

Multifrequency Analysis of the α Relaxation Region of High-Density Polyethylenes: Influence of Thermal History

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SYNOPSIS

The activation energy analysis of the dynamic-mechanical α relaxation has been carried out as a function of thermal history for several high-density polyethylenes. The air-quenched samples display a unique α relaxation whose temperature dependence fits a constant activation energy regardless of the structural features of the samples, whilst the isothermally crystallized samples, on the other hand, display an asymmetric α peak that, often, splits into two, which does not fit a constant activation energy. The asymmetry of the α peak as well as the splitting has been explained accounting for two different relaxation time distributions. The dependence of the intensity of the α and α' relaxations on frequency have been discussed in terms of different mean relaxation times and amorphous layer thickness.

INTRODUCTION

The α relaxation is one of the three relaxations that appear in the isochronal mechanical spectrum of high-density polyethylene. It ranges from 303–340 K, depending on the scan frequency, and it is usually associated with the crystalline phase content.^{1–4} Its position and intensity have generally been related to the crystal thickness⁵ and crystallinity level,⁶ respectively. On the other hand, Mandelkern and coworkers⁷ stated that the position and strength of this relaxation is mainly determined by the fold period. Finally, Boyd⁸ put forward that the mechanism responsible for this transition, when dynamic mechanical measurements are carried out, involves deformation movements into the amorphous region due to reorientations within the crystallites.

The two-site model is the simplest theory that tries to explain the temperature dependence of the viscoelastic behaviour in secondary relaxations.² It states that the relationship between the frequency

of molecular jumps between rotational isomeric states of a molecule is given by an Arrhenius-type equation:

$$\nu = (KT/h)\exp(\Delta S/RT)\exp(-\Delta H/RT) \quad (1)$$

$$\Delta H = -R[\text{dln}\nu/\text{d}(1/T)]_p, \quad (2)$$

where ν is the frequency, R is the gas constant, and T is the absolute temperature. The slope of the representation of the logarithm of the frequency as a function of $1/T$ [eq. (2)] is the negative of the activation energy (ΔH) for the viscoelastic process, in this case the α relaxation of high-density polyethylenes. A unique relaxation time is predicted. This expression establishes that, for high values of the activation energy, a large change in the frequency will be accompanied by a large change in the resonance temperature.

In a previous work,⁹ we stated the influence of molecular segregation^{10,11} on the dynamic-mechanical properties of four high-density polyethylenes that displayed different structural features. This article is aimed at determining the influence of thermal history on the activation energy of the α process on the same polyethylenes using the transition state theory briefly commented on above, as well as at establishing the influence of frequency on this relaxation process.

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Table I Molecular Features of the Materials

Sample Code	M_w (g/mol) ^a	M_n (g/mol) ^a	Density (g/cc) ^a	CH ₃ /1000 CH ₂ ^b
8065	63,000	15,000	0.965	<1
4255	72,000	21,000	0.955	5
2505	40,000	15,000	0.955	5
4005	40,000	11,500	0.955	16

^a Provided by the supplier.^b By infrared spectroscopy (see ref. 8).**EXPERIMENTAL**

The molecular features of the four high-density polyethylene samples have been summarized in Table I.

The dynamic-mechanical analyses were performed in a Polymer Laboratories DMTA apparatus (Traded as Mark II) interfaced to a Hewlett-Packard computer. The mechanical mode used was the bending one sharp knife-like supported.¹² All samples were run according to the following instrumental conditions: a scan rate of 0.5 K/min, a temperature range from 263–383 K, and five frequencies (using the multifrequency mode available in the instrument): 0.1, 0.3, 1, 3, and 10 Hz.

The samples for the analysis were compression moulded for 5 min, ice-water quenched, and isothermally treated for 6 and 24 h in an oven with a temperature accuracy better than ± 0.4 K. The mean dimensions of the samples between the clamps were $10 \times 40 \times 0.65$ mm.

To determine more accurately the transition temperatures, the first derivative of the mechanical

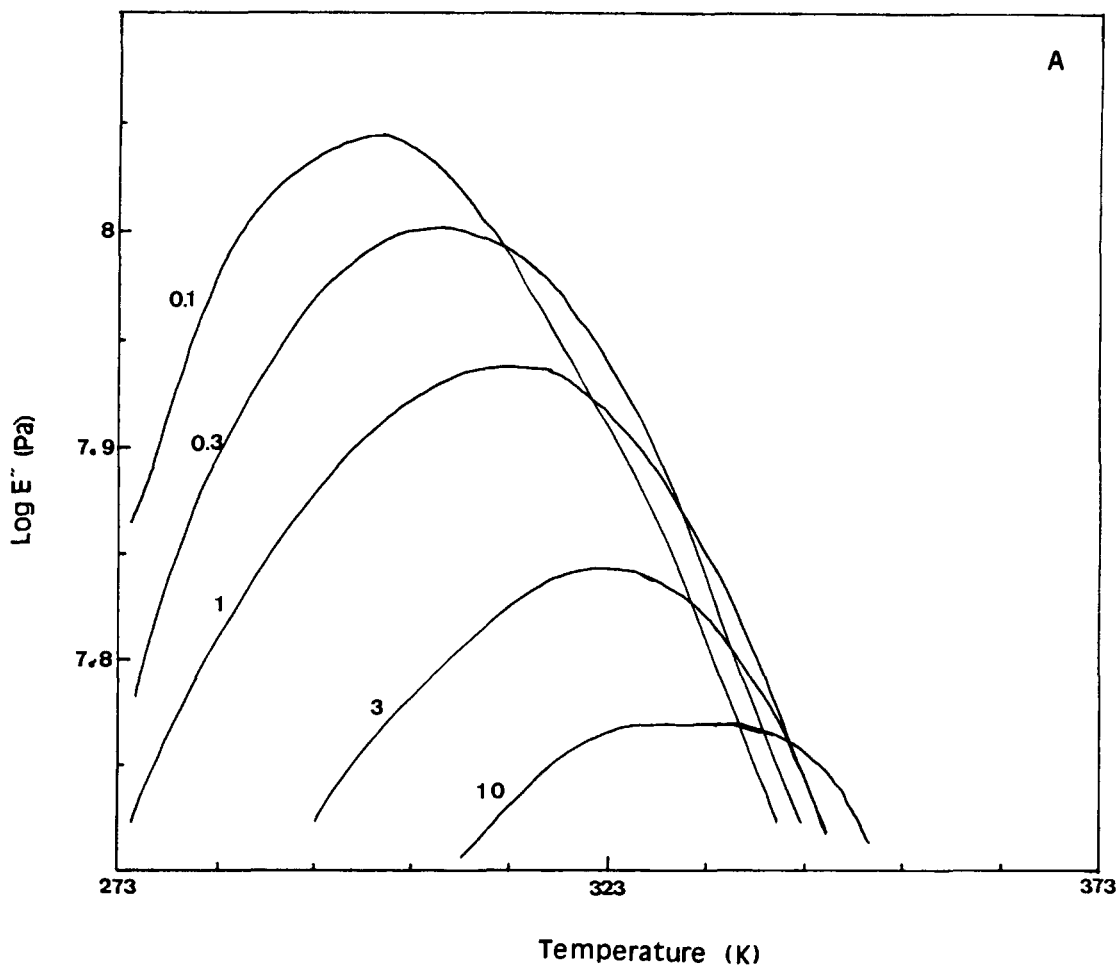


Figure 1 Isochronal mechanical spectra of sample 4005 in the α relaxation region for different scan frequencies. A, airquenched treatment; B and C, isothermal treatment at $T_c = 395$ K and 397 K, respectively (in both cases crystallization time is 6 h). Figure 1(a) shows the frequency associated with each curve.

spectra was obtained using a computer program based on the five-point parabola method.

RESULTS AND DISCUSSION

Three examples of the mechanical spectra [loss modulus (E'') as a function of temperature] corresponding to the multifrequency analysis for sample 4005 are shown in Figure 1. This figure contains data associated with three different thermal histories. The results obtained using eq. (2) are shown in Table II.

The first feature arising from this figure and the table is that the air-quenched samples show a unique peak in the α relaxation region that fits the activated complex theory for all the samples, regardless of structural characteristics (molecular weight distribution and branch content). Moreover, the activation energy value is the same, within the experi-

mental error, for the four polyethylene samples. This result is in accordance with the hypotheses by Boyd⁶ and Bonart and Owen,¹³ who assumed that, to produce a configurational change that is mechanically active in the α region, a sum of a series of movements within the crystalline phase must take place. These cooperative movements, all of them having the same activation energy, give rise to a broad relaxation distribution.

On the other hand, the isothermally crystallized samples show a different behaviour to that observed for the air-quenched ones. The first noticeable difference is the asymmetry displayed by the relaxation peaks, asymmetry that, in some cases, becomes a clear double peak. The appearance of the double peak is apparent for samples 2505 and 4005 and for weight fractions of segregated material, W_s , (see Ref. 9), bigger than 43%. The second difference is that, due to this asymmetry in the peak shape, the isothermally thickened materials do not fit the acti-

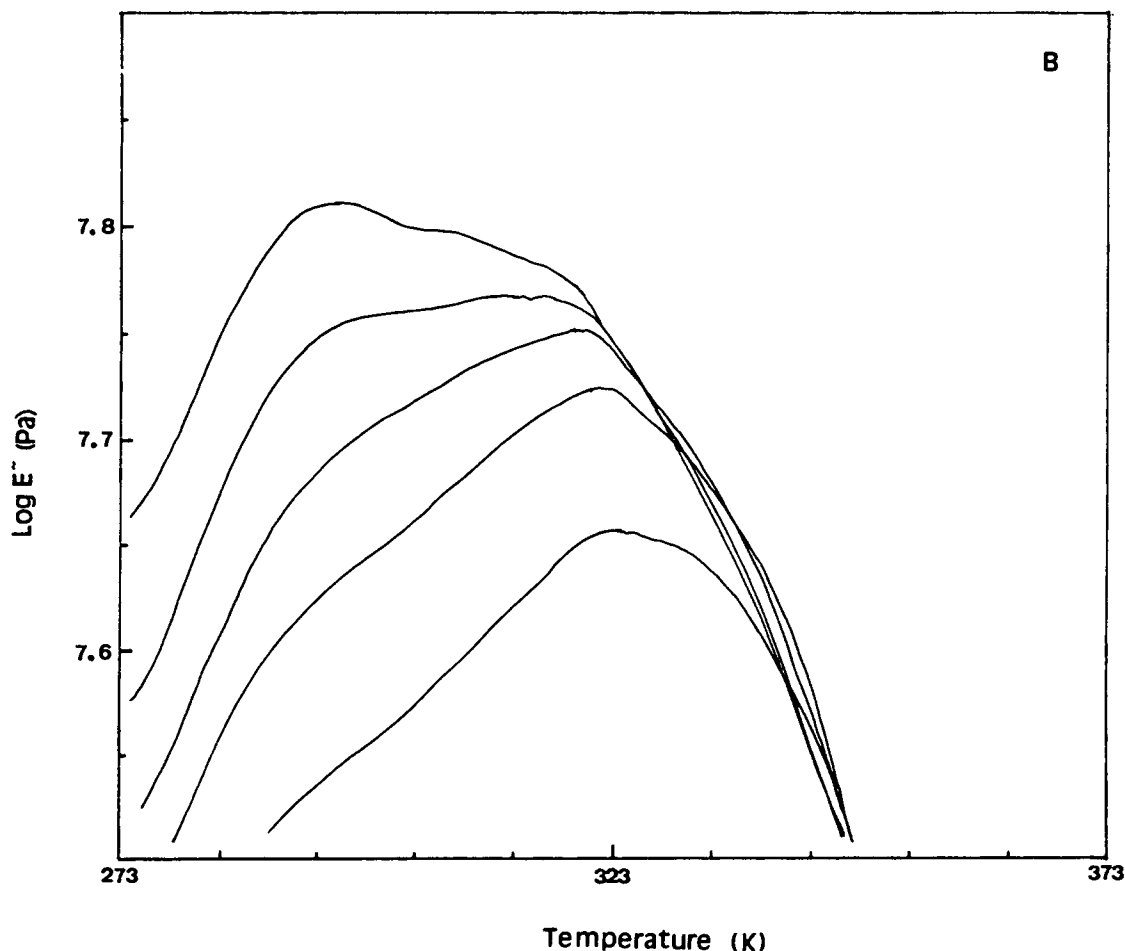


Figure 1 (continued from the previous page)

vated complex theory. The activation energy values given in Table II clearly evidence this observation due to the important scattering found for these values depending on isothermal conditions.

The nature of the two peaks is still a subject for discussion. Whilst some authors^{7,8} suggested that the high-temperature peak (hereafter called α relaxation) is associated with deformation movements within the amorphous region due to reorientations within the largest lamella, others referred to it as to be related to chain movements within the crystalline defect region.⁶ On the other hand, the low-temperature peak (hereafter called α' relaxation) has been explained in two different ways: as reorientations of those lamella that display a smaller lamellar thickness^{7,8} and as the relaxation within the amorphous region.⁶ Our previous work on these samples⁹ and on low-density and linear low-density polyethylenes¹⁴ have shown that the α relaxation temperature depends mainly on the lamellar thick-

ness. Provided this behaviour, we will discuss the activation energy results using the first interpretation of the mechanism of the α relaxation.^{7,8}

Together with the two observations on the isothermally crystallized samples aforementioned, there are two outstanding features to be pointed out, both related to the frequency dependence of the α and α' peaks:

1. Whilst the resonance temperature for the α peak increases steeply as a function of frequency, the resonance temperature for the α' peak experiences a slower increase (see Table III).
2. The strength of both relaxations changes with the frequency: Whilst the α' relaxation undergoes a sharp decrease in its strength as the frequency increases, the α relaxation experiences only a smooth decrease. Thus, whilst the α' peak presents higher intensity

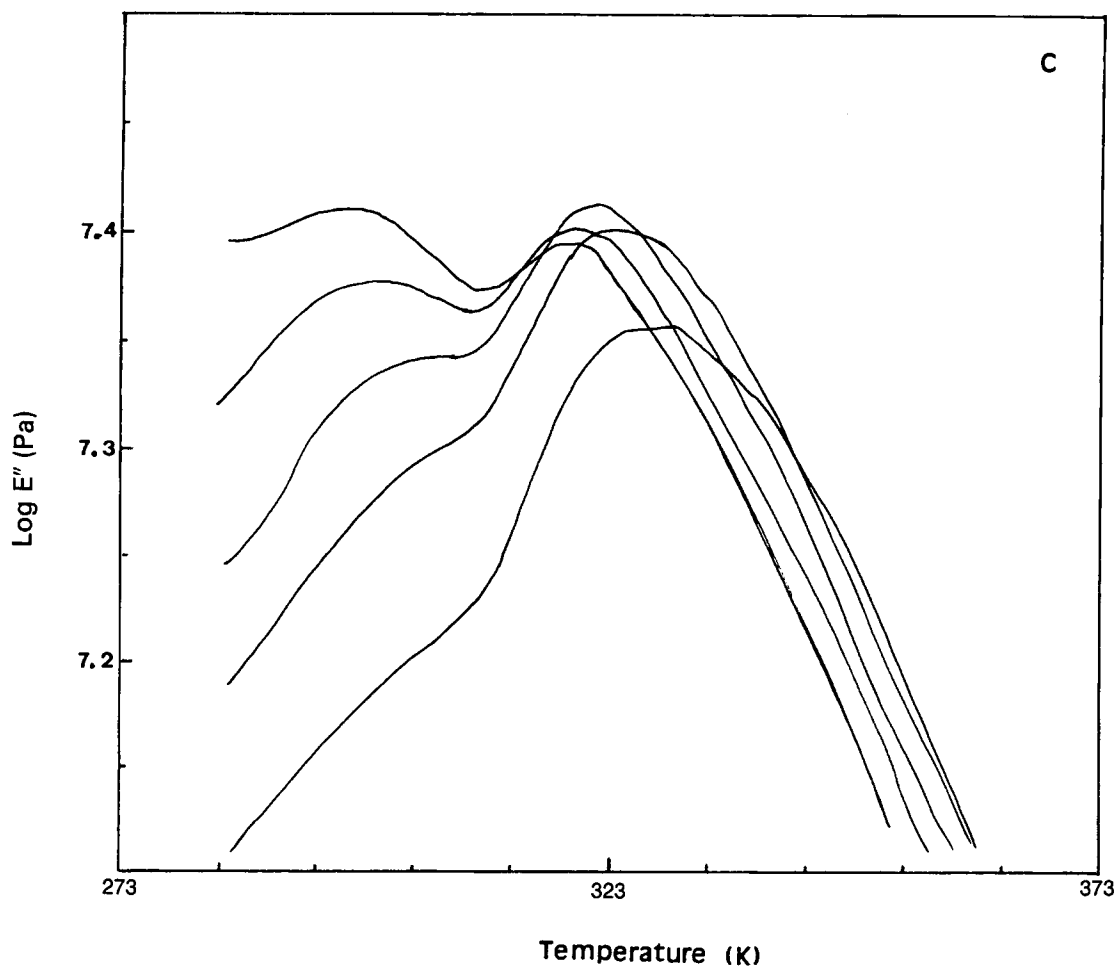


Figure 1c (continued from the previous page)

Table II Activation Energy (kJ/mol) Results

Treatment		8065		4255		2505		4005	
<i>T/K</i>	<i>t/h</i>	W_s^a	E_a	W_s^a	E_a	W_s^a	E_a	W_s^a	E_a
Airquenched		—	122	—	126	—	128	—	120
390	14	—	—	—	—	—	—	35	164
392	6	—	—	—	157	24	127	45	St ^b
	24	—	—	—	130	22	156	43	St ^b
395	6	11	136	20	143	30	115	60	162
	24	9	103	20	170	26	143	54	173
397	6	12	114	29	155	44	St ^b	—	162
	24	11	120	26	136	40	122	—	St ^b
400	6	14	132	—	150	—	142	100	137
	24	12	144	35	154	—	St ^b	100	—
402	6	—	109	100	152	100	126	—	—
	24	24	146	100	131	100	130	—	—
405	6	100	121	100	130	—	—	—	—
	24	100	123	100	—	—	—	—	—

^a Weight fraction of segregated material obtained by differential thermal analysis (see Ref. 8). When this value is 100, we mean that this sample has been air-quenched from the given temperature.

^b Not measured due to the presence of a double peak.

than the α one for low values of the frequency, this latter relaxation shows bigger intensity than the former for high frequencies.

The first observation is due to a different activation energy for each process that would give rise to a different response when the frequency of the sinusoidal force is changed. Although the low resolution displayed by these two peaks makes difficult a quantitative evaluation of the activation energies for both processes for most of these samples, the material 4005 crystallized at 397 K for 24 h allows to calculate a value of 164 kJ/mol for the activation energy of the α' relaxation and a value of 483 kJ/mol for the activation energy of the α relaxation.

Table III Relaxation Temperatures as a Function of Frequency for the Isothermally Crystallized Sample 4005

Frequency (Hz)	$T_c = 392$ K		$T_c = 397$ K	
	$T_{\alpha'}/K$	T_{α}/K	$T_{\alpha'}/K$	T_{α}/K
0.1	294.5	306.5	300	319
0.3	295.5	313	301	320
1	296	320.5	303	322.5
3	297	323	305	324
10	298	324.5	306	326.5

Crystallization temperature: 24 h.

These values agree qualitatively with those calculated by Kahizaki and Hideshima (147 and 209 kJ/mol for the α' and α relaxations, respectively).¹⁵

The second observation must be related to the presence of a heterogeneous lamellar distribution in these isothermally crystallized samples as a consequence of molecular segregation.⁸ As far as the crystallization temperature increases, the amount of segregated material that crystallizes on further cooling increases as well. This brings about two types of lamellar distributions. Although the isochronal experiments are not the most suitable ones for the determination of the relaxation time distributions, the previous comments on molecular segregation as well as the work by Boyd⁶ and Bonart and Owen¹³ allow us to state that the presence of two different relaxation time distributions, rather than the existence of two different relaxation mechanisms, is responsible for the appearance of the asymmetries in the α peak or the splitting of this relaxation in two. Each relaxation time distribution will display a maximum at a different frequency (equal to the inverse of the relaxation time 2) and, therefore, the intensity of the maxima will change as a function of frequency. From Figure 1 it is possible to infer that the relaxation time for the α' relaxation is bigger than for the α one, due to the fact that the former displays its maximum at lower frequencies than the latter. This behaviour can be explained accounting for the morphology of the amorphous phase between

lamellae. The amorphous layer between isothermally thickened lamellae is thinner than the one corresponding to the lamellae formed on cooling, this last one being reached in chain defects. Accepting that the α relaxation takes place in the amorphous phase, it is reasonable to expect the isothermally crystallized lamellae to oscillate faster between the two sites than the lamellae formed on cooling, this being supported by the experimental data.

CONCLUSIONS

The multifrequency analysis carried out on the α relaxation region of four polyethylene samples allow us to draw the following conclusions:

1. The air-quenched samples display a unique α relaxation whose temperature dependence fits a constant activation energy regardless of the structural features of the samples.
2. The isothermal samples, on the other hand, display an asymmetric α peak that, often, splits into two, which does not fit a constant activation energy.
3. The two peaks observed in the isothermal treated samples have been explained accounting for a unique relaxation mechanism and two different relaxation time distributions.
4. The mean α' relaxation time is higher than the α relaxation one.
5. The relaxation time is a function of the amorphous content.

This work has been financially supported by the Departamento de Educación, Universidades e Investigación del

Gobierno Vasco and the Vicerrectorado de investigación de la UPV. The four polyethylene samples provided by Dow Chemical Iberica are gratefully acknowledged.

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Received November 6, 1989

Accepted November 30, 1990