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Influence of chemical composition distribution and thermal history on the mechanical properties and viscoelastic relaxations of ethylene–1-butene copolymers

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The tensile drawing behaviour and the dynamic mechanical properties of four ethylene–1-butene copolymers, with nearly the same comonomer content but obtained with slightly different catalyst systems, have been analysed. It was found that the large strain mechanical properties and the strain-hardening behaviour seem to be affected by the degree of homogeneity in the distribution of comonomer along the different chains, reflecting the differences in the catalyst systems used. However, a parallel trend was not so clear for the small-strain dynamic mechanical properties for a particular thermal history, although the dependence of the relaxations on the crystallization conditions is evident.

1. Introduction

In the last fifteen years, many supported-type catalysts have been employed for the copolymerization of ethylene and alpha-olefins. A high proportion of these new catalysts was developed to permit processes which would not require removal of the catalyst residues from the polymer products. Among them, the systems consisting of titanium compounds supported on $MgCl_2$ are the most interesting (see [1, 2]). One of the factors influencing the relative copolymerization activities of a particular catalyst is the way in which the support is formed. So, different copolymer products with the same whole chemical composition but with varying distributions can be obtained, depending on the physical state of the support. The usual heterogeneity on composition shown by these copolymers, with a higher concentration of comonomer units in the lower molecular weight chains [3, 4], is the result of the existence in the catalyst of centres which exhibit different activity. The activity of these centres can be affected not only by the nature and physical state of the support but also by the addition of different electron-donor substances [1].

Therefore, the catalyst system used in the synthesis will determine some of the structural characteristics of the so-called linear low-density polyethylenes (LLDPEs), and thus the study of the relationship between structure and mechanical properties of ethylene–alpha-olefin copolymers is a task with difficulties added to the inherent structural complexity of semicrystalline polymers, where the thermal treatment imposed on the sample is an important parameter in determining the final properties of the material.

The purpose of the present work was to study the mechanical properties of LLDPEs synthesized with slightly different catalyst systems and crystallized under different conditions. Thus, four ethylene–1-butene copolymers, obtained with different catalyst systems, have been crystallized from the melt under two thermal treatments. The copolymers have been chosen with nearly the same comonomer content in order to analyse in a proper way the effect of differences in the chemical composition distribution, i.e. unequal comonomer content along the chains, produced by the modifications in the catalyst system.

2. Experimental details

2.1. Materials

Four ethylene–1-butene copolymers (A to D, see Table I), were chosen for this study. Sample D was a commercial Lotrex LLDPE, while copolymers A, B and C were synthesized in a high-pressure pilot-plant scale reactor with $MgCl_2$ supported Ziegler-Natta catalysts, with varying Ti/Mg ratios. Thus, the catalyst for sample A was prepared with a ratio of 3%, while those for B and C had a ratio of 5%. The

TABLE I Molecular characteristics of the ethylene–1-butene copolymers

Copolymer	Comonomer content (mol %)	$10^{-3} M_n$	M_w/M_n
A	4.54	20.0	3.61
B	4.45	22.9	3.50
C	4.24	30.8	3.06
D	4.81	24.6	3.62

catalysts for copolymers B and C differ in the preparation of the support: the former was obtained from an organomagnesium compound, while the $MgCl_2$ of the second was a dried commercial material and, due to its low surface area and poor interaction with the $TiCl_4$, both components had to be intensively ball-milled, in order to activate them and to introduce sufficient amounts of titanium into the crystal lattice of $MgCl_2$.

2.2. Characterization of the copolymers

The determination of the comonomer content was carried out by solution ^{13}C nuclear magnetic resonance (NMR) in a Bruker AC300 operating at 75.47 MHz and 7.046 T. Spectra were taken in solution of *o*-dichlorobenzene at 100° C, with the usual acquisition parameters [5]. The comonomer sequence distribution inside the chains was analysed by the method given by Hsieh and Randall [6], concluding that the four copolymers have a nearly random distribution with no appreciable differences among them [7]. The molecular weights and molecular weight distributions were determined in a Waters ALC/GPC 150 gel permeation chromatograph at 145° C in 1,2,4-trichlorobenzene, following standard techniques. The results for the four copolymers are shown in Table I.

The thermal properties of these samples were measured by means of a Perkin Elmer DSC-7 calorimeter interfaced with a data station. The heating rate was $10° C\,min^{-1}$ and the heat of fusion of a perfect crystal, used in the determination of the crystallinity, was taken as $290\,J\,g^{-1}$ [8].

The Raman spectroscopy study was carried out in a Ramanor U 1000 double monochromator equipped with two $1800\,g\,mm^{-1}$ planar holographic gratings. Excitation is provided by ~100 mW 514.5 nm radiation of a Spectra Physics series 2000 Ar^+ laser. The plasma lines are eliminated by use of an Applied Photophysics premonochromator and the scattered light is collected using the 90° geometry. The interfacial contents were calculated from the internal mode region of the spectra, following well-established procedures [9]. Longitudinal acoustic modes (LAM) of the Raman spectra were used to obtain information about the crystallite thickness [10].

2.3. Sample preparation

Polymer granules were placed in a Collin press fitted with smooth-polished plates and hot-pressed at 10 MPa and 150° C for 5 min. The cooling process was carried out following two different routes, either by quenching the molten polymer in ice-water or by slowly cooling it to room temperature (average cooling rate $2° C\,min^{-1}$). The samples obtained in these ways are coded Q and S, respectively.

2.4. Dynamic mechanical properties

Viscoelastic relaxations were studied with a Rheovibron DDV-II-B dynamic viscoelastometer. The complex modulus and the loss tangent were measured at 110, 35, 11 and 3.5 Hz over the temperature range −150 to 100° C. The activation energy (ΔH) values were determined according to the Arrhenius-type equation $f = f_0 \exp(-\Delta H/RT)$, where f and T are the values of frequency and Kelvin temperature, respectively. The absolute errors of ΔH were obtained by assuming a maximum variation of ± 1° C in the temperatures assigned from the plots of loss modulus against temperature.

2.5. Drawing procedures

Dumb-bell-shaped specimens were uniaxially drawn in an Instron dynamometer at strain rates ranging from 0.7 to $6.7\,min^{-1}$. The samples were stretched at 23, 40 and 88° C by using a conditioning chamber. The actual draw ratios, λ, were determined from the displacement of parallel ink marks and the yield stress values have been calculated from the first point having a horizontal tangent in the stress–strain plots.

3. Results and discussion

3.1. Tensile drawing behaviour

The stress–strain behaviour of these samples was studied at three temperatures: 23° C (room temperature), 40° C (approximately the α relaxation temperature) and 88° C (considerably higher than the temperature of that relaxation).

It is important to note that the behaviour of the different polyethylenes has been classified under three categories [11]. The low molecular weight linear polyethylenes ($M_w < 1.5 \times 10^5$) display a well-defined neck as a consequence of their inhomogeneous deformation. On the other hand, a high molecular weight linear polyethylene ($M_w = 8 \times 10^6$) shows no necking and its deformation is uniform. The intermediate category includes low and linear low-density polyethylenes and medium molecular weight polyethylenes, which show stress–strain curves with necking of different intensity. The samples studied in this work are classified under the intermediate category and they will be discussed below according to the main differences in their stress–strain curves. This group is so numerous that polyethylenes belonging to it should be sorted according to the sharpness of the neck, the extent of the draw plateau and the intensity of the strain-hardening phenomenon.

The comparative results at a fixed strain rate, for example $0.7\,min^{-1}$, show a clear difference between samples A and D and the others. In fact, Fig. 1 shows

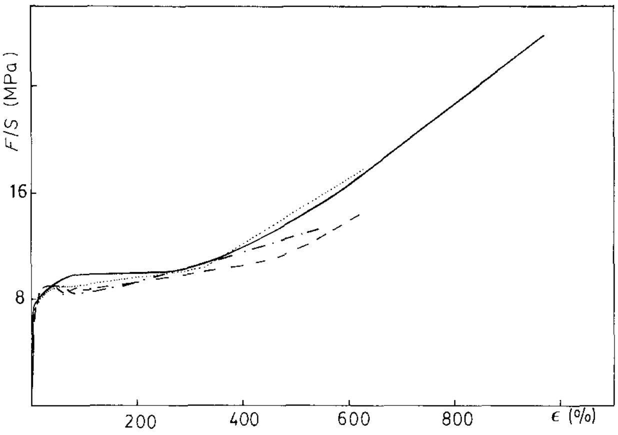

Figure 1 Stress–strain plots for the quenched ethylene–1-butene copolymers stretched at 23° C and strain rate of $0.7\,min^{-1}$. (——) AQ, (– – –) BQ, (–·–·–·–) CQ, (· · ·) DQ.

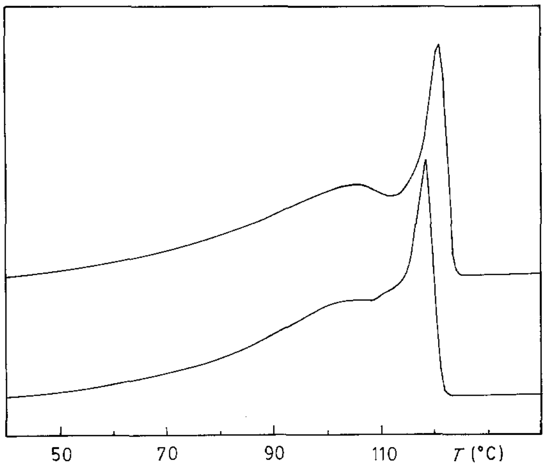

Figure 2 DSC curves of samples A (upper) and D (lower), slowly crystallized from the melt.

a much higher tensile strength and maximum elongation for sample A than for samples B, C. Moreover, samples A and D do not display necking but they show a draw plateau up to 350% strain and strain-hardening behaviour thereafter. On the other hand, samples B and C do not exhibit a draw plateau and they begin the strain-hardening behaviour at 150% strain. An increase in the strain-hardening process with comonomer content has been reported [12] for ethylene-1-hexene copolymers. However, the difference in that content for the samples studied here is very small, especially between samples A and B (see Table I), so that the distinct behaviour mentioned above is difficult to explain only in terms of this parameter.

The pairing of samples A and D on one side, and B and C on the other is also found in the corresponding DSC melting endotherms. Thus, Figs 2 and 3 show these curves for the slowly cooled samples, presenting two maxima typical of LLDPEs crystallized under these conditions, but from their relative intensity it can be deduced that morphological differences do exist between pairs A–D and B–C. It was pointed out above that LLDPEs tend to concentrate a higher proportion of the comonomer in the lower molecular weight chains, mainly depending on the nature of the catalyst system, and the usual existence of two maxima is due to this inhomogeneity in chemical composition. In fact, homogeneous copolymers can be produced [13], giving rise to a single melting peak. Therefore, an idea of the homogeneity of that distribution can be deduced from the relative intensity of the two maxima [4]. Thus, a chemical composition distribution index, DI, has been defined as the ratio of the low-temperature peak area to the total one [4]. It is clear from Figs 2 and 3 that the relative intensity of the low-temperature peak is greater for samples B and C, so that the values of DI for these copolymers are higher than for samples A and D, suggesting a more homogeneous distribution of chemical compositon in the former copolymers. Thus, we believe that the differences between the samples here studied can be explained by a distinct chemical composition distribution of comonomer along the chains between the two pairs of samples, somehow reflecting the particularities of the catalyst systems used.

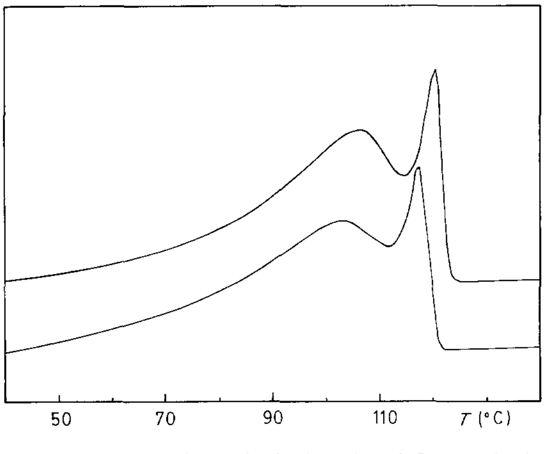

Figure 3 DSC curves of samples B (lower) and C (upper), slowly crystallized from the melt.

The above-mentioned results are confirmed by the maximum draw ratio attainable, values of which are listed in Table II. Samples A and D can be drawn to draw ratios higher than the other samples, although

TABLE II Drawing temperature (T_d), strain rate ($\dot{\varepsilon}$) and maximum draw rates (λ_m) for the various copolymer samples, either quenched (coded Q) or slowly crystallized (coded S)

Sample	T_d (°C)	$\dot{\varepsilon}$ (min^{-1})	λ_m
AQ	23	0.7	7.5
AQ	23	5.0	8.2*
AQ	23	7.1	7.2
AQ	40	0.7	3.7
AQ	88	0.7	7.0
AS	23	7.1	6.7
AS	23	7.1	8.2
AS	40	0.7	3.5
BQ	23	0.7	5.5
BQ	23	6.7	5.7
BQ	40	0.7	5.5
BQ	40	6.7	5.5
BQ	88	0.7	6.8
BQ	88	6.7	6.9
BS	23	0.7	5.5
CQ	23	0.7	5.1
CQ	23	6.7	5.2
CQ	40	0.7	5.8
CQ	40	6.7	4.4
CQ	88	0.7	6.4
CQ	88	6.7	5.1
CS	23	0.7	5.5
CS	40	6.7	7.2
DQ	23	0.7	5.5
DQ	23	6.7	6.0
DQ	40	0.7	6.0
DQ	40	6.7	6.5
DQ	88	0.7	6.5
DQ	88	6.7	6.9
DS	23	0.7	5.2
DS	23	6.7	5.0
DS	40	0.7	6.0
DS	40	6.7	4.5
DS	88	0.7	4.5
DS	88	6.7	7.5

*Partially whitened sample.

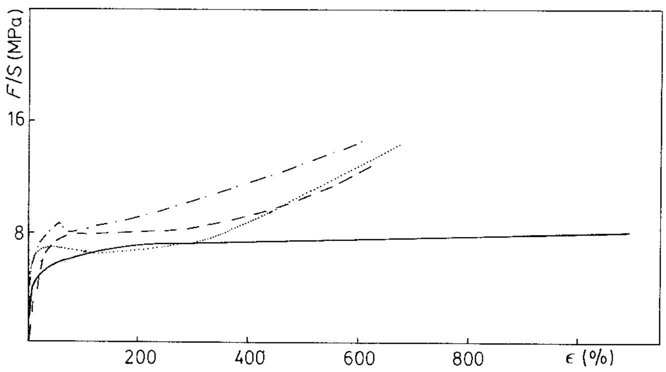

Figure 4 Stress–strain behaviour corresponding to the quenched ethylene-1-butene samples stretched at 40° C and strain rate of 0.7 min^{-1}. For key, see Fig. 1.

sample A whitens when the drawing takes place at room temperature. This phenomenon, due to the formation of microvoids, has been observed in other polymers [14] and also for polyethylene [11]. However, in the latter paper the whitening is found in a sample drawn through a neck whereas the sample A is stretched homogeneously. It can also be observed in Fig. 1 that the yield stress value for sample A is higher than for samples B and C. This behaviour cannot be attributed to differences in crystallinity, because the three samples have similar values (35% to 38% as determined by differential scanning calorimetry (DSC) measurements for the slowly crystallized samples [7]) but rather to the maximum in the crystallite size distribution.

When the stretching process is carried out at 40° C samples A and B do not show necking (the former keeps the draw plateau constant until 1000% strain and the latter begins the strain hardening at ε = 300%) while sample C shows a stress increase after necking for values of strain about 100% (Fig. 4). On the other hand, if the stretching process takes place at 88° C, a temperature well above the α relaxation of the polymers, the stress–strain behaviour is similar for all the samples (Fig. 5). Moreover, the strain hardening pattern is less pronounced than that at room temperature, this result differing from the observed on 1-hexene copolymers, which maintain the strain hardening behaviour even when drawn at 115° C [12].

In relation to the influence of the temperature on drawing, from the joint inspection of Figs 1, 4 and 5 it can be observed for each sample that the stress at a fixed strain decreases as the stretching temperature increases, this feature being more pronounced at temperatures above the α relaxation temperature. This result is in agreement with that obtained for other 1-butene copolymers [15].

The effect of the strain rate on the yield stress has also been observed. In accordance with other results on polyethylene [11] and polyesters [14], the higher strain rate increases the value of the yield stress for the copolymers studied in this work.

The influence of thermal history on the stress–strain behaviour of the copolymers can be assessed by comparing Figs 1 and 6, which correspond to samples quenched and slowly crystallized, respectively. The curves are rather similar and only a slight increase in the stress is observed at low strains. This result agrees with the dependence of yield stress on the level of crystallinity [11], because the latter quantity increases slightly (less than 3%, as determined by DSC [7] and solid-state ^{13}C nuclear magnetic resonance [16]) with the thermal history imposed on the samples studied here. Moreover, the most probable crystallite size of these copolymers (see Table III) fits quite well to the linear relationship between the yield stress and the crystallite size proposed for linear and branched polyethylenes [11].

3.2. Dynamic mechanical behaviour

Polyethylene displays three relaxations, conventionally designated α, β and γ relaxations in order of decreasing temperature, which take place below the melting point. The α, β and γ relaxations have been extensively studied from the earlier days of the dynamic mechanical methods, and their relation to the key structural factors of the polyethylenes (mostly linear and branched) has been recently reported in several important papers [17–19]. In addition to this, the increasing industrial significance of the ethylene-alpha-olefin copolymers has given rise to works focused on the viscoelastic behaviour of some of these copolymers [20–23].

Fig. 7 is an example of the temperature dependence

TABLE III Relaxation temperatures at 11 Hz, loss modulus (E'') maxima and activation energy (ΔH) for the α, β and γ relaxations of the copolymer samples, together with their interfacial content (α_b) and crystallite thickness (l_c) determined by Raman spectroscopy [7]

Sample	T_γ (° C)	E''_γ (MPa)	ΔH_γ (kJ mol^{-1})	T_β (° C)	E''_β (MPa)	T_α (° C)	E''_α (MPa)	α_b	l_c (nm)
AQ	−116	70	68 ± 13	−24	49	27	24	11 ± 8	10.8
BQ	−119	67	65 ± 15	−20	46	20	26	15 ± 8	9.5
CQ	−118	45	60 ± 13	−17	35	25	27	13 ± 8	9.0
DQ	−114	32	–	−18	31	27	24	12 ± 8	10.8
AS	−122	23	–	−20	25	40	22	17 ± 8	15.5
BS	−120	32	36 ± 4	−20	28	40	20	–	–
CS	−120	37	46 ± 7	−20	30	40	22	12 ± 8	11.9
DS	–	–	–	−19	–	35	20	15 ± 8	11.7

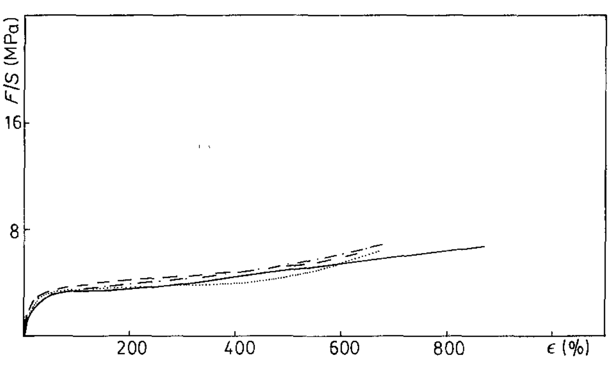

Figure 5 Stress–strain plots for the quenched ethylene–1-butene copolymers stretched at 88° C and strain rate of $0.7\,\mathrm{min}^{-1}$. For key, see Fig. 1.

of the loss modulus for the copolymers studied in the present work and Table III lists the temperature at which each relaxation takes place, together with the maximum value of the loss modulus at the relaxation temperature, the percentage of interfacial content and the crystallite thickness for all the samples. These results will be commented on separately for each relaxation. When the intensity of the relaxations is quoted, it refers to the maximum value of the loss modulus in the relaxation interval, and in order to avoid the possible variations of the absolute values in the loss modulus of the different samples, absolute values in Table III have been normalized, when it is necessary for comparative purposes, dividing them by the minimum loss modulus value of each sample (which occurs in the temperature range around −50° C). The first main conclusion from Table III is, then, that no clear resemblance can be found between the two pairs of samples as in the case of the drawing behaviour.

3.3. α relaxation

The increase of the α relaxation temperature, when the samples studied are slowly crystallized, is related to the increase of the crystallite thickness determined by Raman spectroscopy. This result is similar to that referred of linear and branched polyethylenes and ethylene–vinyl acetate copolymers [17], and the numerical values obtained here fit well the α relaxation temperature–crystallite thickness relation reported in that work (Fig. 8).

It is generally agreed that the α relaxation originates from rotation, translation and twisting of the chains inside the crystals [25, 26]. Owing to the fact that the mobility of the crystals requires deformation of the interfacial regions, a mechanism which attributes the α relaxation to motion in the interfacial and crystalline phases has been proposed [27]. The results of the present work on the relation between crystal thickness and intensity of the α relaxation confirm that this process is affected by the chain mobility of the crystals and, therefore, it takes place at higher temperatures as the crystallite thickness increases. The coupled contributions of the folds, loops and tie molecules of the interfacial region to the α relaxation are in accordance with other previous works [18, 19, 27] and with our results on chlorinated polyethylene [28], where the α relaxation temperature decreases as the chlorine content in the amorphous phase increases. The preferential chlorination in the amorphous phase was assessed because the heterogeneous process was performed in suspension under mild conditions. Moreover, the

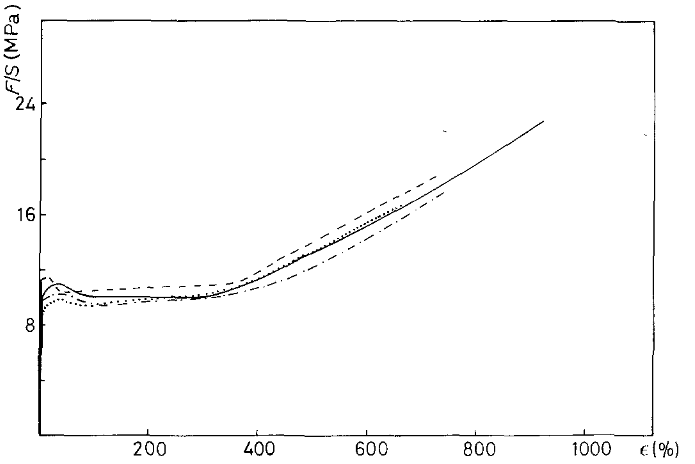

Figure 6 Stress–strain pattern corresponding to the slowly crystallized ethylene–1-butene samples stretched at 23° C and strain rate of $0.7\,\mathrm{min}^{-1}$. For key, see Fig. 1.

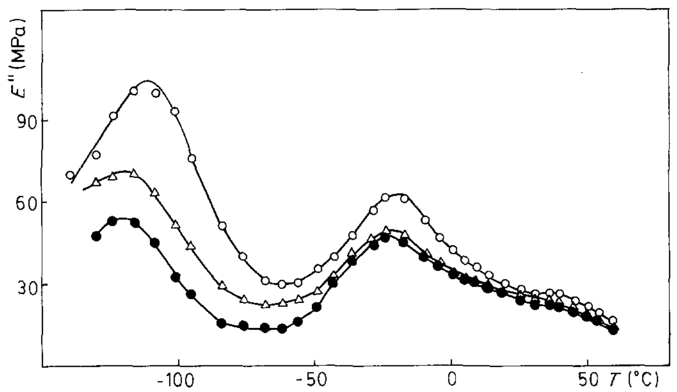

Figure 7 Temperature dependence of the loss modulus of the quenched sample AQ at various frequencies: (○) 110; (△) 11, and (●) 3.5 Hz.

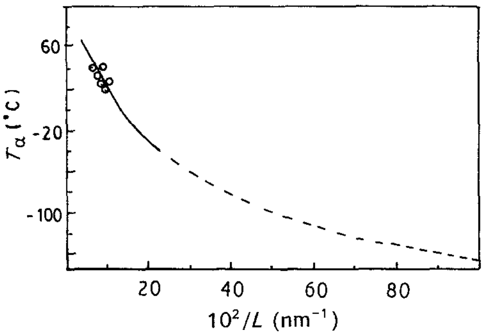

Figure 8 Variation of the relaxation temperature (E'' basis) of polyethylenes as a function of the crystallite thickness: (○) present work; (——) [17]; (- - -) [24].

increase of the α relaxation temperature reported in the present work for the slowly crystallized samples was also previously found for polyethylene filaments [29].

It can be observed (by comparing Figs 7 and 9) that the α relaxation of the quenched samples appears as a shoulder of the neighbouring β relaxation whereas the slowly cooled samples show it as a well-defined peak. This fact may be due to the higher α relaxation temperature for slowly crystallized samples, as well as to the narrower distribution of crystallite thickness for these materials.

3.4. β relaxation

The β relaxation has been universally detected in branched polyethylenes at temperatures around −20° C but it sometimes appears, although weakly, in some samples of linear polyethylene. From the study of various polyethylenes and their copolymers, it has been concluded that this relaxation results from motions of chain units in the interfacial region [17, 30]. Moreover, it was reported [21] that the presence of ethyl branches affects to the β relaxation to a lesser extent than do other longer branches, suggesting that the intensity of the β relaxation depends not only on the interfacial content but also on the comonomer which generates the existence of the interfacial region.

The β relaxation of the samples studied in the present work is located around −20° C. Both temperature and intensity of the β relaxation are constant for each thermal history and this result is readily correlated with the practical constancy of the interfacial content, as shown in Table III.

3.5. γ relaxation

The polyethylenes studied in this work show a relaxation at temperatures around −120° C. This temperature and the low activation energy of the relaxation are typical features of the γ relaxation produced by joint movements of chains containing sequences of three or more methylenic units, either in the main or side chains. Thus, the γ relaxation has also been found in other polymer series such as polyoxides [31], aromatic polyesters [32] and disubstituted polyoxetanes [33]. The movements of the methylenic sequences take place in the amorphous phase as can be deduced from the results listed in Table III, because the quenched samples display intensity values higher than those of the slowly crystallized samples.

4. Conclusion

The large-strain mechanical properties and the strain-hardening behaviour of the ethylene–1-butene copolymers studied here, with nearly the same comonomer content, seem to be affected by the degree of homogeneity in the distribution of comonomer along the different chains, reflecting the differences in the catalyst systems used. However, a parallel trend was not so clear for the small-strain dynamic mechanical properties for a particular thermal history, although the dependence of the relaxations with crystallization conditions is evident. Thus, the α relaxation, which is partially overlapped by the β one, appears more clearly when the copolymer samples are slowly crystallized, being also shifted to higher temperatures. The β relaxation remains constant within a wide range of interfacial content and the intensity of γ relaxation is slightly diminished by a more perfect crystallization.

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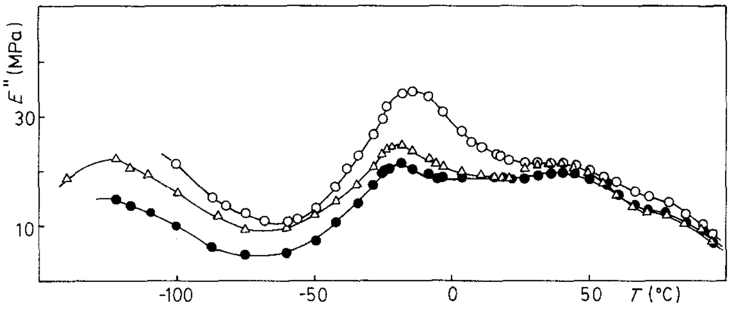

Figure 9 Temperature dependence of the loss modulus of the slowly crystallized sample AS at various frequencies: (○) 110; (△) 11, and (●) 3.5 Hz.

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