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Influence of the comonomer content on the thermal and dynamic mechanical properties of metallocene ethylene/1-octene copolymers

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Abstract

Studies of ethylene/1-octene copolymers prepared by a metallocene catalyst were carried out through dynamic-mechanical experiments (DMTA), differential scanning calorimetry (DSC), Raman spectroscopy and gel permeation chromatography (GPC). The influence of comonomer content on the ethylene/1-octene properties, specially those related to the dynamic-mechanical behaviour were studied. It was observed that the intensity of the β-transition increases as the comonomer content increases and decreases crystallinity. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Linear low density polyethylene (LLDPE) is an important class of polymers because of the specific properties that can be obtained according to the comonomer content and to the copolymerization method. In the ethylene/α-olefin copolymerization, the incorporated α-olefins produce short branches and the catalytic system influences not only the structure but also other characteristics like molecular weight distribution, density and comonomer distribution of the copolymers [1–3].

The development of metallocene catalysts (homogeneous single site catalysts) made possible the synthesis of copolymers with structure and properties completely different from those of traditional linear polyethylenes. Ethylene/α-olefin copolymers obtained by metallocene catalysts show well defined structures, homogeneous comonomer distribution and narrow molecular weight distribution if compared with copolymers obtained by traditional Ziegler–Natta catalysts [2].

In the case of ethylene/1-octene copolymers, the presence of the comonomer decreases significantly the degree of crystallinity [4,5] and highly branched chains may lead to molecular segregation [6,7]. Both the degree of cristallinity and the molecular segregation have great influence on the thermal and mechanical properties of ethylene copolymers [7–9].

One of the characteristics strongly influenced by copolymer structure and composition is the thermal dynamic mechanical behaviour. In general, LLDPE shows some transitions or relaxations besides the melting point. These transitions are called α, β and γ in decreasing order of temperature [9,10].

In general, α-transition is attributed to the vibrational or reorientational motion within the crystals. According to Takayanagi [9,10], α-transition occurs as result of the motions of chain units within the crystal, and the molecular mechanism involved is the same observed in γ-transition. The difference would be that, in γ-transition, this mechanism can be the result of the relaxation of chain units in the amorphous region. Some authors also associate γ-transition to the glass transition of the amorphous regions [9,10]. Another important point to remark is the observable variation in α-transition according to the degree of crystallinity. In general, linear polyethylenes with high degree of crystallinity show strong α-relaxation, but in the case of ethylene copolymers α-transition tends to decrease or even to disappear, as the comonomer content increases (and decreases the degree of crystallinity) [9,10]. The α-transition temperature

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depends on the side-branch content, crystallization method and some possible mechanisms of recrystallization [9–11].

The other transition observed in branched polyethylene and ethylene copolymers is β-transition. This transition has been extensively studied and many discussions and ambiguous explanations about its origin have been published [9–16]. Apparently, the intensity of this transition is related to the branch level and to the degree of crystallinity, since it was observed that as the comonomer content increases, there is an increase in its intensity in many ethylene copolymers. Some authors found a relation between the side branching content of polyethylene and the magnitude of this transition, and attributed it to the onset of diffusional motion of branch points [9]. Other authors attributed β-transition to the glass transition since its intensity increases with the amorphous content [12–14]. Popli et al. [15], in their investigation of ethylene copolymers, attributed this transition to the segmental motions that occur within interfacial regions associated with lamellar crystallites. Based on the correlation time, and through carbon-13 nuclear magnetic ressonance, Dechter et al. [16] found evidences that this transition could not be attributed to glass transition. They concluded that β-transition is related to the segmental motions of disordered chains located in interfacial region and it is not associated with motions of an unrestrained and completely amorphous polymer.

Most of the dynamic-mechanical studies of LLDPE have been done with copolymers obtained with traditional Ziegler–Natta catalysts [17,18]. The properties of copolymers obtained with metallocene catalysts were mainly investigated by DSC [19,20]. In the present study, ethylene/1-octene copolymers prepared by metallocene catalyst were investigated [5,21]. Their properties were also compared to two commercial ethylene/1-octene copolymers prepared by metallocene catalysts. These copolymers show long chain branches besides the short hexyl chain branches [22].

2. Experimental part

The ethylene homopolymer and four ethylene/1-octene copolymers were prepared using metallocene catalyst, $Et[Ind]_2ZrCl_2$, and methylaluminoxane (MAO) [5,21]. Two commercial ethylene/1-octene copolymers manufactured by Dow Chemical Company, also produced by metallocene cataysts, were used: ENGAGE 8100 and AFFINITY 1140.

^{13}C-NMR was employed to determine the compositions of the ethylene copolymers. The ^{13}C-NMR spectra were recorded at 80°C with an acquisition time of 1.5 s, pulse width of 70° and pulse delay of 5 s on a VARIAN XL-300 spectrometer operating at 75 MHz. Sample solutions of the copolymers were prepared with o-dichlorobenzene, benzene-d6 (20% v/v) and chromium (III) acetylacetonate as paramagnetic substance to reduce relaxation times.

The molecular weight of the copolymers was determined by gel permeation chromatography in a Waters 150 CV-plus System, equipped with an optic differential refratometer, a 150 C model, and a set of three columns, Styragel HT type(HT3, HT4, HT6). 1,2,4-trichlorobenzene was used as solvent. The analyses were performed at 140°C and 1.0 ml/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene, polypropylene and polyethylene.

For the DMTA measurements, the samples were melt pressed at 30°C–35°C above their melting points to obtain films with homogeneous thickness (0.2–0.3 mm) and allowed to cool at room temperature. Rectangular films averaging 10 mm wide, 12 mm long and 0.2–0.3 mm thick were used. The dynamic-mechanical experiments were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyser MK II Instrument (DMTA) in the tensile mode. The measurements were carried out in three different frequencies: 1, 3 and 10 Hz. The temperature ranged from -150°C to next to the melting point of each copolymer (50°C to 135°C, depending on the sample used), and the heating rate was 2°C/min.

Differential Scanning Calorimetry (DSC) measurements were performed on a Polymer Laboratories DSC instrument under N_2.atmosphere. The samples were heated from 40°C to 150°C and cooled down to 40°C at a heating rate of 10°C/min to determine the melting temperature. The melting temperature (T_m) and heat of fusion $\Delta(H_f)$ values were taken from the second heating curve. The degree of crystallinity was calculated from ΔH_f and using the equation of Ref. [23] $X_c = \Delta H_f \times 100/64.5$. In order to determine the glass transition temperature, the samples were heated from -150°C to 150°C at a heating rate of 20°C/min and the T_g was determined in the second heating.

The amount of crystalline, amorphous and interfacial contents were determined from the analysis of the internal mode region of the Raman spectra ($960 < \Delta\nu < 1550\ \mathrm{cm}^{-1}$), following a well known method [24]. As excitation source, an HeNe laser (632.8 nm) was used. The scattered light was collected by a microscope, followed by a holographic notch filter and dispersed by Jobin–Yvon HR 320 model monochromator equipped with 1800 lines/mm holographic diffraction gratings. The data acquisition was carried out with an EG and G Princeton Applied Research, 1530-C-1024S model cryogenic CCD detector.

3. Results and discussion

Many studies show that, in general, the alkyl branches cannot enter the polyethylene crystal lattice and only the methyl branches are included in the lattice at an appreciable degree [3,25–27]. The excluded branches form an interfacial region which is more ordered than the amorphous one, showing some degree of crystallinity. In the ethylene/1-octene copolymerization, the comonomer is incorporated

Table 1
Properties of ethylene/1-octene copolymers

LLDPE NMR-^{13}C 1-Octene content (mol%)	Comonomer distribution			Molecular Weight (GPC)		DSC				Raman			DMTA		
	n$_E$	[EOO]	[OEO]	M_w (g/gmol) × 10^{-4}	M_w / M_n	T_m (°C)	T_c (°C)	X_c (%)	T_g (°C)	α_a(%)	α_c (%)	α_b (%)	$T_{\alpha/\alpha'}$ (°C)	T_β (°C)	T_γ (°C)
0.0	—	—	—	35.62	2.9	131	115	62	—	—	—	—	86/49	—	− 115
2.3	45	0	0	9.42	1.9	111	95	43	− 117	31	57	12	46/20	− 20	− 113
5.0	21	0	0	4.95	2.7	98	80	29	− 113	28	57	15	5	—	− 115
6.6^a	16	1.1	0.1	5.90	2.0	98	75^c	30	− 126	23	39	38	− 23	− 39	− 120
8.2	13	0	0.7	4.52	2.0	83	61	14	− 123	—	—	—	—	− 28	− 120
10.3	10	0.7	0.8	4.18	2.0	73	56	05	− 119	50	24	26	—	− 41	− 120
13.1^b	8	3.2	0.9	9.80	1.8	50–70	43^c	n.d.^{d}	− 121	43	12	45	—	− 34	− 121

[a] Affinity.
[b] Engage.
[c] Both presented other minor endotherm peaks at lower temperatures.
[d] Not determined.

as hexyl branches along the polyethylene backbone. As the comonomer content increases, the average number of consecutive ethylene units (n_E) decreases and the crystallizable part of the copolymer becomes smaller. As a consequence, the crystallinity decreases and the amorphous and interfacial contents increase. The n$_E$ of LLDPE obtained with metallocene catalyst is more homogeneous than the one obtained with traditional Ziegler–Natta catalysts.

Through ^{13}C-NMR, it was possible to observe that with low comonomer contents, the 1-octene units were isolated between the ethylene units (or blocks), but, at higher contents, other sequences, like OEO, EOO (where O is the 1-octene comonomer and E is the ethylene monomer), were observed. These results, presented in Table 1, also show that the amounts of these sequences were higher for the commercial samples. Anyway, the results show a tendency to isolate 1-octene units between the ethylene blocks.

Our previous studies [5,21,28] showed that there is a decrease in the melting point and the degree of crystallinity of the ethylene/α-olefin copolymers as the comonomer content increases. As the comonomer content increases, there is also an increase in the amount of amorphous and interfacial regions (Table 1). Apparently, the long chain branches, present in the commercial samples, influence only the interfacial content of the sample with 6.6% 1-octene.

The melting thermograms of ethylene copolymers are influenced by branch distribution and consequently by the distribution of crystallite sizes. In ethylene/1-octene copolymers, as the comonomer content increases, there is a shift of melting endotherms to lower temperatures and also a visible line broadening (Fig. 1). In most of the cases, broadening of endothermic lines can be attributed to a diversity in crystal size, to broad molecular weight distribution, and also to different thermal histories of the copolymers [5,26]. As all the samples were prepared in a similar way and all the DSC scans were taken at the same conditions, we can eliminate the influence of the thermal history and crystallization method in the differences observed. The M_w drops with addition of the comonomer up to 5.0% comonomer. The copolymers with more than 5.0% of 1-octene show similar molecular weight, and molecular weight distribution around 2.0. Considering these small variations, the influence of molecular weight distribution can be neglected for these copolymers. Then, broadening of these lines can be attributed to the difference in crystal sizes and degree of perfection of them, caused by the introduction of 1-octene comonomer in the polyethylene chain.

The degree of crystallinity was determined by the analysis of the internal mode region of Raman spectra of the copolymers (α_c in Table 1) and also by the heat of fusion (ΔH_f) obtained from the DSC measurements. By the analyses of Raman spectra it is also possible to determine the amorphous (liquidlike region, α_a) and interfacial content (α_b). Crystallinity and amorphous amounts were obtained through integral intensities of the bands at 1416 cm^{-1} and

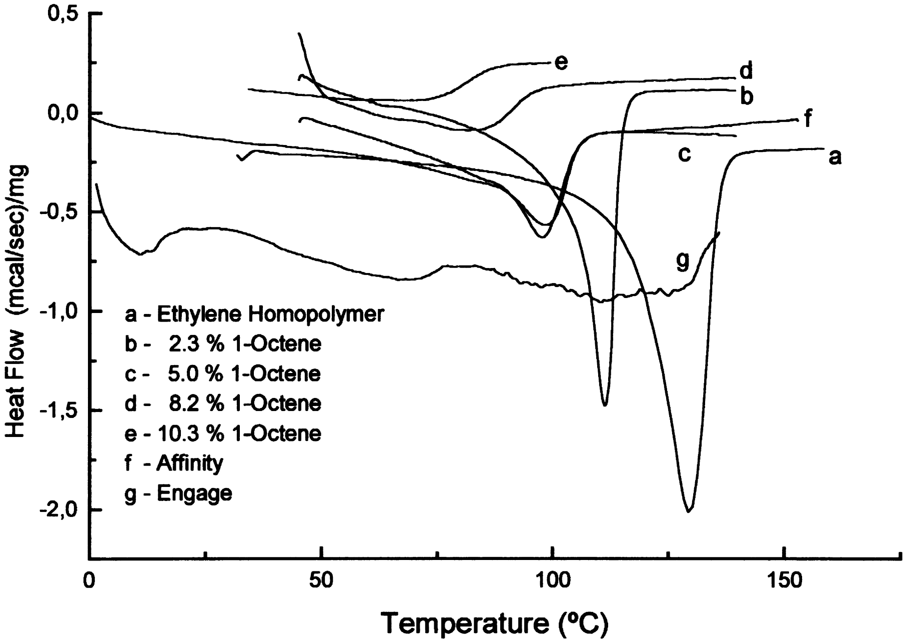


Fig. 1. DSC melting curves of ethylene/1-octene copolymers, at 10°C/min.

1303 cm^{-1}, respectively ($\alpha_c = I_{1416}/I_T \times 0.46$ and $\alpha_a = I_{1303}/I_T$, where I_T is the total intensity in the CH_2 twisting range, around 1300 cm^{-1}). The interfacial content was obtained by the relation $\alpha_b = 1 - \alpha_a - \alpha_c$ [16]. Fig. 2(a) shows typical Raman spectrum obtained for these copolymers. It is possible to observe that in the spectrum (a), which represents the copolymer with 5.0% of 1-octene, the band at 1416 cm^{-1} is in evidence, while in the copolymer with 10.3% of 1-octene (b), this band is not very clear. On the other hand, the band at 1303 cm^{-1}, used to calculate the amount of amorphous phase is broader in the spectrum (b). Analyzing Table 1, it is possible to observe that as the comonomer content increases, there is an increase in the interfacial content. The only exception is the copolymer with 6.6% of 1-octene, which also presents long chain branches. Its interfacial content is higher than the ones shown by the other copolymers with higher comonomer contents. It seems that, in this case, the longer chain branches could be affecting the crystallization behaviour. Another interesting point to remark is that when we compare our samples with those of Clas et al.[18] (copolymers with similar 1-octene content and molecular weight), which were obtained by traditional catalysts, it is possible to observe a great difference in the amount of crystalline and amorphous regions determined by Raman spectroscopy. These differences could be explained on account of the influence of the catalytic systems on the structure of the copolymers [29,30].

Fig. 3 shows the logarithms of the storage (a) and loss (b) modulus versus temperature curves for ethylene/1-octene copolymers with different compositions. In general, the storage modulus decreases with increasing comonomer content, showing that the stiffness of these copolymers decreases with increasing comonomer content. In analyzing

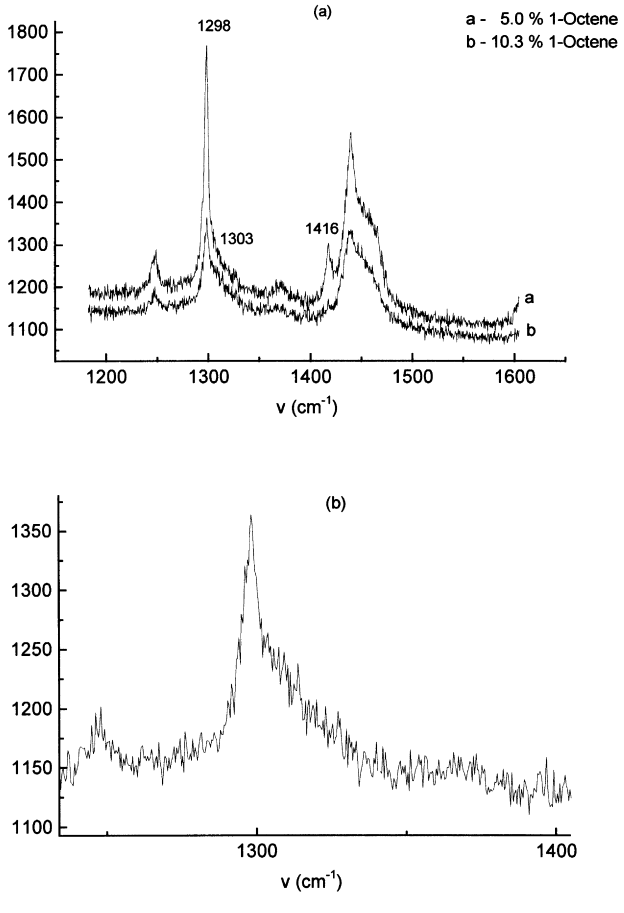
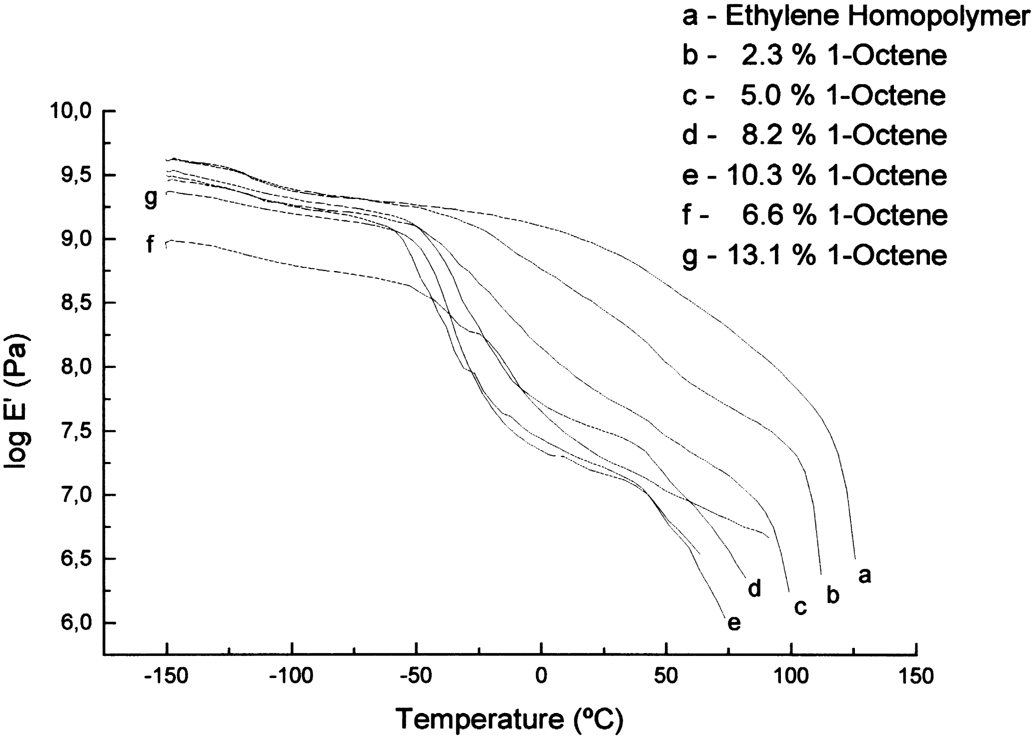


Fig. 2. (a) Typical Raman spectra obtained for ethylene/1-octene copolymers. (b) Expanded Raman spectra of ethylene/1-octene copolymer (10.3% octene) in the range 1200–1350 cm^{-1}.



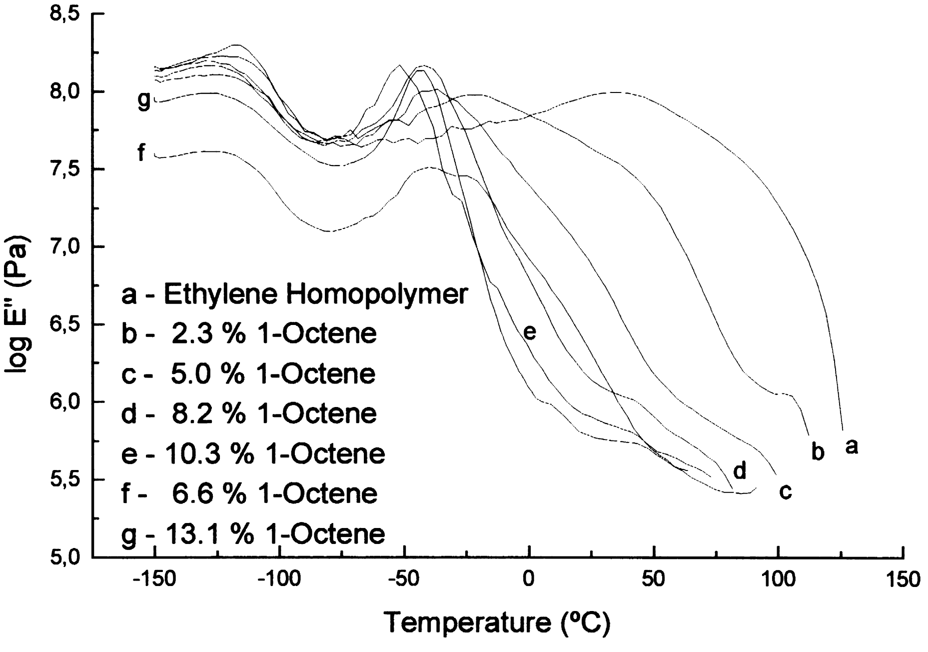


Fig. 3. Logarithms of the storage modulus (a) and loss modulus (b) versus temperature curves of ethylene/1-octene copolymers with different comonomer contents, at 1 Hz.

Fig. 3(a), it is interesting to observe that the sample with 6.6% of 1-octene presents the lowest storage modulus. As we have commented before, in this case, the long chain branches, which were not quantified by ^{13}C-NMR, could be affecting the mechanical behaviour, although the same has not been observed for the other commercial sample (13.1% of 1-octene). From the loss modulus curves it can be clearly seen that high temperature transitions (α) shift to lower temperatures with increase of comonomer content.

Fig. 4 shows the loss tangent versus temperature curves

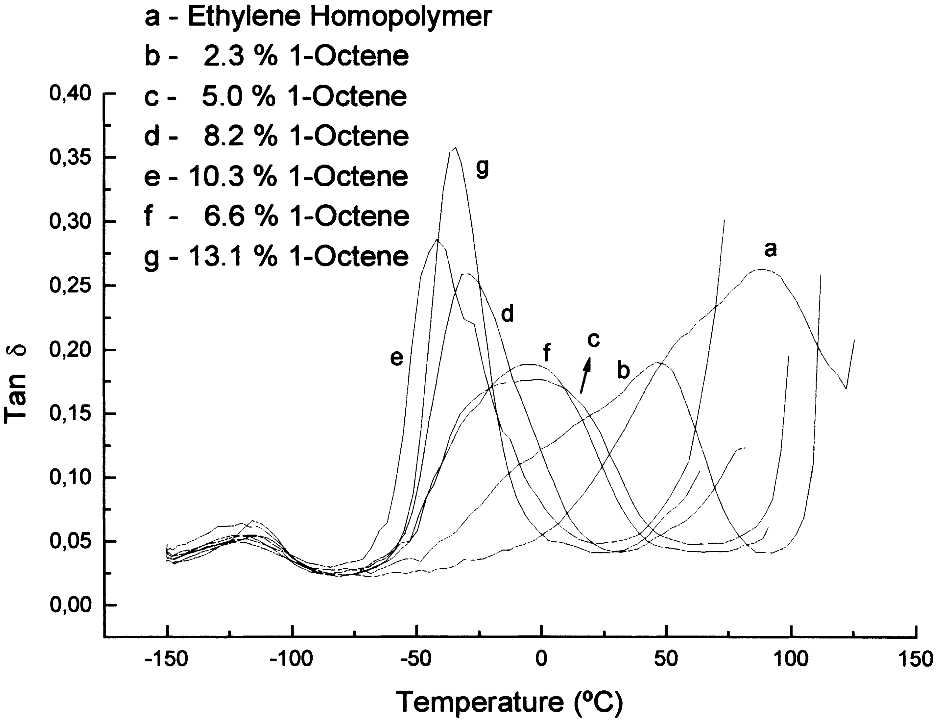


Fig. 4. Loss tangent (tan δ) versus temperature curves of ethylene/1-octene copolymers with different comonomer contents, at 1 Hz.

for the copolymers with different 1-octene content. Three regions should be considered in the analysis. The first one corresponds to temperatures above 0°C, where α-transition normally occurs. Ethylene homopolymer shows a large peak ranging between 0°C and 100°C. Considering the shape of this peak, it is possible to consider the presence of a second transition overlapping α-transition. This transition is often called α'-transition [10]. For the copolymer with 2.3% of 1-octene, a transition with a form similar to that of the homopolymer is observed, though in this case the transition occurs at a lower temperature. It can also be observed that the intensity of α'/α-transition decreases with increasing comonomer content, which does not occur with the copolymers with 8.2%, 10.3% and 13.1% of 1-octene in the experimental window. According to the literature [9,10], α-transition originates from the motion of CH_2 units of polyethylene within the crystal lattice. The origin of α'-transition is not well defined. Some authors have attributed it to an intercrystalline grain boundary slip process or to motions within crystallites of different sizes [9,10]. This interpretation agrees with our observation that the intensity of these transitions decreases with increasing comonomer content and with the results of the DSC and Raman spectroscopy which show that the degree of crystallinity decreases with increasing comonomer content.

At temperatures ranging between −75°C and 25°C, β-transition can be observed in the copolymers, but not in the homopolymer. β-transition is not apparent for the copolymer with 2.3% of 1-octene. If there is one, it overlaps α'-transition. For the copolymers with 8.2%, 10.3% and 13.1% of 1-octene, an intense and relatively narrow peak can be observed in this temperature range. β-transition also shifts to lower temperatures with increasing comonomer content. For the copolymers with 5% and 6.6% of 1-octene only a very broad peak in the range of − 50°C to 50°C can be observed. Apparently in this composition, α- and β-transitions strongly overlap. There are different interpretations for β-transition in the literature [9–16]. Some authors attribute this transition to the glass transition of the polyethylene amorphous phase [12–14]. Other authors attribute it to the interfacial phase [9,15,16]. Analyzing Raman spectroscopy data (Table 1), it is possible to observe that with the increase of comonomer content, the interfacial content also increases. This is a strong indication that β-transition is related to the interfacial content and is in agreement with Clas et al. [18].

The third region corresponds to γ-transition and occurs below − 100°C. γ-transition is normally attributed to the motions of CH_2 units in the amorphous region [7]. This region is almost independent of comonomer content, since only a slightly broadening of the peaks can be observed with increasing comonomer content. The intensity of γ-transition is quite low and γ-transition temperature observed for each copolymer is near to glass transition temperature (T_g) obtained from the DSC measurements (Table 1).

4. Conclusions

The comonomer content has great influence on the thermal dynamic-mechanical properties of ethylene/1-octene copolymers obtained by using a metallocene catalyst. From the dynamic-mechanical experiments it was possible to observe that as the comonomer content increases, there is an increase in the intensity of β-transition, meanwhile it was observed a decrease in the intensity of α-transition. From Raman spectroscopy and DSC data, it was also observed that as the comonomer content increases there is an increase in the interfacial content and a decrease in the melting temperatures and crystallinity, indicating that the changes observed in β-transition region are probably related to movements of the chain segments that are located in the interfacial region. As to the commercial samples, which have also long branches, it seems that the influence of these branches is similar to that of the short ones. Apparently, the influence of the long chain branches is stronger on the commercial sample with 6.6% of 1-octene than on the one with 13.1%.

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