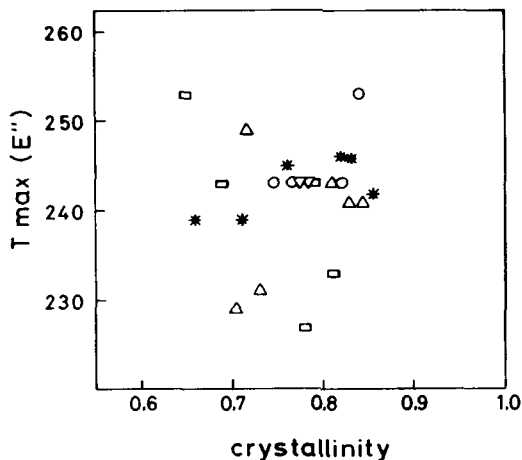
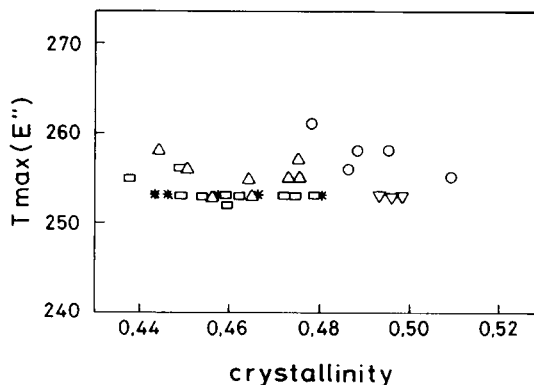Fig. 6. Temperature of the peaks in the polyethylenes: (*) XZ-86658; (□) 25055; (△) 10062; (▽) 25057; (○) 6067.

Fig. 7.   Temperature of the peaks in the polyethylenes: (△) XP-5204; (□) 519; (○) 710; (▽) 549; (∗) 980.

oscillates around $-20°C$ in all low density polyethylenes, irradiated as well as unirradiated. However, the position of the β peak, measured in E'', is between -40 and $-30°C$ in all high density polyethylenes, irradiated as well as unirradiated.

The E'' maximum values of the β peak are generally lower in the polyethylenes with greater crystalline content. We studied the relationship
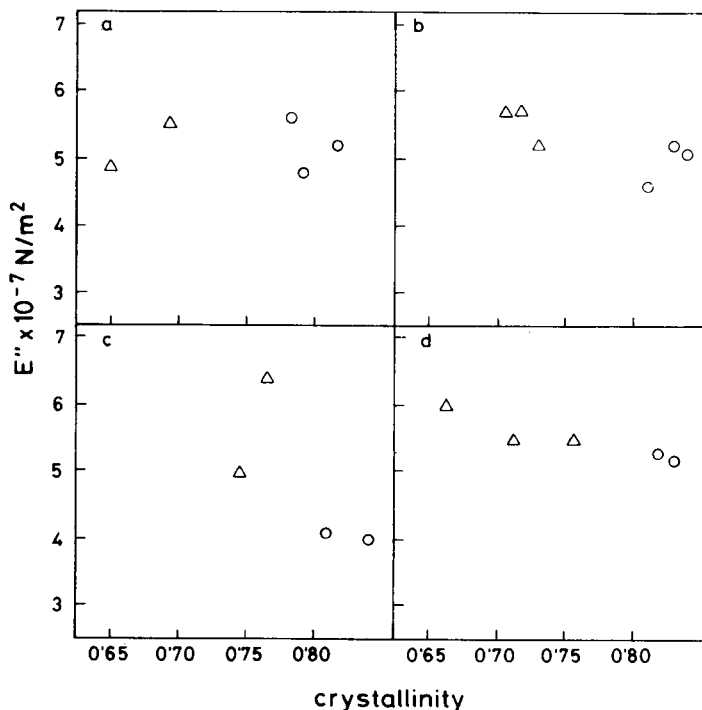

Fig. 8.   Maximum values of dynamic loss modulus (E'') vs. crystalline content for irradiated polyethylenes (△) and unirradiated ones (○), subjected to the D, G, and H annealing processes. D: 100°C, 41 h; G: 85°C, 48 h; H: 121°C, 6 h. (a) The 25055 polyethylene; (b) the 10062 polyethylene; (c) the 6067 polyethylene; (d) the XZ-86658 polyethylene.
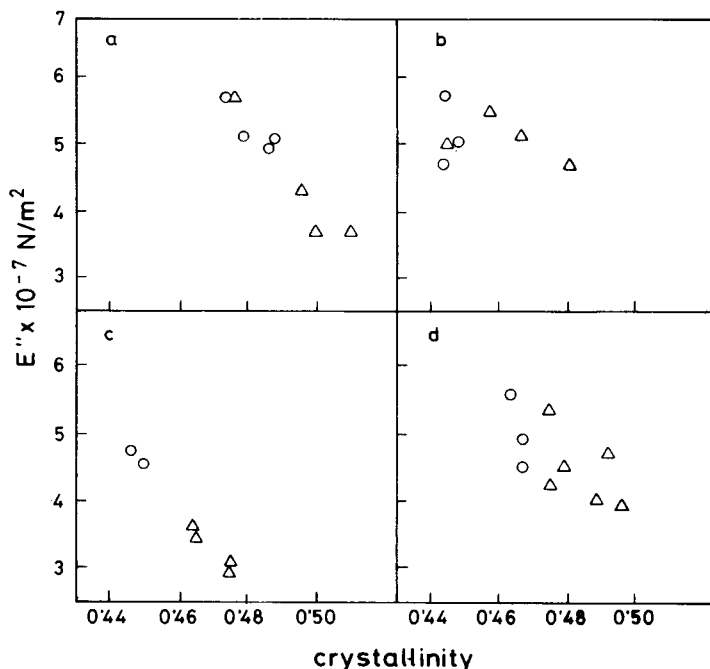
Fig. 9. Maximum values of damping factor vs. crystalline content for irradiated polyethylenes (○) and unirradiated ones (△), subjected to the A, B, C, D, E, and F annealing processes: A: 75°C, 46 h; B: 82°C, 48h; C: 90°C, 6 h; D: 100°C, 41 h; E: 102°C, 48 h; F: 107°C, 48 h. (a) The 710 polyethylene; (b) the 980 polyethylene; (c) the 549 polyethylene; (d) the 519 polyethylene.

between the values of E'' maximum and the crystalline content for each of polyethylenes, which is shown in Figures 8 and 9. In these figures it can be seen that the values of E'' maximum increase when the crystalline content decreases, for the same polyethylene.

These results suggested to us that the crystalline morphology, and not the degree of branching, as suggested other authors,[15] is the parameter which governs the height of β mechanical relaxation. The β-relaxation is more intense in branched polyethylenes because in these the amorphous content is greater. Again, the irradiation and annealing of the samples would modify the β mechanical relaxation if these processes increased the amorphous content.

α-Relaxation

The α-relaxation occurs between 0°C and 100°C at 1 Hz for the polyethylenes studied. It is a complex process formed by two or more over-lapped relaxations. The form and temperature of the peaks depend upon the type of polyethylene. The mechanical spectrum of high density polyethylenes represented by the values of E'' vs. temperature show two or three overlapped relaxations, which are labeled α_I, α_{II}, and α_{III} in order of increasing temperature (Fig. 2). We were not able to separate these relaxations, and we analyzed this process as a whole. Meanwhile, the mechanical spectrum of low density polyethylenes represented by the values of tan δ vs. temperature showed two
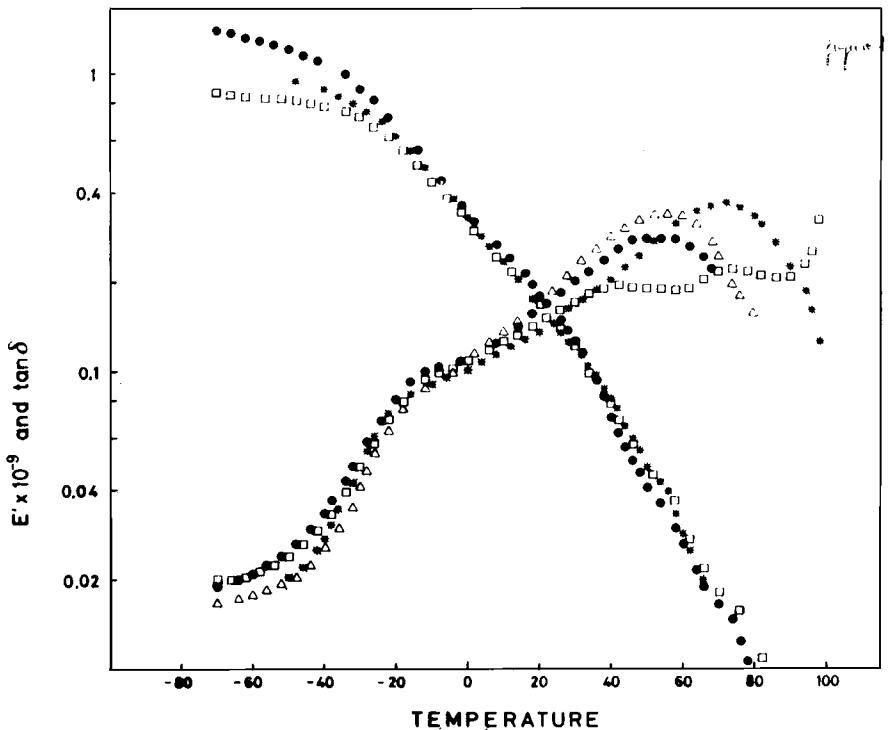
Fig. 10.   Dynamic storage modulus (E') and damping factor (tan δ) vs. temperature of the irradiated (20 Mrad) polyethylene 519 subjected to annealing processes: ($\triangle$) A; ($\bullet$) C; ($*$) D; ($\square$) F. A: 75°C, 46 h; C: 90°C, 6 h; D: 100°C, 41 h; F: 107°C, 48 h.

overlapping relaxations, which were labeled α_I and α_{II} in order of increasing temperature (Fig. 10).

We have proved in an earlier work[6] that the relaxations in low density polyethylenes are related to the melting peaks and their temperature is governed by the most probable crystallite thickness. Now, we have checked that this result can also be stated for high density polyethylenes.

We have plotted the temperature of the maximum values of E'' vs. the reciprocal of the melting point of each high density polyethylene (Fig. 11), and found that the temperature of the E'' maximum increases when the melting point increases in all the irradiated samples as well as in the unirradiated samples.

Since the melting point may be related to the most probable crystallite thickness,[6] this result suggested to us that the parameter which governs the position in the temperature axis of the α mechanical relaxations in all the polyethylenes studied is the most probable crystallite thickness. Thus the 20-Mrad dose of irradiation followed by annealing will have an effect on the position of α mechanical relaxations if this process modifies the most probable crystallite thickness of the samples. We observed that the α peaks in irradiated polyethylenes are lower than in unirradiated ones, because irradiation modifies the molecular structure and hinders the growth of the crystallites during annealing.
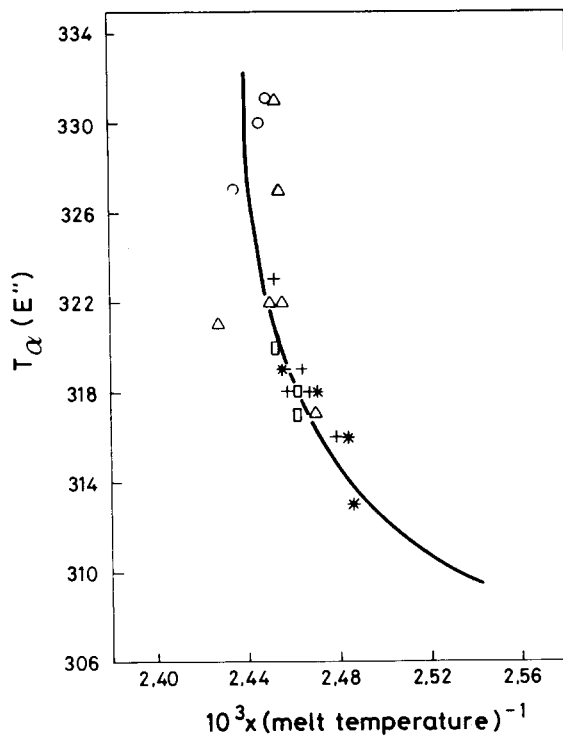
Fig. 11.   Relationship between temperature of E''_{max} values and the melting temperature for the polyethylenes; (△) 10062; (∗) 25055; (□) 25057; (○) XZ86658; (+) 6067.

CONCLUSIONS

The γ-relaxation is formed by the γ_I- and γ_{II}-relaxations in low and high density polyethylenes. The height of the γ_I-relaxation increases with the amorphous content of the samples.

The β-relaxation is present in both high and low density polyethylenes and seems not to be related to the branching index.

The α-relaxation is formed by the α_I and α_{II} in low density polyethylenes and by the α_I, α_{II}, and α_{III} overlapping relaxations in high density ones, which are not separated. The α-relaxation zone in low and high density polyethylenes is representative of the crystalline phase and its position depends on the most probable crystallite thickness of the crystalline phase, because it is related to the melting temperature.

The 20-Mrad dose of irradiation modifies the chemical structure of polyethylenes because it increases the internal unsaturations and the number of ketone and aldehyde groups, while decreasing the number of vinyl and vinylidene groups. The annealing modifies the morphology of the samples. Both processes affect to the dynamic-mechanical relaxation spectrum in low and high density polyethylenes. Thus the height of the γ_I-relaxation increases in irradiated samples because of the increases in the total amorphous content. The position of the α-relaxation shifts to lower temperatures because imperfections in the molecular chains hinder the growth of crystallites during the annealing.

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