Revisiting the Dielectric Relaxation of Ethylene-Vinylacetate Copolymers: Influence of Microstructure

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ABSTRACT

The dielectric relaxation behavior of a series of ethylene-vinylacetate (EVA) copolymers was investigated by measuring the complex dielectric permittivity in a broad frequency and temperature range. Crystallinity of EVA copolymers was estimated by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). The shape of the higher temperature relaxation, appearing above the glass transition temperature T_g depends on the VA content. It was found that this relaxation was asymmetric for VA concentrations higher than 40 wt% and changed to a symmetric shape at lower VA values. Concurrently, as the VA content decreased, a major broadening of the relaxation over a wide frequency range was observed. It is found that the dielectric relaxation was preserved on going through the melting range of the semicrystalline samples, although it exhibited changes of its characteristic parameters that are typical for segmental relaxation appearing at T_g . This finding allows one to associate this relaxation to the segmental motions at T_g in the amorphous phase and not to the existence of interfacial regions.

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Q1
[102] OK

INTRODUCTION

In spite of the extensive research work performed in polyethylene (PE) copolymers to characterize the structure-dynamics relationships, the relaxation behavior of these materials is still under discussion [1–4]. Owing to the nonpolar character of PE, until now the assignment of the relaxation processes of PE using dielectric spectroscopy is a rather open subject [4]. The introduction of polar groups in the PE chain has been used commonly to characterize dielectrically the relaxation behavior of PE and its copolymers [5]. Three main dielectric relaxation processes appear in PE: α , β , and γ in order of decreasing temperature. It is widely accepted that the α -process involves molecular motions in the crystalline phase [5]. However, while the β - and γ -processes are associated without ambiguity with the amorphous phase, it is not yet fully clear which of the two, β or γ , can be assigned to the dielectric relaxation process associated with the glass transition temperature [4,6,7]. For PE copolymers, only two main relaxation processes associated with the amorphous phase are reported: α and β , which correspond to the β and γ of the PE homopolymer, respectively. In addition, in PE random copolymers, the temperature position of the α -relaxation does not follow the theoretical comonomer content dependence expected for random copolymers [6].

As far as we know, there are at least two hypotheses concerning the above question [6,8,9]. Popli and Mandelkern [6] associate the α -relaxation of PE copolymers to the crystal-amorphous interfacial regions, attributing the β -relaxation to the glass transition [6]. On the contrary, Reding et al. [8] relate the α -relaxation of PE copolymers to the glass transition [8].

This hypothesis has been supported by molecular dynamics simulations [4]. Copolymerization of ethylene (E) and vinyl acetate (VA) yields copolymers (EVA) with a hydrocarbon backbone and pendant polar acetate groups attached to the main chain at random [10]. EVA copolymers are widely used in industry in applications to obtain rubbery materials resembling low-density PE with improved technical properties. Dielectric studies of these copolymers, with VA contents lower than about 40 wt%, have been restricted to a rather narrow frequency range (5 Hz–50 kHz) [1–3]. The extension of dielectric measurements to a higher frequency range offers the possibility of characterizing the dielectric relaxation of these materials in the molten state.

With this idea in mind, we have applied broadband dielectric relaxation spectroscopy (10^{-1} Hz– 10^9 Hz) to EVA copolymers to follow the α -relaxation process through the melting region. The aim of the present study was to characterize the influence of crystallinity on this relaxation and to examine whether this relaxation process can be assigned to the glass transition in PE copolymers.

EXPERIMENTAL

Materials

EVA copolymers from Repsol (Madrid, Spain) with different VA weight contents between 6 wt% and 70 wt% were investigated (Table 1). The schematic structure of EVA copolymer is presented below.

[T1]

TABLE 1
Weight Percentage Crystallinity, Glass Transition Temperatures, and Melting
Range of Ethylene-Vinylacetate Copolymers

Sample	VA content, wt%	X_c (DSC), wt%	X_c (WAXS), wt%	T_g (DSC), °C	T_m interval °C
EVA6	6	33.8	36.9	-24	30-105
EVA12	12.5	33.7	23.3	-20.5	22-94
EVA18	18	27.6	18.2	-20.4	22-96
EVA33	33	10.3	6.6	-20.2	20-80
EVA40	40	5.2	2.3	-18.1	20-72
EVA70	70	0	0	-16.3	—
PVAc	100	0	0	30.7	—

Polyvinyl acetate (PVAc) was considered as the sample with the highest VA content (100 wt%). Cast films with an average thickness of about 40 μ were prepared from chloroform solutions under slow evaporation conditions at room temperature. Thereafter, the cast films were kept in vacuum overnight to remove traces of solvent. The sample EVA6 was prepared by melt compression.

Techniques

Calorimetric measurements were carried out using a Perkin-Elmer (Madrid, Spain) DSC-7 differential scanning calorimeter (DSC) at a scanning rate of 20°/min under constant nitrogen flow. Calibration of the equipment was made by measuring indium and zinc standard samples. Wide-angle X-ray scattering (WAXS) experiments were performed at room temperature using a SeifertTM (Hamburg, Germany) XRD 3000 θ/θ diffractometer with nickel-filtered $\text{CuK}\alpha$ radiation in the 5°–45° 2 θ angular range. A scanning speed of about 1° (2 θ)/min was employed.

Complex dielectric permittivity measurements ($\epsilon^* = \epsilon' - i\epsilon''$) were performed over a broad frequency window, 10^{-1} Hz < F < 10^9 Hz, in a temperature range of $-150^\circ\text{C} < T < 150^\circ\text{C}$. To cover the above frequency interval, three different experimental setups were used.

First, from 10^{-1} Hz to 10^5 Hz, a Novocontrol (Huntsangen, Germany) system integrating an SR 830 lock-in amplifier with a dielectric interface was employed. Second, in the range 10^6 Hz– 10^8 Hz, dielectric measurements were obtained by means of an HP 4291⁴ coaxial line reflectometer. In this case, the complex permittivity was calculated by measuring the reflection coefficient at a particular reference plane [11]. These equip-

(Hewlett-Packard 4291)
(Hyogo, Japan)

[Q2]

ment were integrated in a Novocontrol broadband dielectric spectrometer. The temperature in this spectrometer is controlled by a nitrogen jet with a temperature error, for every single sweep in frequency, of $\pm 0.1^\circ\text{C}$. Third, the frequency gap from 10^5 Hz to 10^6 Hz was covered using an HP 4192 impedance analyzer. Dielectric measurements in this frequency range were performed using a home-made cryostat operating with a temperature-controlled nitrogen atmosphere. Circular gold electrodes were sputtered onto the free surfaces of the films with a diameter of 3 cm for the measurements up to 10^6 Hz and 0.5 cm for measurements at $F > 10^6$ Hz.

RESULTS

Calorimetry

Thermograms of the EVA copolymers and PVAc studied in the -70°C to 130°C temperature range are shown in Fig. 1. All samples were scanned at a heating rate of $20^\circ\text{C}/\text{min}$. PVAc appears as an amorphous polymer with a glass transition temperature T_g near 31°C . This value is in agreement with those reported in the literature [12]. As the VA content decreases to 70 wt%, a shift of the glass transition temperature to around -18°C is observed. A further VA content decrease leaves T_g almost unaffected, and only minor temperature variations were detected. The T_g values derived from the DSC are presented in Table 1. For the samples with VA content less than 70 wt%, the appearance of endothermic peaks indicating the presence of a crystalline phase is noteworthy. The melting temperature range for the crystalline phase in all samples is rather broad. The lower limit starts around 20°C – 25°C , and the higher temperature limit depends on VA content (105°C for EVA6 to 75°C for EVA40) (see Table 1). The shape of the observed

[F1]

FIG. 1. DSC thermograms of EVA samples at a heating rate of $20^\circ\text{C}/\text{min}$.

melting endotherms is rather complex, suggesting the existence of distinct crystalline populations with a possible crystalline phase reorganization on melting. The nature of the melting process in EVA copolymers has been discussed in the literature [13]. An estimation of the weight percentage crystallinity was made by considering the area under the curve of the melting endotherms normalized by the sample mass. Crystallinity was obtained by assuming the value for the 100% crystalline phase of pure PE as 70 cal/g [14]. It is generally accepted that the crystalline phase in EVA copolymers is formed by the packing of linear PE chain segments, leaving the comonomer units excluded into the amorphous phase [15]. As the VA content decreases, the crystallinity exhibits an increase from 0 to around 40 wt%. A quantitative summary of data extracted from DSC scans and from wide-angle X-ray diffraction is compiled in Table 1.

Wide-Angle X-Ray Diffraction

[F2]

X-ray diffraction patterns of the investigated copolymers are shown in Fig. 2. The existence of a crystalline phase for VA content lower than 40 wt% starts becoming detectable from the presence of the incipient 200, 110 reflections of the orthorhombic

FIG. 2. Wide-angle X-ray diffraction patterns for selected EVA samples. The peak separation procedure for Bragg reflections is presented for the EVA12 sample.

unit cell of PE [15]. A systematic shift of the Bragg maxima toward lower 2θ angle is observed on increasing the amount of VA groups in the copolymer. This effect, which indicates an expansion of the unit cell, has been reported previously to occur in ethylene copolymers [15,16]. The weight fraction crystallinity X_c was estimated from the ratio between the crystalline peak and the total area of coherent scattering after subtraction of the incoherent background [17,18]. Separation of the diffracted peaks was done assuming Voigt functions for the 200, 110 reflections (see Fig. 1) [19]. X_c values for the different investigated copolymers are presented in Table 1. It is seen that crystallinity notably increases for VA concentrations less than 40 wt%. The slight difference between WAXS crystallinity values and those derived from DSC experiments is common for measurements done using these two techniques. Among other reasons, it can be mentioned that WAXS measurements were restricted to the 5° – 45° (2θ) angular range. In addition, recrystallization processes that appear during DSC experiments may increase the crystallinity value estimated from calorimetry.

[Q3] OK

Dielectric Relaxation Measurements

[F3]

Figure 3 illustrates the dielectric loss values ϵ'' of EVA copolymers in the case of EVA40 as a function of temperature and frequency. The dielectric relaxation data reveal the existence of a main relaxation process α that appears at T_g in agreement with previous results [1–3,6]. The frequency of the maximum loss shifts toward higher values as the temperature increases. In addition, at lower frequencies, a dramatic increase in ϵ'' that is associated with a conduction process σ appears. The dielectric relaxation data of EVA

FIG. 3. Dielectric loss ϵ'' as a function of temperature and frequency for the EVA40 sample taken with the three different experimental setups (see text).

copolymers in the investigated temperature and frequency range reveals also the existence of a low-temperature relaxation process that was in accordance with previously reported data [1,3].

Figure 4 illustrates that β -relaxation can be detected for copolymers with a VA content higher than 40 wt% (samples EVA70 and PVAc). With decreasing VA content, the β -relaxation weakens, and for VA content less than 70%, it appears as just a weak wide shoulder in the plot of ϵ'' versus F . In addition, the α -relaxation shifts toward lower temperatures and overlaps strongly with the β -process. In PVAc, the β -relaxation has been associated with a hindered rotation of the pendant ester group around the linkage to the main polymer chain. The activation energies for the β -process of EVA70 and PVAc samples were calculated, and the obtained value of 9.3 kcal/mol for PVAc is in good agreement with data published elsewhere [8]. It is noteworthy that EVA 70% exhibits a similar value for the activation energy even though, in this case, the β -relaxation appears at higher temperatures.

Figure 5 represents the experimental ϵ'' data as a function of frequency for PVAc and two selected EVA copolymers for different temperatures in the region of the α -relaxation. The frequency variation of maximum loss $F_{\max}$ as a function of the reciprocal temperature for the different EVA copolymers is presented in Fig. 6. Here, we indicate by arrows the melting temperature range of the semicrystalline samples (EVA12–EVA40) according to the DSC measurements. As mentioned above, the melting temperature range depends on the VA content. Therefore, for the sake of clarity, we present lower and higher temperature limits (Table 1). From our data, it can be seen that we have been able

FIG. 4. Dielectric loss curves at 1 kHz for selected samples in the secondary (β) relaxation region: ●, PVAc; ■, EVA70; ○, EVA40; △, EVA18.

FIG. 5. Isothermal plots of the dielectric loss ϵ'' versus frequency in the α -relaxation region. The continuous solid lines represent the results of fitting experimental points to the HN equation. The solid points show temperatures at which the fitting procedure of the loss curves was not accomplished.

FIG. 6. $\log(F_{\max})$ as a function of reciprocal temperature for the α -relaxation in EVA samples. Solid lines are fittings to the VFT equation. Symbols are experimental data (●, PVAc; ■, EVA70; ○, EVA40; ▲, EVA33; △, EVA18; ▼, EVA12; □, EVA6). Arrows indicate the limits of melting range in semicrystalline samples.

to follow the α -relaxation process well above the melting temperatures of the crystalline phase of the corresponding samples. It is noteworthy that, while important modifications in the microstructure of the sample such as reorganization and melting occur, no remarkable changes are observed in the $F_{\max}$ behavior in the temperature region shown.

For EVA copolymers with VA greater than 40 wt%, the temperature position of the α -relaxation decreases with decreasing VA content. However, for VA less than 40 wt%, the temperature position of the α -relaxation is observed to remain almost unaffected. This effect seems to be similar to the behavior followed by the T_g value (Table 1). From Fig. 6, it can be seen that the α -process exhibits a characteristic non-Arrhenius temperature dependence similar to that observed for the relaxations associated with the segmental motions appearing above the glass transition temperature [20]. In this case, it is known that the temperature dependence of $F_{\max}$ follows a Vogel-Fulcher-Tamann (VFT) behavior [20]:

$$F = F_0 \exp \frac{-DT_0}{(T - T_0)} \quad (1)$$

where F_0 is a characteristic frequency, T_0 is referred as the Vogel temperature [20], and D is the fragility strength parameter [21]. Fits of the $F_{\max}$ experimental values to the VFT equation are represented in Fig. 6 by the continuous lines; the corresponding parameters

are collected in Table 2. It was not possible to obtain accurate fits in the case of the EVA6 sample due to low dielectric loss values. In graphical terms, the parameter D describes the curvature of $F_{\max}$ in a reciprocal temperature plot scaled by a reference temperature $T^* = T[F_{\max} = 1/(2\pi 10)]$.

[T2]

Havriliak-Negami Analysis

The Havriliak-Negami (HN) formalism has been employed to evaluate the ϵ'' dielectric relaxation curves [22]:

$$\epsilon^*(\omega) = \frac{\epsilon_o - \epsilon_\infty}{[1 + (i\omega\tau_o)^b]} + \epsilon_\infty - i \frac{\sigma}{\epsilon_{vac}\omega^s} \quad (2)$$

where $\epsilon_o - \epsilon_\infty = \Delta\epsilon$ is the dielectric strength, τ_o is the central relaxation time, and b and c are parameters that describe the shape of the relaxation time distribution function [22]. The contribution of the conductivity process is taken into account by the last term of the equation. Here, σ is related to the direct current electrical conductivity, ϵ_{vac} is the dielectric constant of vacuum, and the value of the coefficient $0 < s < 1$ depends on the conduction mechanism.

Dielectric data (ϵ' and ϵ'') from isothermal scans were fitted to Eq. 2. Graphical results of this fitting procedure for ϵ'' are presented in Fig. 5 by the continuous curves. The solid points in these graphs indicate the temperatures at which the fitting procedure could not be accomplished, owing either to the conspicuous broadening (EVA12.5 at low temperatures) of the α -relaxation or to truncations at high frequency (EVA40, $T = 100^\circ\text{C}$).

The values of the fitting parameters are presented in Fig. 7 as a function of the corresponding $F_{\max}$ values. By scaling the data in this way, it is possible to compare the characteristic parameters of the relaxation process for similar dynamic conditions.

[F7]

From Fig. 7, it can be seen that the dielectric strength $\Delta\epsilon$ of the α -relaxation process decreases with the VA content in the copolymers. In addition, the data in Fig. 7 show that the broadening parameter b systematically decreases with reduction in VA content, indicating that relaxation becomes broader at low VA contents. For a fixed

TABLE 2
Vogel-Fulcher-Tamann Parameters for the
Ethylene-Vinylacetate Copolymers

VA content, wt%	D	T_0 , K	F_0
6	—	—	—
12.5	3.74	218.53	10.82
18	3.64	216.91	10.70
33	3.94	211.98	10.62
40	4.59	208.56	10.92
70	5.90	218.26	11.09
100	6.10	257.62	11.37

FIG. 7. Characteristic parameters of the dielectric loss curves obtained from fitting to the HN equation: (a) asymmetry parameter c ; (b) symmetric broadening parameter b and dielectric strength $\Delta\epsilon$. Symbols are the same as in Fig. 6.

VA content, the b value tends to increase with the temperature, pointing to the narrowing of the relaxation time distribution curves. At the same time, the symmetry of the relaxation curves is also affected. At low VA content (6–33 wt% VA), the distribution of relaxation times is symmetric, as indicated by values of c close to unity (1). However, further growth in VA content induces an increase of asymmetry of the relaxation, reaching a maximum value for the sample with 70 wt% VA.

DISCUSSION

According to the model proposed by Richert and Angell [21], one may classify glassy materials in two broad categories: strong (Arrhenius temperature dependence of F_{max}) and fragile (non-Arrhenius temperature dependence of F_{max}). According to this description, high D values indicate the occurrence of a strong VFT behavior, promoting an Arrhenius-like type of behavior.

The strength-fragility parameter D is presented in Table 2. One observes a systematic decrease of D values with decreasing VA content. The trend is in agreement with previous dielectric measurements of EVA copolymers [1]. Ngai and Roland [23] suggested that, for the α -relaxation, the enhancement of intermolecular interactions associated with the polarity of pendant groups and steric effects increases the degree of intermolecular coupling, giving rise to a decrease of the D parameter [23]. Accordingly, for the EVA copolymers, a decrease of the VA content should induce a reduction of dipolar interactions owing to the "dilution" effect caused by the nonpolar ethylene units intercalated along the polymer chain. Consequently, one should detect an increase in D that is at variance with our findings (Table 2). Considering that, in EVA copolymers, only the ethylene units are capable of crystallizing, an exclusion of the polar VA groups from the crystalline into the amorphous phase is likely to occur [9,15]. This effect provokes an effective enrichment of the amorphous phase in VA group content, enhancing the dipolar interaction among them. This could explain the apparent contradiction and the observed decrease of the D parameter.

As mentioned in the introduction, there is still some uncertainty about the origin and molecular assignment of the α -relaxation process in PE and its copolymers as well as its composition dependence, atypical for copolymers. In our experiment, the temperature position of the α -relaxation remained almost constant for VA contents less than 40 wt% and increased for higher VA content, reaching that of PVAc (VA = 100 wt%).

There are two major viewpoints to explain this dependence. The first [6,9] associates this behavior with the existence of crystallinity. Nielsen [9] suggested that, despite the change in the overall composition of the copolymer, the VA concentration in the amorphous phase remains approximately constant due to the exclusion of the copolymer units from the PE-rich crystalline phase. Popli and Mandelkern [6] assigned the relaxation to the existence of an interfacial region. The second one [8] disregarded this explanation, arguing that the change in the T_g dependence occurs somewhere around 65 wt% VA content, although the last traces of crystallinity disappear at 45 wt% VA content. These authors concluded that the α -relaxation has a localized nature involving tertiary carbons and just a few neighboring CH_2 groups along the main chain. In this way, the relaxing segments suffer from a dilution effect when the length of the PE segment separating them increases. On the contrary, when the VA content increases, the dipolar and sterical interactions among the pendant VA groups set in, causing the increase of the relaxation temperature. According to this concept, it follows that crystallinity does not affect significantly the change in the relaxation temperature.

From the results presented in Fig. 6, one sees that the α -relaxation not only does not disappear on going through the melting region of the semicrystalline samples, but also does not even suffer major changes. Our measurements indicate that the VFT trend tested by F_{max} , which is characteristic of the segmental motions appearing above T_g [20], is not affected in the melting region. As far as the shape of the relaxation is concerned, we can see that the copolymers without crystallinity (PVAc and EVA70) exhibit an asymmetry that is characteristic of the α -relaxation of amorphous polymers [24]. However, for EVA = 40 wt%, the relaxation is asymmetric only in the melting region and becomes symmetric ($c = 1$) in the temperature region outside the melting range. This can be interpreted as caused by the increase of the amorphous phase at the expense of the crystalline one on melting.

A similar interpretation can be drawn from the temperature dependence of the dielectric strength $\Delta\epsilon$. While in the amorphous samples $\Delta\epsilon$ decreases with temperature,

as expected from the Frölich-Kirkwood equation [20], in the semicrystalline samples, this trend is followed only in the melting region. At lower temperatures, $\Delta\epsilon$ remains almost constant.

These observations are characteristic for the influence of crystallinity on the α -relaxation [24]. Therefore, our results support the assignment of the α -relaxation to the segmental motions appearing in the amorphous phase above the glass transition temperature rather than to the interfacial regions, which would be strongly modified in the molten zones.

CONCLUSIONS

1. The characteristics of the segmental relaxation process in EVA copolymers depends on VA percentage comonomer ratio and on the crystalline content of the material.
2. The dielectric strength of the relaxation process gradually decreases with increasing amount of the nonpolar PE comonomer units.
3. The shape of the relaxation becomes wider and changes from an asymmetric to a symmetric shape with decreasing VA content.
4. The dielectric relaxation not only not disappears when going through the temperature beyond the melting point of the semicrystalline samples, but also does not suffer major changes in its characteristic parameters.
5. Broadband dielectric spectroscopy measurements, when extended to the temperatures across the melting range, support the assignment of the α -relaxation to the segmental motions appearing in the amorphous phase at the glass transition temperature and cannot be assigned to the interfacial regions.

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