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Viscoelastic relaxations in poly(ethylene-*co*-1-octadecene) synthesized by a metallocene catalyst

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Abstract

The viscoelastic relaxations of four copolymers of ethylene and 1-octadecene, with different comonomer contents, synthesized with a metallocene catalyst, have been analysed and compared to those of the corresponding polyethylene homopolymer. Similar to other ethylene copolymers, the temperature for α relaxation decreases with the increase in the comonomer content, attributed to the reduction of the crystal size. In fact, a linear relation has been found between the temperature location of α relaxation and the crystal thickness estimated from the SAXS long spacing. However, the position of β relaxation experiences very little dependence with the comonomer content and it overlaps to α relaxation for the higher comonomer contents. As to γ relaxation, there is also a clear effect of the comonomer content on the breadth and on the location of this relaxation.

Keywords: Ethylene–1-octadecene copolymers; Dynamic mechanical properties; Metallocene catalyst

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1. Introduction

Linear low-density polyethylene (LLDPE) is an important family of ethylene polymers. Appearing in the industry 20 years after the discovery of high-density polyethylene, it was an industrial revolution. Density (or crystallinity) control is obtained by copolymerization of ethylene with α-olefins and typical values are in the range 0.915–0.925 g/cm^3. When the comonomer content is above 10%, special very low density products are obtained (0.88–0.915 g/cm^3) called very low density polyethylenes, VLDPE. In the beginning, these copolymers were synthesized by Ziegler–Natta catalysts, and they presented non-homogeneous distribution of comonomer and wide molecular weight distributions. Recently, the development of new technologies led to the appearance of metallocene catalysts. These new catalysts are revolutioning the polymer industry in general, and that of polyolefins in particular. This new generation of single-site metallocene catalysts leads to copolymers with a homogeneous comonomer distribution along the chains as well as narrow molecular weight distribution. Moreover, their very high activities allow to incorporate high comonomer contents in the case of long-chain α-olefins, which are difficult to obtain with classical Ziegler–Natta catalysts, due to the progressive decrease in the reactivity of α-olefin in relation to ethylene as the length of the lateral branch increases [1].

The extraordinary ability of these catalyst to polymerize and copolymerize new monomers in combination with the known processes, as well as with new processes, is producing a new family of materials, which are eliminating the differences between the so called commodity and engineering polymers and between thermoplastics and elastomers. These thermoplastics are increasingly elastic and the elastomers are increasingly thermoplastic.

Consequently the mechanical and physical properties of polyethylene are drastically changed by copolymerization with small amounts of α-olefins. This change will depend primarily not only on the amount of co-units, but also their distribution along the chain and even the nature of the side branches arising from the α-olefin affect the final properties [2–4].

Several works have analysed the properties of homogeneous copolymers of ethylene and 1-octadecene prepared with vanadium catalysts [1,5,6] focusing the

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attention on the structural characterization and mechano-dynamic properties of the copolymers in order to establish the possible participation of the relatively long side branches of 1-octadecene in the crystallization and relaxation of ethylene sequences. Other studies have been published on such copolymers synthesized with metallocene catalysts, analysing the influence of the metal (Zr or Hf) on the incorporation of comonomer and other polymer characteristics [7,8].

We have previously studied [9–11] some aspects of synthesis, structure characterization and mechanical properties of ethylene–1-octadecene copolymers synthesized with a metallocene catalyst. Following these investigations, this work reports on the dynamic mechanical properties of several copolymers of ethylene with 1-octadecene (a long branched α-olefin). These properties are analysed basically in terms of the comonomer content and of the crystallinity exhibited by the sample. These new results are compared and discussed in relation to similar ones, previously reported on copolymers synthesized by Ziegler–Natta catalysts. We have tried to clarify the origin of the different relaxations, because at present the interpretation of the dynamic mechanical properties of polyethylene and its copolymers is somewhat controversial.

2. Experimental part

Copolymerizations of ethylene and 1-octadecene were performed as described elsewhere [9]. The catalyst used was *rac*-Et(Ind)$_2$ZrCl$_2$. The results about the comonomer content, determined by ^{13}C NMR spectroscopy, are shown in Table 1.

The molecular weights, determined by gel permeation chromatography [9] and corrected for the non-linearity of the chains [12,13], are also shown in Table 1.

Sheets of each polymer were prepared by compression moulding between hot plates (about 20 °C above the melting temperature) in a Collin press at a pressure of about 20 MPa. The samples were cooled between water plates at the same pressure. The thickness of the moulded sheets was around 0.5 mm.

Density determinations were performed at 23 °C in a water–ethanol gradient column which had been calibrated with glass floats. The degree of crystallinity was calculated from the equation

$$(f_c)_d = (\rho_c/\rho)((\rho - \rho_a)/(\rho_c - \rho_a)) \qquad (1)$$

using the values $\rho_a = 0.8532$ g/cm^3 and $\rho_c = 1.000$ g/cm^3 for the amorphous and crystalline phase densities, respectively [14]. The density of the different samples and the corresponding values of the crystallinity are shown in Table 1.

The thermal properties were determined with a Perkin-Elmer DSC-7 calorimeter connected to a cooling system and calibrated with different standards. The sample weights ranged from 7 to 10 mg, and the used heating rate was 20 °C/min. A value of 290 J g^{-1} has been taken as the enthalpy of a perfect polyethylene crystal, [15] in order to calculate crystallinities from the enthalpies of melting.

Wide-angle X-ray diffraction patterns [10] were recorded in the reflection mode at room temperature by using a Philips diffractometer with Geiger counter connected to a computer. Ni-filtered Cu Kα radiation was used. The crystalline diffractions and the amorphous component have been separated with a fitting program that allows us to estimate the crystallinity of the samples. The baseline has been taken just as a straight line in the 2θ range from 10 to 30 °, and no further correction has been applied. The different diffraction peaks were fitted to Voigt functions. The amorphous peak of the different samples was found to be centred at 2θ between 19.5 and 19.8 °. The X-ray crystallinity values, f_c^{WAXD}, are displayed in Table 2.

The samples were also studied by small-angle X-ray scattering (SAXS) employing synchrotron radiation (with $\lambda = 0.150$ nm) in the beamline A2 at HASYLAB (Hamburg, Germany). A linear position-sensitive detector was used, at a distance of 235 cm from the sample, calibrated with the different orders of the long spacing of rat tail cornea ($L = 65$ nm). It was found to cover a spacing range from 5 to 55 nm.

Dynamic mechanical relaxations were measured with a Polymer Laboratories MK II Dynamic mechanical thermal analyser, working in the tensile mode. The storage modulus, E', loss modulus, E'' and the loss tangent, tan δ, of each sample were obtained as functions of temperature over the range from − 140 to 120 °C at fixed frequencies of 1, 3, 10–30 Hz and at heating rate of 1.5 °C/min. Strips from sheets were cut around 2.2 mm wide and 15 mm length. The apparent activation enthalpy values were calculated on loss

Table 1
Characterization of the ethylene–1-octadecene copolymer samples

Sample	Comonomer content (%)	$10^{-3}M_w$	M_w/M_n	Density (g cm^{-3})	f_c^{density}
PE	0	291	3	0.94	0.63
C1	1.7	173	2.5	0.9285	0.55
C2	2.4	160	2.3	0.9247	0.53
C3	4.7	164	2.3	0.9128	0.44
C4	5.7	140	2.1	0.903	0.38

Table 2
Results from the X-ray analysis of the samples: X-ray crystallinity, f_c^{WAXD}, long spacing, L, and crystallite thickness, l_c

Sample	Comonomer content (%)	f_c^{WAXD}	L (nm)	l_c (nm)
PE	0	0.68	25.8	17.5
C1	1.7	0.58	17.4	10.1
C2	2.4	0.53	15.9	8.4
C3	4.7	0.41	14.7	6
C4	5.7	0.37	14.9	5.5

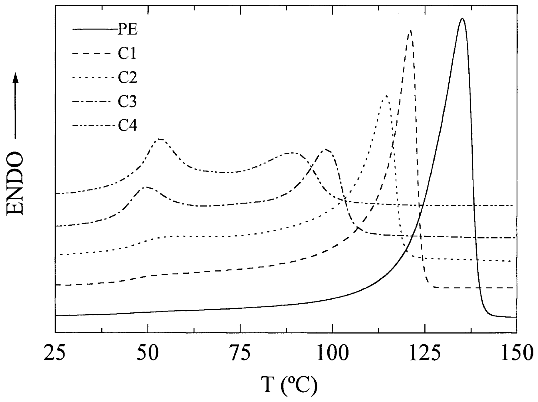

Fig. 1. DSC melting curves (first melting) of the different samples.

moduli according to an Arrhenius-type equation, considering an accuracy of ± 1 °C in the temperature assignment from the maxima.

3. Results

The DSC melting curves of the different samples, corresponding to the first melting, are shown in Fig. 1. As expected, the melting temperature and the enthalpy of melting decrease with increasing incorporation of comonomer [10,11]. It is important to comment that the samples were left at room temperature for several days before any analysis, since the melting range extends to subambient temperatures and important annealing effects are produced when standing at room temperature. These annealing effects have a very important influence on the mechanical [11] and dynamic properties, and are, of course, more evident in the high comonomer contents. In such cases, two different endothermic processes are observed: one at lower temperature, associated with the melting of crystallites annealed during the stay of the material at room temperature after processing, and the other one, at higher temperatures, that corresponds to the main melting endotherm, associated with crystals formed by the classical nucleation-controlled chain-folded lamellar crystals. The low-temperature one is attributed to those very imperfect, bundle-like crystals, which exhibit almost reversible crystallization–melting processes [16]. The endotherm at low temperature appears around 40–45 °C (depending upon thermal history) and it disappears in the second heating scan.

The wide-angle X-ray analysis of these samples has been reported before [10]. The results show that the presence of comonomer leads to a considerable decrease in the crystallinity of the copolymers, though the (110) and (200) diffraction peaks of the typical orthorhombic lattice of PE [17,18] are observed even in the copolymer C4. Evidently diffractions are broadened and shifted to lower angles, indicating a diminishment in the crystallite size and less perfect crystals, respectively, as the comonomer content increases [10].

The crystallinity estimated from X-ray diffraction exhibits a value practically coincident to that determined from the density (Tables 1 and 2). On the contrary, both determinations (density and WAXD) provide a higher value than that assessed by DSC measurements [10], in ethylene copolymers, what is attributed to the fact that the interfacial content is not contributing to the enthalpy [19].

A division of ethylene–1-octene copolymers as a function of density has been suggested [2]. Such a classification scheme shows a broad range of solid-state structures in this type of copolymers synthesized under a particular polymerization conditions and a specific catalyst. Copolymers with densities higher than 0.93 g/cm^3 exhibit a lamellar morphology with well-developed spherulitic superstructure. If density values are in the 0.93–0.91 g/cm^3 range, the copolymers have thinner lamellae and smaller spherulites. Materials with densities between 0.91 and 0.89 g/cm^3 have mixed morphology of small lamellae and bundled crystals. These materials can form small spherulites. Finally, copolymers with densities less than 0.89 g/cm^3 have no lamellae or spherulites: fringed micellar or bundled crystals are inferred from the low degree of crystallinity and the granular, non-lamellar morphology. Subsequent work on very low density copolymers has shown that even copolymers with densities in the range 0.88–0.89 present two crystal populations attributed to a mixture of lamellar and bundled crystal [20]. This division may be approximately valid for the present ethylene–1-octadecene copolymers. In such case, and from the density values reported in Table 1, the present samples will be included in the first three of those subdivisions.

Fig. 2 shows the Lorentz-corrected SAXS profiles corresponding to the homopolymer and the four copolymers

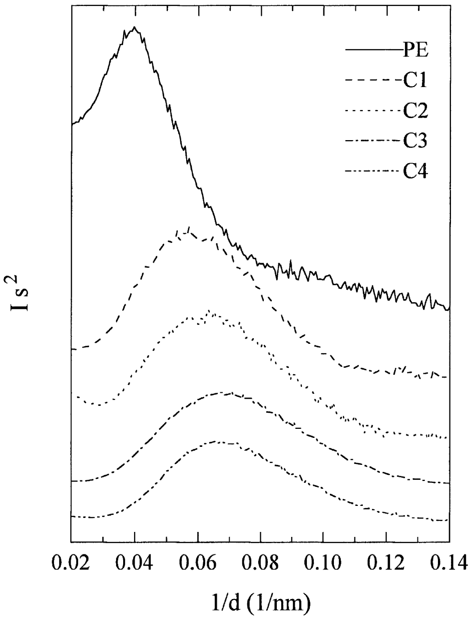

Fig. 2. Lorentz-corrected SAXS profiles of the different samples.

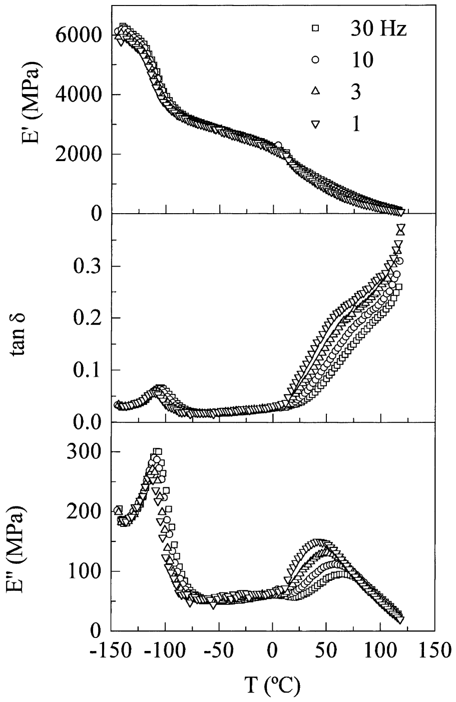

Fig. 3. Variation of the storage modulus (E'), tan δ and loss modulus (E'') as a function of temperature, at the indicated frequencies, for polyethylene homopolymer.

at room temperature. A very clear long spacing is exhibited by all samples, indicating the presence of a lamellar structure in all of them, although, considering the density of the present samples and the division mentioned before, copolymer C4 may be composed of a mixed morphology of lamellae and bundled crystals. In spite of this possibility, we have estimated the crystallite thickness, l_c, from the long spacing, L, assuming a simple two-phase lamellar model in all the cases, i.e. $l_c = f_c L$, f_c being the crystallinity degree. For that, we have employed the X-ray crystallinity values (which are similar to those obtained from the density). All these results are presented in Table 2, and decrease of the crystallite thickness is deduced, as the comonomer content increases.

3.1. Dynamic–mechanical properties

The viscoelastic behaviour of polyethylene and copolymers is strongly influenced by variables that affect the crystalline regions such as crystallinity, lamellar thickness and the interface. Linear and branched polyethylenes, as well as copolymers of ethylene, display a series of relaxations, which can be detected by dynamic mechanical thermal analysis, among other techniques. They are called α, β and γ relaxation in order of decreasing temperature.

3.1.1. Homopolymer: linear polyethylene

Plots of storage, loss moduli and tan δ as a function of temperature are shown in Fig. 3 for the linear polyethylene sample at four frequencies. Two clear relaxations, α and γ in order of decreasing temperature, are observed, but the β relaxation, characteristic of branched polyethylene, is not readily observed. The tan δ and loss modulus maximum corresponding to the relaxations (α and γ) are accompanied by a pronounced decrease of the storage modulus at the same temperature.

It is generally agreed that the α relaxation is due to motions of chain units which lie within the crystalline portion of the polymer. It is now well documented that, during α relaxation the chains in the inside crystal are mobilized (chain rotation, translation and twist) [21,22] and it seems to be a very complex process associated not only with the crystalline phase but also with the amorphous phase [23]. Long time ago, Sinnott [24] demonstrated that α relaxation is due to the motion of the chain folds at the crystal surfaces. Boyd [25] has shown that the motion occurs in the amorphous phase but requires mobility of the crystals. Takayanagi and Kajiyama [26] have considered the α relaxation as two overlapping processes, which allow to resolve the experimental results in two different peaks with different activation energies. Popli et al. [27] associated the α relaxation with the mobility in the crystalline phase. A second relaxation α′ is observed as a shoulder on the main α process (asymmetric relaxation) resulting from crystallites of different lengths [7,28]. In a previous work [29], it was found that there exists a relation between crystal thickness and intensity of the α relaxation, confirming 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. In general, its position and intensity have been related to the crystal thickness and crystallinity level, respectively. We will analyse these aspects later on, when discussing the results on the copolymers.

In the present PE sample, the α relaxation appears centered at 51 °C (at 3 Hz). Its intensity increases with increasing frequencies, this behaviour not usually found in transitions associated with the amorphous content. The apparent activation energy, ΔH, calculated from E'' curves assuming a single process, takes the values of 158 kJ/mol. The α relaxation in tan δ does not show a clear maximum, the data sweeping up steeply towards the melting temperature of the polymer. This result is in line with earlier finding for HDPE and LLDPE, as a consequence of larger size crystals present in PE [30].

The β relaxation process in polyethylene has been also extensively studied [27,31]. Its molecular origin, however, still remains obscure and ambiguous. This process either has not been observed at all in some linear polyethylenes samples [27,32] or it has been barely detected in others [28,33,34]. However, the β relaxation has been universally detected in branched polyethylenes at temperatures around −20 °C, but scarcely appears, although weakly, in some samples of linear polyethylene. Some authors have concluded that the β relaxation results from motions of chain units in the interfacial region [27] whereas some

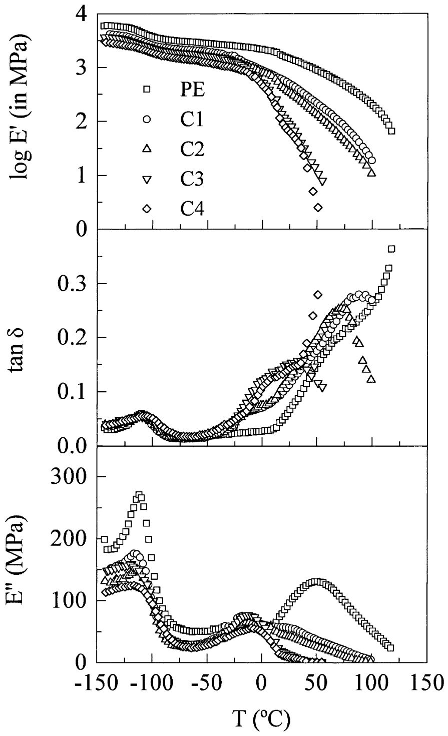

Fig. 4. Variation of the storage modulus (E'), tan δ and loss modulus (E'') with temperature, at 3 Hz, for different samples.

others have attributed this process to the glass transition [35, 36]. A recent paper [37] has suggested a different molecular origin of the β relaxation in linear polyethylene with high molecular weights quite dissimilar to those aforementioned for branched polyethylene. Because of the formation of loose tie and loop molecules in the amorphous layers in polyethylene with high molecular weights, the β relaxation seems to be a consequence of the motion of the loose tie molecules in this type of polyethylene. The absence of the β relaxation in typical linear polyethylene having a thinner amorphous layer thickness (which is considered to promote taut tie molecules) can be directly attributed to the lack of loose tie molecules [37].

In the present case, a very weak β relaxation is observed for the PE homopolymer sample in the loss modulus plots (see lower part of Fig. 3), centred at around 0– − 25 °C, depending on the frequency.

Finally, the γ relaxation has been associated with a single relaxation process predominantly of amorphous origin. This relaxation is typical of the joint movements of chains containing three or more methylene units in the main chain. There is a body of opinions with support one or more of the several models for restricted conformational transitions as kind formation, inversion and migration [31,38,39]. This γ-process has also been found in polyesters containing oxyethylene spacers, where the oxygen atom plays an equivalent role than the methylenic groups [40–42].

The γ relaxation appears at − 113 °C in the homopolymer sample analysed here (Fig. 3). The apparent activation energy is 110 kJ/mol, of the same order of other PE homopolymers [31].

3.1.2. Copolymers

Fig. 4 and Table 3 show the DMTA results of the different samples, at 3 Hz. In the upper part of the figure, it is observed that the storage modulus at low temperature slightly decreases as the 1-octadecene content increases. This modulus reduction is more remarkable at higher temperature. This behaviour is a consequence of the stiffness decrease as the content of crystallinity is reduced.

Three relaxations have been observed, α, β and γ in order of decreasing temperature, similarly to the homopolymer. The γ relaxation appears as a maximum around − 110 °C in tan δ and at a slightly lower temperature in loss modulus, with a corresponding decrease in storage modulus. There is a clear effect of comonomer content on the breadth and on the location of the relaxation: this process is shifted to lower temperature, as comonomer content increases as a consequence of increase in the amorphous content. The temperature and the apparent activation energy of the relaxation (Table 3) display typical values of the γ relaxation produced by motions of methylene units preferably in the amorphous region. Therefore, the apparent activation energy determined from the loss modulus and tan δ curves decreases as the comonomer content increases. This behaviour is similar to the value found for 1-octene and 1-octadecene copolymers synthesized by Ziegler–Natta catalysts [28] and copolymers with 1-hexene and 1-octene prepared with metallocene catalysts [4,31].

Regarding the other two relaxations, it can be observed in the lower part of Fig. 4 that the α relaxation is moved to lower temperatures and intensity decreases when the comonomer content increases. Simultaneously, the β relaxation appears clearer but does not move very much in temperature. Consequently, the two processes show a severe overlapping in the copolymers, and for C4, a single peak is observed, due to the merging of the two relaxations (and/or very small intensity of the α peak). Anyway, previous studies [27] have concluded that, in some cases, where a single peak is observed, it may be due to the superposition of the two relaxations.

For the accurate determination of the peak temperature in the α/β relaxation, a separation procedure was used which

Table 3
Temperatures and apparent activation energies of the relaxations α, β and γ, at 3 Hz, for polyethylene and copolymers

Samples	T (°C)			ΔH (kJ mol^{-1})		
	T_α	T_β	T_γ	ΔH_α	ΔH_β	ΔH_γ
PE	51	− 20	− 113	158	83	110
C1	18	− 19	− 116	197	202	102
C2	7	− 11	− 118	134	274	89
C3	− 4	− 14	− 119	145	304	82
C4	− 9	− 9	− 117	–	–	57

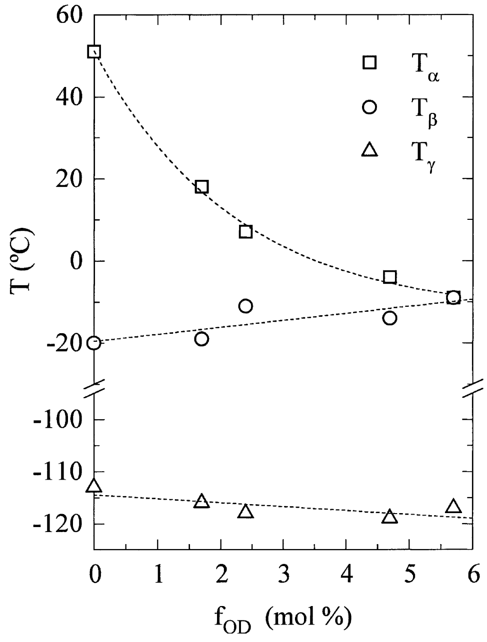

Fig. 5. Variation of the temperature location of the α, β and γ relaxations as a function of 1-octadecene comonomer content.

involved fitting two Gaussian functions and the results were used to determine the apparent activation energies. Such a convolution does not have a theoretical basis that can explain satisfactorily the shape of the dependence of loss modulus on temperature, though some factors that can influence it are known. In other works [31,43] Gaussian functions were applied and provided the best fitting. This convolution allows the estimation of the relative areas and position of the different relaxation mechanism when they are overlapping. The results for the temperature location and activation energy of the relaxations are shown in Table 3. These values of the activation energies are consistent with those found previously for LLPDEs [29]. The fact that the two processes have very different activation energies is a consequence of sensitivity of the two peaks to frequency: the α relaxation shows a bigger frequency dependence than the β relaxation. The activation energy of the α process decreases as the comonomer content increases due to the decrease in the crystal size and crystallinity. On the contrary, the β activation energy increases as the comonomer content increases as a consequence of the major proportion of amorphous regions.

The dependence of the temperature location of the three relaxations on the comonomer content is clearly observed in Fig. 5. The merging of the α and β relaxations and the great decrease in the α position are the more important features. However, the β relaxation shows very little change with the comonomer content and even a small increase seems to be obtained, contrary to the case of ethylene copolymers with comonomers of smaller branches, namely 1-butene, 1-hexene, 1-octene and 1-dodecene [4,27,28,43,44]. In these cases, the β relaxation moves down in temperature rather appreciably with the comonomer content.

One interpretation of the behaviour is the assignment of the β relaxation to the glass transition in these copolymers, and, for instance, in the case of ethylene–1-octene copolymers, the value of T_g decreases to a constant value of around −65 °C for very high comonomer contents [45] (of the order of 40 mol%) which is precisely the reported value for the T_g of poly-1-octene homopolymer. Moreover, the β relaxation has also been identified with the T_g of ethylene–1-butene copolymers [43], where there is a very clear decrease in T_β with the increase in comonomer content. The fact that the present 1-octadecene copolymers show a slight increase of T_β may have two different interpretations: either the glass transition of poly-1-octadecene homopolymer is higher than −20 °C or there may be some lateral crystallization of the relatively long branches of 1-octadecene. It is well known that poly-1-octadecene homopolymer and other long-chain poly-α-olefins [46–48] display lateral crystallization of the side branches irrespective of the tacticity of the polymer. In such case, the T_g cannot be detected by DSC. In a previous work [49], the constancy of the β relaxation position in 1-octadecene copolymers was interpreted as being due to restraint of chain movement near the branch point caused by the crystallization of the side chain. Moreover, in another work [6] the observation of a peak at around 19.5–20 ° in the diffractograms of ethylene–1-octadecene copolymers was considered as indicative of the side branches of 1-octadecene participating in the crystalline structure.

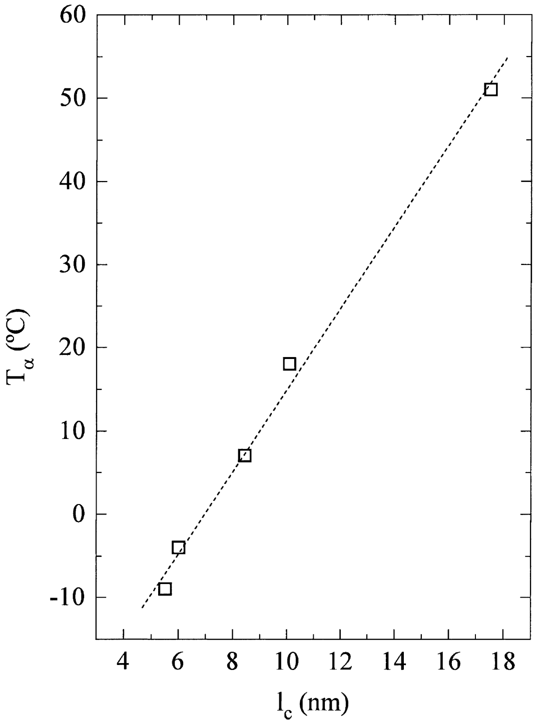

Fig. 6. Variation of the temperature of the α relaxation with the crystallite thickness.

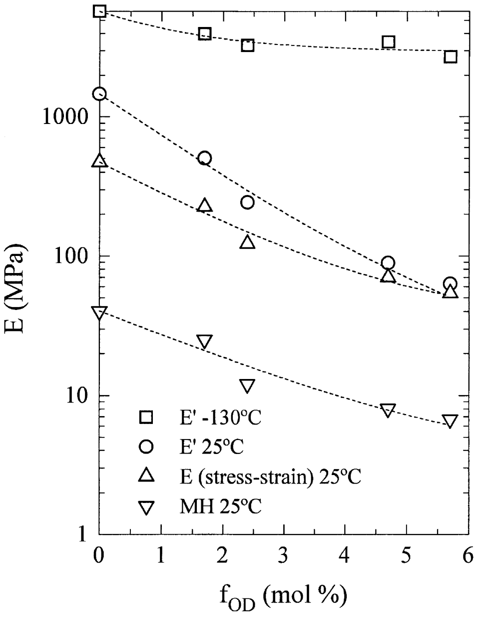

Fig. 7. Young's moduli obtained by different methods as a function of 1-octadecene comonomer content.

However, it was shown [10] that such peak is also present in the diffractograms of ethylene–1-hexene copolymers (and in other ethylene copolymers with small side branches [4, 45,50]). So it is not clear if the side branches of 1-octadecene can really participate in the crystalline structure of these copolymers of relatively low comonomer contents, although such possibility certainly exists for copolymers of very high comonomer content.

Anyway, the results in Figs. 3 and 4 and in Table 3 show a dependence of the α and β relaxations in different way. Thus, the α relaxation decreases with temperature and intensity as the comonomer increases. On the other hand, the β relaxation increases in intensity, but the temperature is almost constant.

As previously commented, a dependence of the temperature location of the α relaxation, T_α, with the crystal thickness has been proposed. From the values of the long spacing, reported in Fig. 2, and assuming a simple two-phase model, the crystallite thickness has been estimated. Fig. 6 shows the variation of T_α with the crystal thickness. A rather good linear dependence is observed, with values very similar to those previously reported [27] for other PE samples. In that report, however, the study is extended to samples with higher crystal thickness and a non-linear dependence is found. It seems to follow, therefore, that the linear behaviour of the present samples is just due to the reduced interval of crystal thickness studied here.

It is also interesting to analyse the variation of the storage modulus as a function of the comonomer content. The corresponding variation is displayed in Fig. 7, analysing the behaviour at two well different temperatures: at −130 °C, below all relaxations, and at room temperature (25 °C), comparing the results with the moduli determined by other techniques: the Young's modulus (from stress–strain measurements) and the microhardness of these copolymers [11]. At very low temperatures, the variation is rather small, the values of the moduli are all very high and the samples are very rigid since they are below T_g (irrespectively of the relaxation assigned as the T_g of PE). However, at room temperature, the modulus decay with the comonomer content is rather high, the samples are now above T_g and the key feature is the crystallinity of the sample, which decreases very much with the comonomer content. This variation is parallel to that of either the Young's modulus or the microhardness (although the latter value, as usual [51, 52] which is about one order of magnitude smaller).

4. Conclusions

Three relaxations α, β and γ in order of decreasing temperature have been found in the studied samples. Similar to other ethylene copolymers, the temperature for the α relaxation decreases with the increase in the comonomer content, attributed to the reduction of the crystal size. In fact, a linear relation has been found between the temperature location of the α relaxation and the crystal thickness estimated from the SAXS long spacing. However, the position of the β relaxation experiences very little dependence with the comonomer content and it overlaps to the α relaxation for the higher comonomer contents. As to the γ relaxation, there is also a clear effect of the comonomer content on the breadth and on the location of this relaxation.

Acknowledgements

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