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The effect of tensile drawing on the structure and relaxation processes in vinyl alcohol–ethylene copolymers

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Abstract

The influence of the tensile drawing on the structure and dynamic mechanical relaxations of vinyl alcohol–ethylene (VAE) copolymers with higher content in the former counit is studied. The structure of VAE copolymers is considerably modified by drawing, which produces a disordered crystalline form, as revealed by WAXD and DSC measurements. The structural changes have significant effects on the viscoelastic relaxations of the stretched samples. A remarkable increase in the storage modulus is observed in the direction parallel to the draw direction in detriment to those found in specimens cut transverse and diagonally to the draw direction. The drawn copolymers show an additional α' relaxation, attributed to motions within the crystalline regions, taking place at temperatures higher than that of the α relaxation (glass transition). A clear anisotropy $\tan\delta_{45} > \tan\delta_0 \approx \tan\delta_{90}$ is exhibited in this α' relaxation similar to that observed in oriented LDPE where the chain axes are aligned in the draw direction while the lamellae are inclined at 45° to the draw direction, and the pattern of anisotropy thus suggests chain shear as a mechanism for the loss process. The α' process in the VAE copolymers is thus assigned to chain shear while the α and β processes are assigned to interlamellar shear. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Vinyl alcohol–ethylene copolymers; Anisotropy; Relaxation processes

1. Introduction

The growing interest in developing packaging materials with enhanced gas-barrier properties has led to a renewal of the research on copolymers of vinyl alcohol and ethylene (VAE) with a high molar fraction (from 0.6 to 0.8) of vinyl alcohol. The use of VAE copolymers as a barrier layer in the production of multilayer films for the packaging of foods and pharmaceuticals [1] involves a close control of the specifications of these copolymers, mainly the comonomer content. In addition, the manufacturing processes of barrier laminates imply various drawing procedures which can be simulated in order to study the influence of the stretching parameters on the orientation and on the corresponding final properties of the laminate [2–4]. The behavior of those anisotropic materials can be analyzed from the several mechanical relaxations taking place in an oriented sample, since relaxation processes can be dependent on the direction of the applied stress [5]. The analysis of viscoelastic mechanisms at different chosen angles provides a further information concerning the origin of the distinct relaxations. Cold-drawn low density polyethylene (LDPE) sheets with very well defined crystallographic and lamellar orientations have been attained and classified into two main categories: a roof-top structure, with tilted lamellae, or a parallel lamella structure, giving rise to well different SAXS patterns and dynamic mechanical spectra [5]. A particular case of roof-top structure causes a relaxation process in LDPE that shows a striking anisotropy with maximum loss for the specimen cut at 45° to the original draw direction. This is the anisotropy to be expected for a relaxation which involves shear parallel to the drawn direction in a plane containing the draw direction [5]. This relaxation has been termed as 'c-shear relaxation'. In this structure, the *c* axes of the polyethylene crystallites lye along the initial draw direction, the *b* axes in the plane of the sheet and the *a* axes normal to the plane of the sheet, while the lamellae are inclined at about 45° to the draw direction.

On the contrary, cold-drawn and annealed LDPE sheets with a parallel lamellae orientation also show a relaxation at about 0°C but with different anisotropy. The losses are now greatest when the stress is applied along the 0° direction and a similar anisotropy has been observed for high density polyethylene sheets (HDPE). It was proposed that this other relaxation mechanism, which corresponds to the β relaxation in LDPE and to the α relaxation in HDPE, is an interlamellar shear process. In this case, the lamellar

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planes are normal to the initial draw direction and the *c* axes now make an angle of about 45° with this direction [5].

The aim of this work is to analyze the influence of the tensile drawing on the structure, thermal behavior and viscoelastic response in VAE copolymers, for specimens cut parallel, perpendicular and at diagonal respect to the draw direction. In addition, the mechanical origin of the different relaxation processes exhibited by VAE copolymers is established. Moreover, the anisotropic behavior in the different relaxations of these copolymers is compared with that found in LDPE since one of the structural parts of these copolymers is LDPE.

It should be noted that crystallographic conventions require that the chain axis is the *b* axis in the crystal structures adopted by the copolymers studied in this paper. The relaxation mechanism known as '*c* shear' in polyethylene would thus be '*b* shear' in these structures. This mechanism will generally be referred to as 'chain shear' to apply to either case.

2. Experimental

Three commercially available random VAE copolymers, VAE1, VAE2 and VAE3 (from Solvay, Kuraray and Du Pont, respectively), were used. Table 1 shows the composition in vinyl alcohol, determined by means of ^{1}H and ^{13}C n.m.r. spectroscopies, as well as other characteristics of the samples. Sheet specimens were obtained as films by compression molding in a Collin press between hot plates (210°C), and at a pressure of 2.5 MPa for 15 min. The thickness of such films ranged from 200 to 250 μm.

Each one of the VAE samples has been crystallized by a fast cooling between plates cooled with water after melting in the press. Such a thermal treatment has been labeled as Q. The corresponding cooling rate is, approximately, 100°C min^{-1} for these Q specimens.

The 'parent' homopolymer LDPE was a commercial grade. Its manufacturing conditions (pressure and temperature) were similar to those used for the production of the VAE copolymers studied. LDPE films were obtained by melt compression at 140°C.

The LDPE homopolymer and VAE copolymers were deformed by uniaxial tensile stretching. Dumb-bell shaped specimens, with gauge dimensions 35 mm in length and 37 mm in width, were cut from the sheets. Tensile testing was carried out using an Instron Universal testing machine calibrated according to standard procedures. Specimens were drawn at 80°C and at two crosshead speeds of 0.5 and 10 cm min^{-1}. The elongation of the samples is given by the draw ratio, $\lambda = l_f/l_{0,}$ being l_f = final length and l_0 = initial length. The actual draw ratio, λ, was directly determined from the displacement of parallel ink marks printed 5 mm apart prior to drawing, and its value was about 4 in all the cases.

Wide-angle X-ray diffraction patterns were recorded in the reflection mode at room temperature by using a Philips diffractometer with a Geiger counter connected to a computer. Ni-filtered CuK_α radiation was used. The diffraction scans were collected over a period of 20 min between 2θ values from 3 to 43°, using a sampling rate of 1 Hz. The goniometer was calibrated with a standard silicon sample.

The stretched copolymers were characterized by DSC, in a Perkin-Elmer DSC7 calorimeter, connected to a cooling system and calibrated with different standards. The scanning rate used was 20°C min^{-1}.

Viscoelastic properties were measured with a Polymer Laboratories MK II dynamic mechanical thermal analyzer working in a tensile mode. The complex modulus and the loss tangent (tan δ) of each sample were determined at 3, 10 and 30 Hz over a temperature range from −150 to 150°C at a heating rate of 2°C min^{-1}. Specimens cut at 0, 45 and 90° to the drawing direction [6], were measured to study the anisotropy of relaxations. In the three different directions analyzed, specimens for dynamic mechanical analysis were rectangular strips 2.2 mm wide and over 10 mm long. Due to the fragility of specimens in VAE1 and VAE2 at 45° and transverse direction, the measurements of these two copolymers were started at temperatures higher than −150°C. The apparent activation energy values were estimated according to an Arrhenius-type equation, employing an accuracy of 1°C in the temperature assignment of tan δ maxima.

3. Results and discussion

3.1. Morphological aspects of stretched VAE copolymers

It has been reported that the undrawn corresponding 'parent' homopolymers, PVAL and LDPE, crystallize, independently of thermal treatment, into a monoclinic and an

Table 1
Vinyl alcohol (VA) composition and sample characteristics of VAE copolymers

Copolymer	Composition (f_{VA})			Density (g cm^{-3})	MFI[a] (g 10 min^{-1})
	Nominal	^{1}H n.m.r.	^{13}C n.m.r.		
VAE1	0.71	0.76	0.77	1.20	2.8
VAE2	0.68	0.73	0.72	1.19	3.1
VAE3	0.56	0.61	0.62	1.15	16.0

[a] MFI: melt flow index.

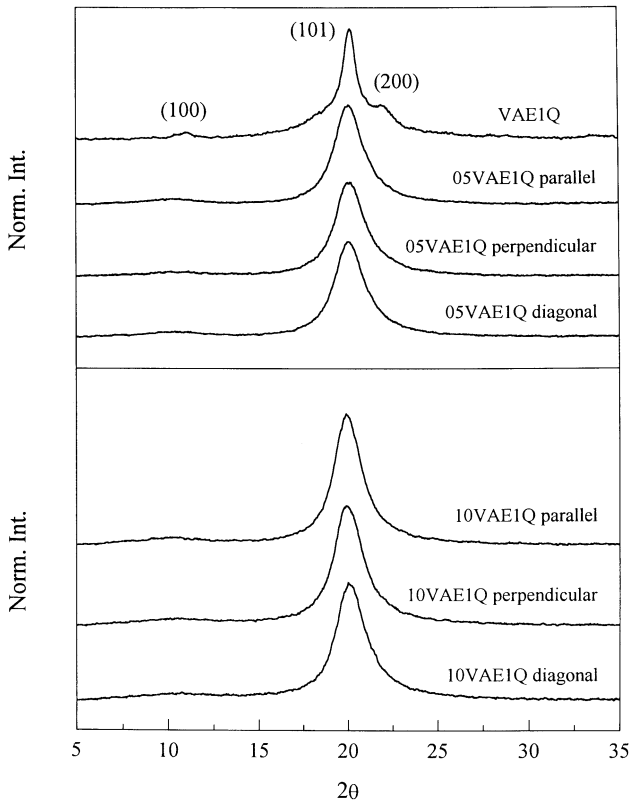

Fig. 1. X-ray diffraction patterns of the original and stretched VAE1Q specimens for the two crosshead speeds, 0.5 and 10 cm min^{-1}, at the different directions analyzed with respect to the draw direction. The two first numbers indicate the strain rate.

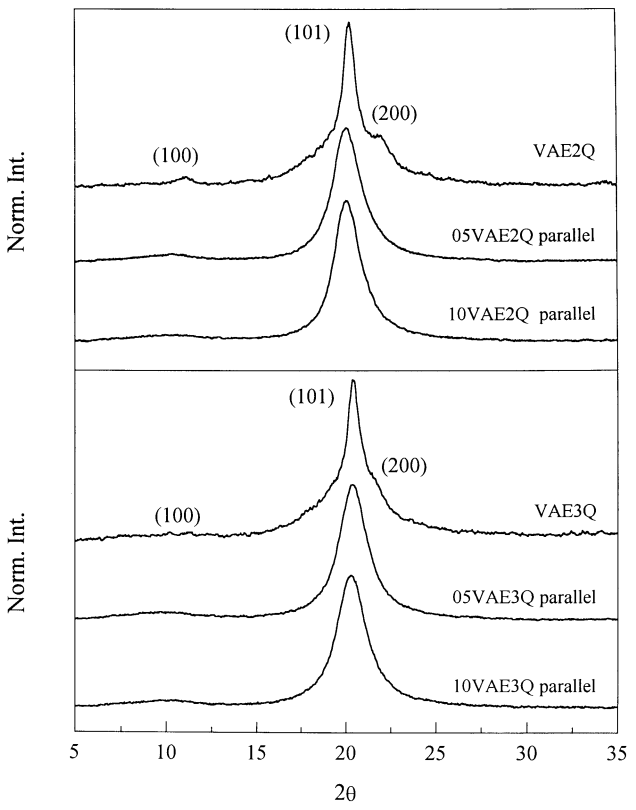

Fig. 2. X-ray diffraction patterns of the original and stretched specimens referred to VAE2Q (upper plot) and VAE3Q (lower plot) for the two crosshead speeds, 0.5 and 10 cm min^{-1}, at parallel direction with respect to the stretching one. The two first numbers indicate the strain rate.

orthorhombic lattice, respectively [7–9]. Nevertheless, the unstretched VAE copolymers show a polymorphic behavior depending on composition [2,9,10] and thermal treatment [2,9]. The polymorphism exhibited by these copolymers is not the usual one of two different unit cells with well-defined lattice parameters. VAE1 and VAE2 show a continuous change of some of the lattice constants, caused by the influence of the cooling rate [9]. The three quenched VAE copolymers under study crystallize in a monoclinic lattice with the angle β very close to 90° [9]. As a consequence the $(10\bar{1})$ and (101) diffraction spots are no longer resolved (Figs. 1 and 2) and the structure appears virtually orthorhombic.

The morphological structure of these VAE copolymers is considerably modified due to the drawing process, as shown in Figs. 1 and 2. Under the empirical protocol used in this work, the deformation process in VAE copolymers takes place through necking formation. The distinct X ray diffraction patterns suggest a strain-induced phase change. In Fig. 1, it can be observed that the diffraction pattern presented by VAE1 is altered. A disappearance of the (200) diffraction and a broadening of the (101) one is noticed, at both strain rates. Moreover, the (100) diffraction becomes wider and the maximum is shifted to lower angles. Fig. 2 shows identical features in VAE2Q and VAE3Q, just pointed out for VAE1Q. It seems that after stretching, the (200) reflection has merged into the main (101) reflection displayed in the quenched VAE2. The (200) diffraction in isotropicVAE3Q has become a slight shoulder on the (101) diffraction. After stretching, as with the other copolymers, the (200) diffraction is not observed.

The strain-induced phase change, just commented in the different VAE copolymers, is consistent with the loss of lateral ordering, judging from the vanishing of the (200) reflection and the broadening of the (100) one. A similar phenomenon has been found in vinyl alcohol–ethylene copolymers within the same composition range, but studied under distinct empirical backgrounds. A transformation from the original undrawn lattice into a disordered crystalline form of mesomorphic character has been suggested [11,12]. These common findings in this type of copolymers are in favor of a smectic-like order as pointed out previously for uniaxially oriented polypropylene [13].

Evidently, a much better picture of the induced anisotropy in the samples is obtained by performing two-dimensional small angle scattering experiments. We plan to analyze this point under real-time conditions by performing scattering experiments in a synchrotron source as a function of the draw ratio by using a two-dimensional detector. We have already analyzed these copolymers in their isotropic state.

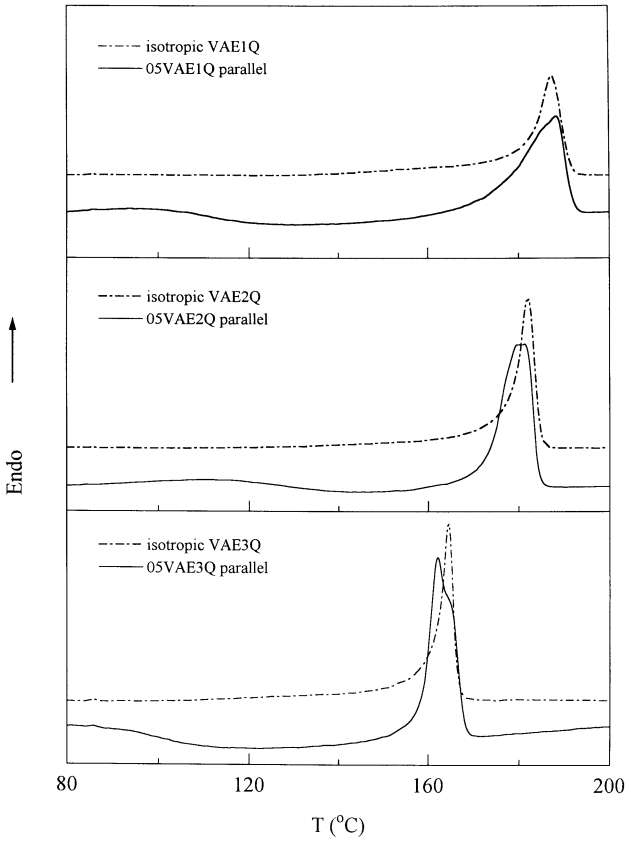

Fig. 3. D.s.c. curves corresponding to specimens isotropic and stretched at 0.5 cm $min^{-1}$and cut at parallel direction with respect to draw direction. From top to bottom: VAE1Q, VAE2Q and VAE3Q.

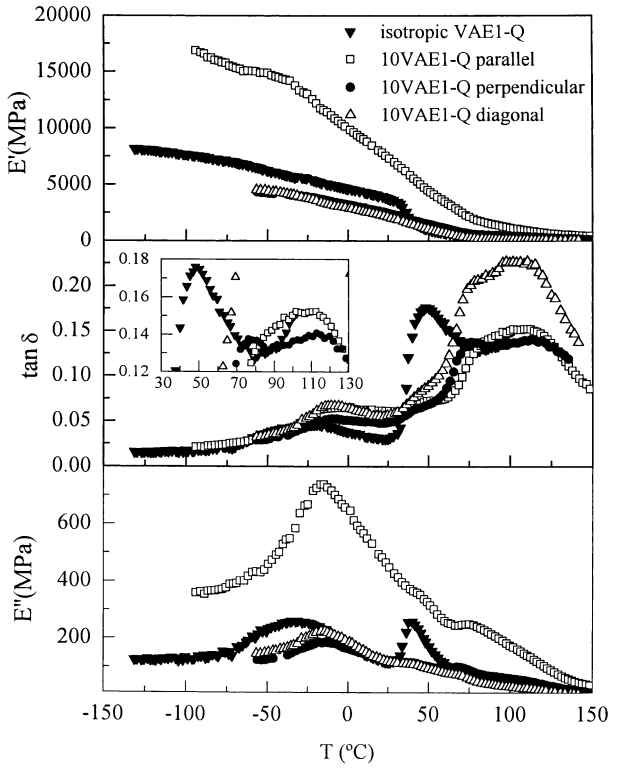

Fig. 4. Temperature dependence of the storage and loss modulus and loss tangent of either original or stretched (at 10 cm min^{-1}) specimens measured at the three different directions with respect to the draw one in VAE1Q copolymer.

The results show [14] well defined long spacings, centered around 13 nm for the quenched samples, which is indicative of a lamellar structure.

Fig. 3 shows the differences found in the melting behavior between isotropic and stretched specimens. In the upper part, the traces of isotropic specimens show a single peak at the temperature range represented, which corresponds to the melting of crystallites in the different VAE copolymers. On the contrary, a significant exotherm, at temperatures below the main endotherm, also appears in the stretched specimens. The exothermic peak is ascribed to the reorganization of the mesomorphic phase into the orthorhombic one of quenched specimens. It is worth noticing that an analogous exothermic transition has been observed for compression-drawn [15,16] as well as quenched polypropylene [13,15,16], and a first order smectic-to-crystal transition has been proposed to explain this feature [13].

3.2. Viscoelastic behavior of stretched VAE copolymers

Three different relaxation processes (in tan δ results at 3 Hz) have been observed for both homopolymers, PVAL and LDPE [17]. On the one hand, PVAL-Q shows relaxation mechanisms at −53, 82 and 113°C, being named as β, α and α' in order of increasing temperatures. On the other hand, the three viscoelastic relaxations found for LDPE-Q are located at approximately −120, −10 and 37°C, though the two latter processes are overlapped. In this case, the relaxations have been labelled γ, β and α, respectively [17]. On the contrary, only two different viscoelastic processes are exhibited in the three original VAE copolymers, at approximately −25 and 50°C in loss tangent, as seen in Fig. 4 for isotropicVAE1Q. These peaks are called as β and α, as referred previously [17,18]. In addition, VAE3 displays an additional relaxation at lower temperatures, around −125°C, being named γ. This relaxation process is seen more clearly in the loss modulus plot.

The viscoelastic behavior of the different specimens at the three directions with respect to the stretching direction is shown in Figs. 4–8. Some important data about the dynamic mechanical behavior of the investigated materials, such as temperature location and apparent activation energy of the relaxations, are listed in Tables 2–4.

It can be observed that the structural strain-induced phase changes provoked by the deformation process, mentioned above, have a very significant effect on the viscoelastic behavior exhibited in the stretched specimens. Drawing produces alignment of the macromolecules along the stretching direction. Consequently, the storage modulus considerably increases in the direction parallel to the draw direction but the moduli found in the transverse and

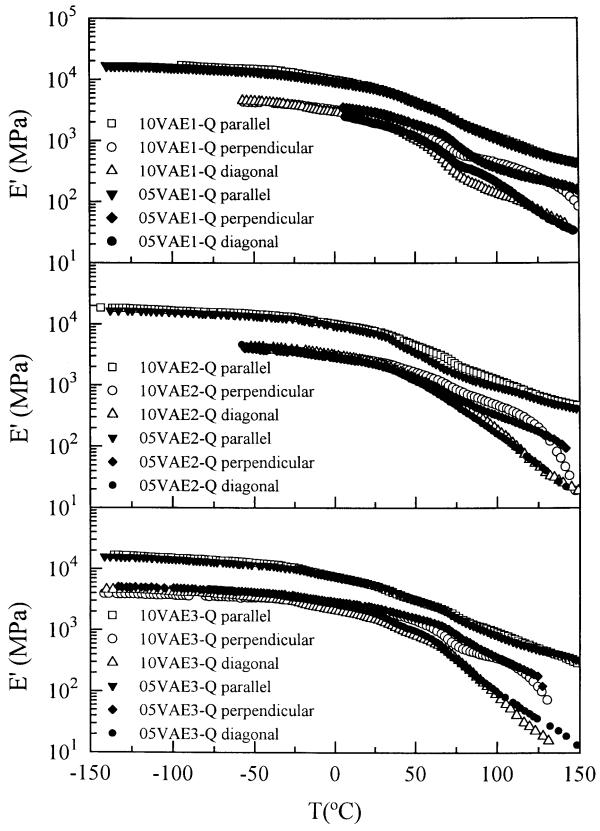

Fig. 5. Temperature dependence of the storage modulus for the three quenched VAE copolymers stretched at two crosshead speeds, 0.5 and 10 cm min^{-1}, and at the three different directions analyzed with respect to the draw direction. The two first numbers indicate the strain rate.

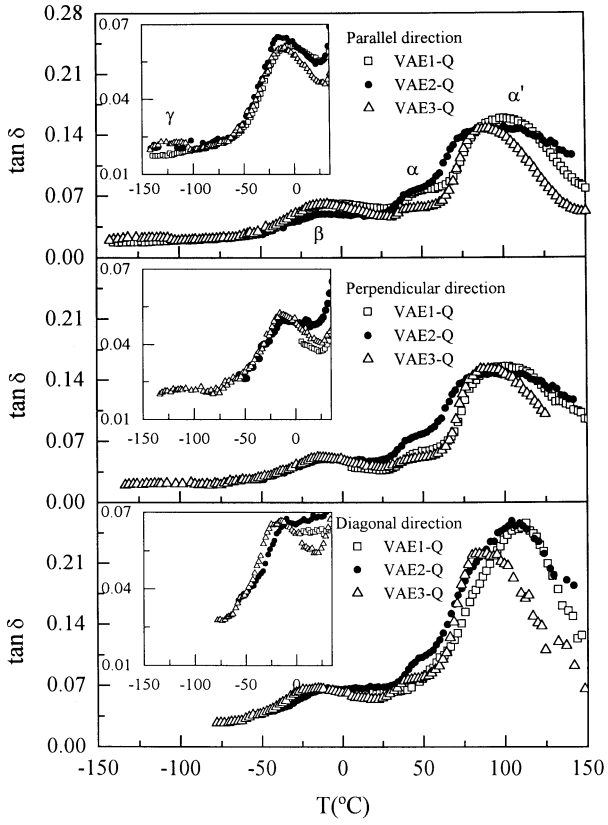

Fig. 6. Temperature dependence of tan δ for the three quenched VAE copolymers stretched at 0.5 cm min^{-1}, and at the three different directions analyzed with respect to the draw direction.

diagonal direction with respect to the drawing direction remarkably decrease, as depicted in Fig. 5. The storage modulus in the transverse and diagonal stretched specimens exhibits values even lower than in the corresponding isotropic copolymer, as depicted in Fig. 4 for VAE1. In addition to this dependence with the analyzed direction, modulus values are dependent upon composition and strain rate. Therefore, a storage modulus diminishment in stretched specimens measured in the different directions is shown as vinyl alcohol content decreases in the copolymer, since such a comonomer is the more rigid component owing to the intra and intermolecular hydrogen bonds between its macromolecules. The alignment of chains parallel to the draw direction is higher as strain rate increases, and, hence, specimens stretched at 10 cm min^{-1} exhibit in a given copolymer a higher modulus due to their higher orientation [19].

As can be seen in Figs. 4, 6 and 7, an additional relaxation mechanism is observed at high temperatures in the stretched copolymers. This process, which we designate the α' process, is seen in all testing directions and sometimes appears split into two well defined contributions.

The temperature dependence of tan δ was modeled as the sum of four Gaussian curves (two for the α' process and one for each of the other processes). Though such a representation has no a theoretical basis, the validity of this empirical approximation has been demonstrated for dynamic mechanical loss curves of several polymers in the region of their glass transition [20] and it provides a useful method of determining the peak positions. The distinct observed relaxation processes are analyzed separately as follows.

3.2.1. γ Relaxation

The relaxation at the lowest temperature takes place exclusively in LDPE and VAE3, as depicted in Figs. 6–8. The γ relaxation in LDPE has been attributed to crankshaft movements of polymethylenic chains [21]. Though a lot of work concerning the γ relaxation in polyethylene has been done, there remains no clear consensus regarding the details of the underlying motional process [22,23]. There is, however, a body of opinions which support one or more of the various model for restricted conformational transitions [24–27]. This γ process has also been found in polyesters containing oxyethylene spacers, where the oxygen atom plays an equivalent role to the methylenic group [28–30]. The position of the γ loss peak and the calculated low activation energy suggest the same molecular origin for VAE3 copolymer without stretching [17,18]. This type of motion requires chains containing sequences of three or more methylenic units. Because of this requirement, the γ relaxation is only displayed in the sample with the highest ethylene content, VAE3, but its

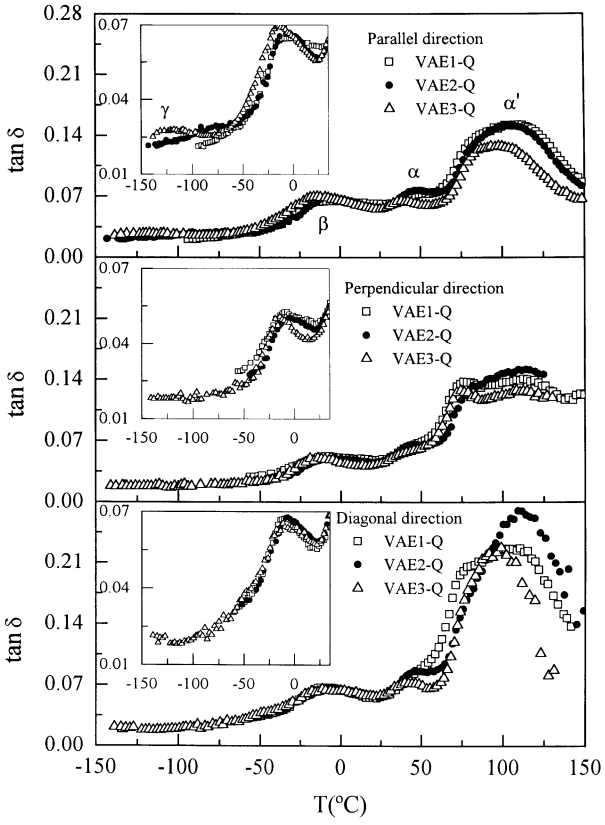

Fig. 7. Temperature dependence of tan δ for the three quenched VAE copolymers stretched at 10 cm min^{-1}, and at the three different directions analyzed with respect to the draw direction.

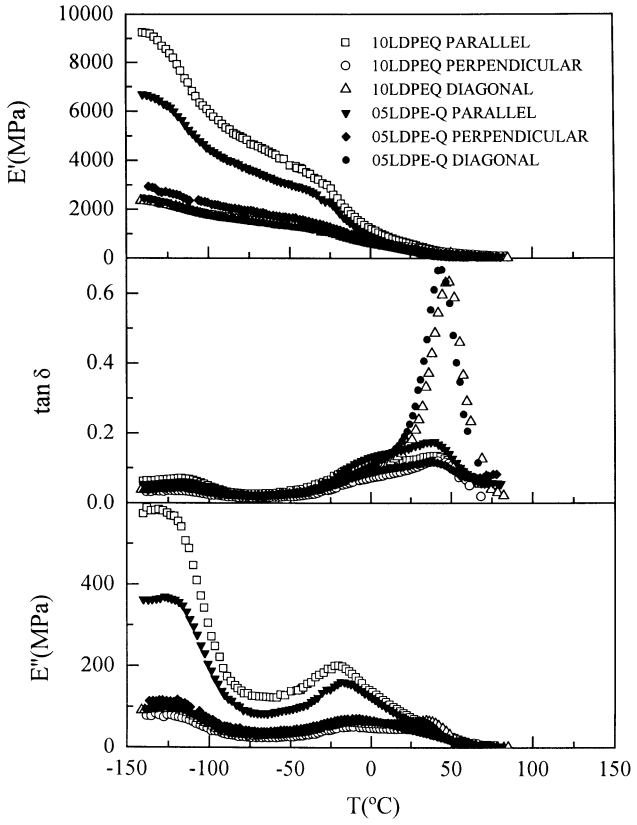

Fig. 8. Temperature dependence of the storage and loss modulus and loss tangent of stretched LDPEQ specimens measured at the three different directions with respect to the draw one at the two crosshead speeds (0.5 and 10 cm min^{-1}).

magnitude is very weak. Drawing causes a shift to higher temperatures of this relaxation measured in the different directions because the amorphous phase is more constrained than before stretching. Consequently, the apparent activation energy required for this motion is higher in the stretched specimens than in the isotropic one. A difference in intensity is not observed for the VAE3 specimens measured at the different directions perhaps because such a relaxation is so weak. Nevertheless, it has to be noted that

Table 2
Temperatures (in tan δ, at 3 Hz) and activation energies for the different relaxations of homopolymers and VAE copolymers, stretched at 80°C at two crosshead speeds, 0.5 and 10 cm min^{-1}, in specimens cut at 0° to the draw direction

Sample	T (°C)					ΔH (kJ mol^{-1})				
	γ	β	α		α'	γ	β	α		α'
PVAL-Q	–	−53	82	113	–	–	50	>400	–[a]	–
PVAL-Q-0.5	–	–	–	–	–	–	–	–	–	–
PVAL-Q-10	–	–	–	–	–	–	–	–	–	–
VAE1-Q	–	−22	48	–		–	110	>400	–	–
VAE1-Q-0.5	–	−5	51	84	115	–	85	>400	230	260
VAE1-Q-10	–	−6	52	86	119	–	70	>400	220	270
VAE2-Q	–	−20	48	–	–	–	110	>400	–	–
VAE2-Q-0.5	–	−10	46	83	113	–	95	>400	230	250
VAE2-Q-10	–	−7	48	85	118	–	80	>400	230	260
VAE3-Q	−125	−28	46	–		25	95	>400	–	–
VAE3-Q-0.5	−120	−11	42	81	99	60	80	>400	220	250
VAE3-Q-10	−116	−14	44	84	116	45	90	>400	220	260
PE-Q	−122	−8	38	–	–	60	230	105	–	–
PE-Q-0.5	−117	19	38	–	–	58	210	220	–	–
PE-Q-10	−117	18	40	–	–	54	200	240	–	–

[a] Results are not clearly observed in tan δ at all the frequencies.

Table 3
Temperatures (in tan δ, at 3 Hz) and activation energies for the different relaxations of homopolymers and VAE copolymers, stretched at 80°C at two crosshead speeds, 0.5 and 10 cm min^{-1}, in specimens cut at 45° to the draw direction

Sample	T (°C)					ΔH (kJ mol^{-1})				
	γ	β	α		α'	γ	β	α		α'
PVAL-Q	–	−53	82	113	–	–	50	>400	–[b]	–
PVAL-Q-0.5	–	–	–	–	–	–	–	–	–	–
PVAL-Q-10	–	–	–	–	–	–	–	–	–	–
VAE1-Q	–	−22	48	–		–	110	>400	–	–
VAE1-Q-0.5	–	–[a]	50	88	119	–	85	>400	160	210
VAE1-Q-10	–	−8	48	77	108	–	70	>400	160	220
VAE2-Q	–	−20	48	–	–	–	110	>400	–	–
VAE2-Q-0.5	–	−8	49	83	117	–	95	>400	150	190
VAE2-Q-10	–	−4	47	80	114	–	80	>400	150	190
VAE3-Q	−125	−28	46	–		25	95	>400	–	–
VAE3-Q-0.5	–[c]	−13	44	78	105	–[c]	80	>400	140	170
VAE3-Q-10	–[b]	−9	46	83	107	–[b]	90	>400	140	180
PE-Q	−122	−8	38	–	–	60	230	105		–
PE-Q-0.5	−121	−19	44	–	–	60	210	220	–	–
PE-Q-10	−121	18	48	–	–	60	200	240	–	–

[b] Results are not clearly observed in tan δ at all the frequencies.
[a] Measurements start at 0°C.
[c] Measurements start at −100°C.

the magnitude of this relaxation does considerably decrease for LDPE in specimens measured at 45 and 90° respect to the draw direction (Fig. 8). This suggests that the γ process is activated most strongly by tensile stresses in chains aligned with the draw direction.

3.2.2. β Relaxation

The β relaxation is very broad in all the samples analyzed. It has been reported [17] to take place around −20°C in VAE1 and VAE2 and at a lower temperature (about −30°C) in VAE3. The β relaxation of the stretched samples measured at the different directions with respect to the draw direction occurs at higher temperatures, around −10°C. This shift to higher temperatures is provoked by the orientation introduced during deformation of the chains. The different origins of this process in PVAL, LDPE and the three VAE copolymers should be noted [17]. On the one hand, the β mechanism in PVAL has been attributed either to hindered rotations of water molecules bound by hydrogen bonds to the polymer chains [31,32] or to local torsion

Table 4
Temperatures (in tan δ, at 3 Hz) and activation energies for the different relaxations of homopolymers and VAE copolymers, stretched at 80°C at two crosshead speeds, 0.5 and 10 cm min^{-1}, in specimens cut at 90° to the draw direction

Sample	T (°C)					ΔH (kJ mol^{-1})				
	γ	β	α		α'	γ	β	α		α'
PVAL-Q	–	−53	82	113	–	–	50	>400	–[b]	–
PVAL-Q-0.5	–	–	–	–	–	–	–	–	–	–
PVAL-Q-10	–	–	–	–	–	–	–	–	–	–
VAE1-Q	–	−22	48	–		–	110	>400	–	–
VAE1-Q-0.5	–	–[a]	47	85	115	–	85	>400	180	230
VAE1-Q-10	–	−7	44	75	116	–	70	>400	180	230
VAE2-Q	–	−20	48	–	–	–	110	>400	–	–
VAE2-Q-0.5	–	−11	47	82	114	–	95	>400	170	240
VAE2-Q-10	–	−7	48	80	113	–	80	>400	170	240
VAE3-Q	−125	−28	46	–		25	95	>400	–	–
VAE3-Q-0.5	−118	−12	49	81	109	60	80	>400	160	200
VAE3-Q-10	–[c]	−12	47	75	113	45	90	>400	160	210
PE-Q	−122	−8	38	–	–	60	230	105	–	–
PE-Q-0.5	−121	19	37	–	–	58	210	220	–	–
PE-Q-10	−121	17	41	–	–	54	200	240	–	–

[b] Results are not clearly observed in tan δ at all the frequencies.
[a] Measurements start at 0°C.
[c] Measurements start at −100°C.

movements around main chain bonds [33]. Such a mechanism takes place in PVAL at temperatures markedly lower than in VAE specimens. On the other hand, the β relaxation has been universally detected in branched polyethylenes at temperatures around -20°C but it sometimes appears, though 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 [34,35]. The temperature location of the β peak and the value of the apparent activation energy suggest a mechanism for the VAE copolymers similar to that found in LDPE [2,17,18]. Orientation has affected the whole VAE copolymers structure introducing alignment and constraints to chains placed into crystalline, amorphous and interfacial phases. The amount of interfacial material seems to have increased on deformation since the intensity of the β relaxation increases irrespective of the direction of measurement. This increase of intensity is higher in specimens cut parallel and diagonal than in those cut in the transverse direction, indicating that motions involved in the process are more preferred in these two directions. This pattern of anisotropy is consistent with an interlamellar shear process in a material with lamellae inclined at 45° to the draw direction as has been seen for the β process in LDPE [5].

3.2.3. α Relaxation

The α relaxation is considered to be the glass transition of the three copolymers and the PVAL sample, due to its intensity and to the correspondingly strong decrease of the storage moduli at the relaxation maximum (as depicted in Figs. 4–7). The value of the apparent activation energy is very high (>400 kJ mol^{-1}) calculated through either loss moduli or tan δ values (as listed in Tables 2–4). This apparent activation energy has been calculated, of course, by assuming an Arrhenius behavior over the narrow range of frequencies involved despite the fact that the process is non-Arrhenius over a wider range of frequencies. To corroborate the assignment of this α relaxation to the glass transition, the 'steepness index', m, has been also evaluated [36] from a cooperativity plot (i.e. log τ vs T_g/T). The m values found in stretched VAE copolymers are much higher than 16. In addition, the consideration of this relaxation process as associated to long-range motions taking place in the glass transition zone of the VAE copolymers agrees with the baseline change in the specific heat obtained in the calorimetric analysis [2]. On the contrary, the mechanism associated to this relaxation in LDPE is different and it involves motions within crystalline regions [29], as commented above.

The temperature of the α relaxation in undrawn specimens increases with vinyl alcohol content, approaching to the glass transition temperature of PVAL [17]. This feature is due to the major rigidity of vinyl alcohol as a consequence of the intra and intermolecular hydrogen bonds. Stretching induces chains alignment along the draw direction joined to the strain-induced phase modification and chains within the amorphous phase are, consequently, oriented and constrained. Therefore, the α relaxation intensity (associated to the amorphous regions) decreases strongly, irrespective of the direction of measurement, as seen in Fig. 4 for VAE1.

The temperature of this α relaxation increases with the vinyl alcohol content, as detailed in Tables 2–4 and noticed in Figs. 6 and 7. However, this process is strongly overlapped by the α' relaxation, which is the more intense mechanism of VAE specimens stretched under the empirical protocol used in the current work.

3.2.4. α' Relaxation

VAE copolymers are semicrystalline irrespective of composition [1,10]. Consequently, they could be expected to show a crystalline relaxation mechanism at temperatures higher than the relaxation associated to the glass transition, since crystallinity developed by these VAE copolymers is quite high [2,9] under both crystallization conditions (S and Q). Nevertheless, undrawn specimens did not exhibit a high temperature α' relaxation [17,18], as can be observed in the tan δ curve of Fig. 4 for the unstretched VAE1 specimen. It may be that this relaxation is not observed in undrawn material because it does not have sufficient mechanical strength for measurements to be performed at the appropriate temperature. Anyway, this α' relaxation is not shown in original specimens (in tan δ plots), as mentioned above, and in the loss modulus plot it is overlapped by the high temperature side of the α relaxation process.

In PVAL, such a relaxation has been assigned to motions within the crystalline phase, and can be caused either by the relaxation of hydrogen bonds between the hydroxyl groups in this phase [37,38] or to movements close to the crystal lamellae surface [39]. Though its molecular origin is different, LDPE shows a relaxation process related to motions in its crystalline regions [5]. It appears at lower temperatures than in PVAL (around 40°C) and it is labelled as α.

The additional α' mechanical relaxation, as commented above, is displayed in all the stretched samples measured at different directions with respect to the draw direction, at temperatures well above to the process associated to the glass transition (α relaxation). Orientation has aligned chains and induced a phase transformation, as seen in X ray diffraction and calorimetric measurements. Such a change has restructured either crystalline or amorphous phases and, hence, a new process associated to motions within crystals is now observed, as depicted in Figs. 4, 6, 7. This relaxation seems to be composed of two contributions, one taking place around 82°C and other at higher temperature, around 115°C. In polyethylene, sometimes, the relaxation related to movement in the crystalline regions is split into two mechanisms. The one appearing at higher temperature is due to a translational motion of the molecule in the direction of the molecular axis [21]. On the other hand,

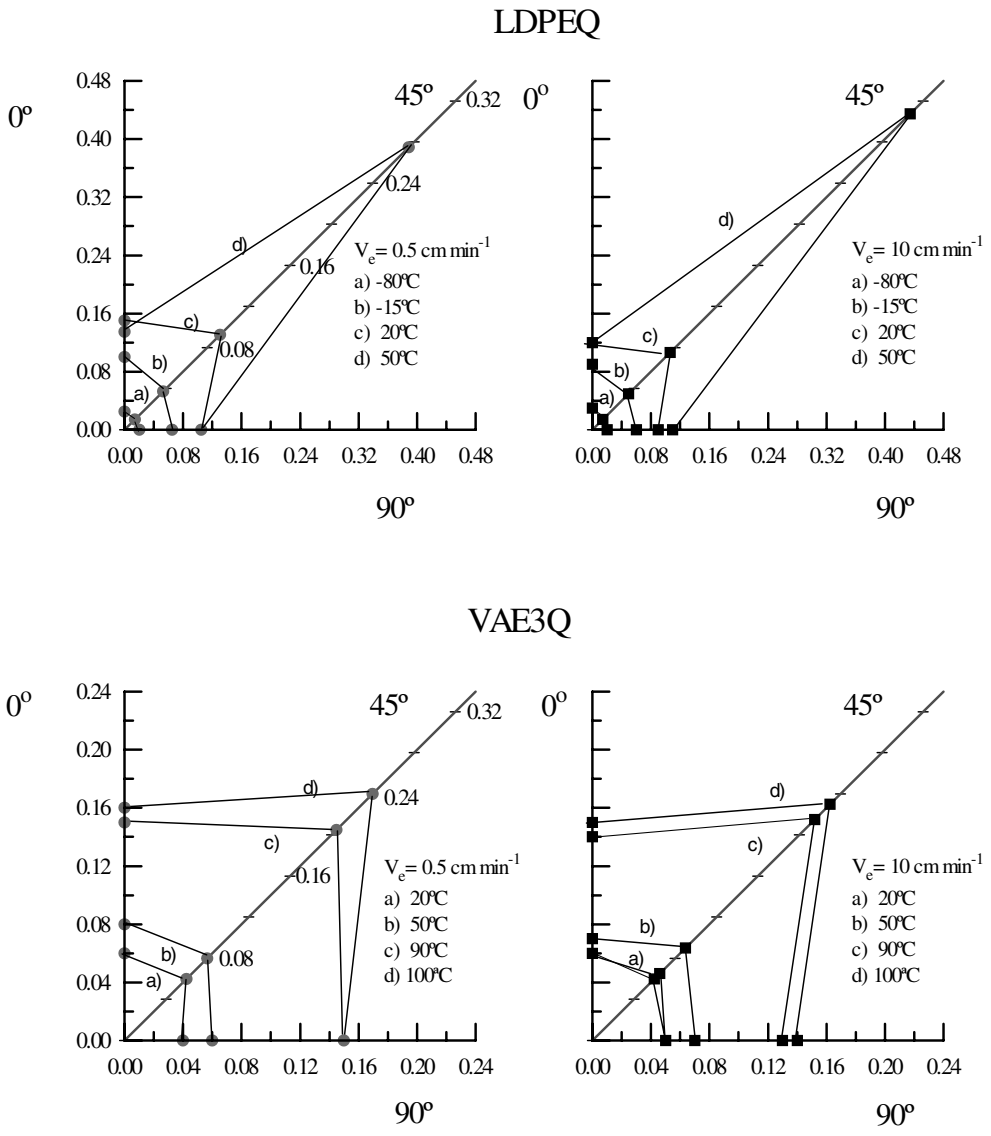

Fig. 9. Polar plots of the variation of loss tangent as a function of the angle between the cutting and stretching directions, at the temperatures and strain rates indicated in LDPEQ (upper plots) and VAE3Q (lower plots).

the crystalline relaxation at lower temperatures is related to vibrational and reorientational motion within the crystals [21]. In the case of VAE copolymers two different explanations can be suggested. On the one hand, as in polyethylene (one of the two 'parent' homopolymers), the higher temperature component could be due to the translational motion within the crystalline regions. This type of movement is more constrained and, consequently, is shifted to higher temperatures and implies a higher activation energy, as empirically observed. The lower temperature component, which is not always explicitly exhibited, would be associated with the vibrational and reorientational motions within the crystallites. The other possible explanation is given in terms of motions in the mesomorphic region for the relaxation occurring around 85°C, which is in agreement with the exotherm seen by DSC, whereas the contribution at the highest temperatures could be caused by motions within crystallites.

The temperature location and the intensity of this α' process are dependent upon comonomer content, in general terms, as seen in Figs. 6 and 7. Because of the greater orientation in specimens stretched at 10 cm min^{-1} [19], the intensity is lower and the relaxation time distribution becomes narrower in specimens stretched at that high crosshead speed. On the other hand, the apparent activation energy associated with this α' relaxation is higher than those found for secondary processes (β and γ) because of the restricted motions in the crystalline phase and its value is quite similar for all the stretched VAE copolymers.

It should be noted that the intensity of this process is much greater in specimens measured at 45° to the draw direction while the intensities of the process in parallel and transverse specimens are similar to each other. This is a characteristic pattern of anisotropy discussed below.

Table 5
Relative values of the anisotropy of storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) for stretched LDPE cut in parallel (0°), perpendicular (90°) and diagonal (45°) directions with respect to the draw direction

V_s (cm min^{-1})	T (°C)	Anisotropy	Relative values		
			0°	45°	90°
0.5	−80	$E'_0 > E'_{90} > E'_{45}$	1	0.4	0.5
	−15	$E'_0 > E'_{90} > E'_{45}$	1	0.5	0.7
	20	$E'_0 > E'_{90} > E'_{45}$	1	0.7	0.9
	50	$E'_{90} > E'_0 > E'_{45}$	0.9	0.1	1
	90	–	–	–	–
	100	–	–	–	–
10	−80	$E'_0 > E'_{90} = E'_{45}$	1	0.3	0.3
	−15	$E'_0 > E'_{90} = E'_{45}$	1	0.4	0.4
	20	$E'_0 > E'_{90} > E'_{45}$	1	0.6	0.7
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.9
	90	–	–	–	–
	100	–	–	–	–
0.5	−80	$E''_0 > E''_{90} > E''_{45}$	1	0.3	0.5
	−15	$E''_0 > E''_{90} = E''_{45}$	1	0.4	0.4
	20	$E''_0 > E''_{45} > E''_{90}$	1	0.8	0.6
	50	$E''_0 > E''_{90} > E''_{45}$	1	0.7	0.8
	90	–	–	–	–
	100	–	–	–	–
10	−80	$E''_0 > E''_{45} = E''_{90}$	1	0.2	0.2
	−15	$E''_0 > E''_{45} = E''_{90}$	1	0.3	0.3
	20	$E''_0 > E''_{45} > E''_{90}$	1	0.7	0.5
	50	$E''_{45} > E''_0 = E''_{90}$	0.9	1	0.9
	90	–	–	–	–
	100	–	–	–	–
0.5	−80	$\tan\delta_0 > \tan\delta_{45} = \tan\delta_{90}$	1	0.8	0.8
	−15	$\tan\delta_0 > \tan\delta_{45} > \tan\delta_{90}$	1	0.8	0.7
	20	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.8	1	0.6
	50	$\tan\delta_{90} = \tan\delta_0 < \tan\delta_{45}$	0.2	1	0.2
	90	–	–	–	–
	100	–	–	–	–
10	−80	$\tan\delta_0 > \tan\delta_{45} = \tan\delta_{90}$	1	0.7	0.7
	−15	$\tan\delta_0 > \tan\delta_{45} > \tan\delta_{90}$	1	0.8	0.7
	20	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.8	1	0.6
	50	$\tan\delta_{90} = \tan\delta_0 < \tan\delta_{45}$	0.2	1	0.2
	90	–	–	–	–
	100	–	–	–	–

Table 6
Relative values of the anisotropy of storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) for stretched VAE1-Q cut in parallel (0°), perpendicular (90°) and diagonal (45°) directions with respect to the draw direction

V_s (cm min^{-1})	T (°C)	Anisotropy	Relative values		
			0°	45°	90°
0.5	−80	–	–	–	–
	−15	–	–	–	–
	20	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.4
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.4
	90	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.3
	100	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.3
10	−80	–	–	–	–
	−15	$E'_0 > E'_{90} = E'_{45}$	1	0.3	0.3
	20	$E'_0 > E'_{90} = E'_{45}$	1	0.3	0.3
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.3
	90	$E'_0 > E'_{90} > E'_{45}$	1	0.1	0.3
	100	$E'_0 > E'_{90} > E'_{45}$	1	0.1	0.4
0.5	−80	–	–	–	–
	−15	–	–	–	–
	20	$E''_0 > E''_{45} = E''_{90}$	1	0.3	0.3
	50	$E''_0 > E''_{90} = E''_{45}$	1	0.3	0.3
	90	$E''_0 > E''_{90} = E''_{45}$	1	0.3	0.3
	100	$E''_0 > E''_{90} = E''_{45}$	1	0.3	0.3
10	−80		–	–	–
	−15	$E''_0 > E''_{45} > E''_{90}$	1	0.3	0.2
	20	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.3
	50	$E''_0 > E''_{90} = E''_{45}$	1	0.3	0.3
	90	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.3
	100	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.3
0.5	−80	–	–	–	–
	−15	–	–	–	–
	20	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.7
	50	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.7
	90	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.7	1	0.7
	100	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.7	1	0.7
10	−80	–	–	–	–
	−15	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.9	1	0.8
	20	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.8
	50	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.8	1	0.8
	90	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.7	1	0.6
	100	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.7	1	0.6

3.3. Anisotropy of the viscoelastic processes in VAE copolymers

The relative values of storage modulus, loss modulus and loss tangent at the three directions are collected in Tables 5–8 for LDPE and the three VAE copolymers. They are compared at six temperatures, corresponding to the mean global α' relaxation (around 100°C), α relaxation (about 50°C) and β relaxation (approximately −15°C) of the three copolymers and at two temperatures (−80 and 20°C) where no relaxation is detected. Tables 5–8 show that the values of the storage moduli in parallel direction are, in general, higher than the ones in perpendicular and diagonal directions ($E_0 > E_{90} > E_{45}$) for VAE copolymers and LDPE. This trend is maintained for copolymers in all the temperature range and shows that stresses are mainly transmitted through taut molecules in the drawing direction. For LDPE, the tendency mentioned above is sustained in almost all the range of temperatures, except for the higher one in which an inversion of the storage modulus is observed. A simple model was proposed to explain this behavior [5]. Application of stress in the parallel direction gives a large fall in modulus with increasing temperature and the stiffness at high temperature is primarily determined by the amorphous regions, which are very compliant above the relaxation transition. The basic assumption is that the crystalline and the amorphous regions are in series in the parallel direction and in parallel in the perpendicular one. In physical terms, above the relaxation transition the crystalline regions support the applied stress and a comparatively high stiffness is maintained.

Table 7
Relative values of the anisotropy of storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) for stretched VAE2-Q cut in parallel (0°), perpendicular (90°) and diagonal (45°) directions with respect to the draw direction

V_s (cm min^{-1})	T (°C)	Anisotropy	Relative values		
			0°	45°	90°
0.5	−80	–	–	–	–
	−15	$E'_0 > E'_{45} = E'90$	1	0.3	0.3
	20	$E'_0 > E'_{45} = E'_{90}$	1	0.3	0.3
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.4
	90	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.4
	100	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.3
10	−80	–	–	–	–
	−15	$E'_0 > E'_{45} = E'_{90}$	1	0.3	0.3
	20	$E'_0 > E'_{90} = E'_{45}$	1	0.3	0.3
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.4
	90	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.4
	100	$E'_0 > E'_{90} > E'_{45}$	1	0.2	0.4
0.5	−80	–	–	–	–
	−15	$E''_0 > E''_{45} > E''_{90}$	1	0.3	0.2
	20	$E''_0 > E''_{45} > E''_{90}$	1	0.4	0.3
	50	$E''_0 > E''_{45} > E''_{90}$	1	0.4	0.3
	90	$E''_0 > E''_{90} = E''_{45}$	1	0.4	0.4
	100	$E''_0 > E''_{90} = E''_{45}$	1	0.3	0.3
10	−80	–	–	–	–
	−15	$E''_0 > E''_{45} > E''_{90}$	1	0.3	0.2
	20	$E''_0 > E''_{45} = E''_{90}$	1	0.3	0.3
	50	$E''_0 > E''_{45} = E''_{90}$	1	0.3	0.3
	90	$E''_0 > E''_{90} > E''_{45}$	1	0.3	0.4
	100	$E''_0 > E''_{90} > E''_{45}$	1	0.3	0.4
0.5	−80	–	–	–	–
	−15	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.8
	20	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.9	1	0.7
	50	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.9	1	0.8
	90	$\tan\delta_0 < \tan\delta_{90} < \tan\delta_{45}$	0.6	1	0.7
	100	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.6	1	0.6
10	−80	–	–	–	–
	−15	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.8
	20	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.8
	50	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.9	1	0.8
	90	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.7	1	0.7
	100	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.6	1	0.6

Table 8
Relative values of the anisotropy of storage modulus (E''), loss modulus (E'') and loss tangent (tan δ) for stretched VAE3-Q cut in parallel (0°), perpendicular (90°) and diagonal (45°) directions with respect to the draw direction

V_s (cm min^{-1})	T (°C)	Anisotropy	Relative values		
			0°	45°	90°
0.5	−80	$E'_0 > E'_{45} > E'_{90}$	1	0.4	0.3
	−15	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.4
	20	$E'_0 > E'_{90} = E'_{45}$	1	0.4	0.4
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.5
	90	$E'_0 > E'_{90} > E'_{45}$	1	0.1	0.5
	100	$E'_0 > E'_{90} > E'_{45}$	1	0.1	0.4
10	−80	$E'_0 > E'_{45} > E'_{90}$	1	0.3	0.2
	−15	$E'_0 > E'_{90} = E'_{45}$	1	0.3	0.3
	20	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.4
	50	$E'_0 > E'_{90} > E'_{45}$	1	0.3	0.5
	90	$E'_0 > E'_{90} > E'_{45}$	1	0.1	0.4
	100	$E'_0 > E'_{90} > E'_{45}$	1	0.1	0.4
0.5	−80	$E''_0 > E''_{45} > E''_{90}$	1	0.3	0.2
	−15	$E''_0 > E''_{45} = E''_{90}$	1	0.3	0.3
	20	$E''_0 > E''_{45} = E''_{90}$	1	0.3	0.3
	50	$E''_0 > E''_{90} = E''_{45}$	1	0.4	0.4
	90	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.5
	100	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.4
10	−80	$E''_0 > E''_{45} > E''_{90}$	1	0.5	0.2
	−15	$E''_0 > E''_{45} > E''_{90}$	1	0.3	0.2
	20	$E''_0 > E''_{45} > E''_{90}$	1	0.4	0.3
	50	$E''_0 > E''_{90} > E''_{45}$	1	0.4	0.5
	90	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.3
	100	$E''_0 > E''_{90} > E''_{45}$	1	0.2	0.4
0.5	−80	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.7
	−15	$\tan\delta_0 = \tan\delta_{45} > \tan\delta_{90}$	1	1	0.7
	20	$\tan\delta_0 > \tan\delta_{45} > \tan\delta_{90}$	1	0.8	0.7
	50	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.9	1	0.6
	90	$\tan\delta_{90} = \tan\delta_0 < \tan\delta_{45}$	0.7	1	0.7
	100	$\tan\delta_{90} = \tan\delta_0 < \tan\delta_{45}$	0.7	1	0.7
10	−80	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.7	1	0.5
	−15	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.9	1	0.6
	20	$\tan\delta_{90} < \tan\delta_0 < \tan\delta_{45}$	0.7	1	0.5
	50	$\tan\delta_0 = \tan\delta_{90} < \tan\delta_{45}$	0.7	1	0.7
	90	$\tan\delta_{90} = \tan\delta_0 < \tan\delta_{45}$	0.5	1	0.5
	100	$\tan\delta_{90} = \tan\delta_0 < \tan\delta_{45}$	0.5	1	0.5

The behavior of the loss tangent is more complex. As noted above, a clear anisotropy is exhibited in the α' relaxation region for the VAE copolymers in that $\tan\delta_{45} > \tan\delta_0 \approx \tan\delta_{90}$ (See Figs. 7 and 9 and Tables 5–8). This anisotropy is also exhibited by the α process in LDPE (Fig. 8). The tensile stress applied to the 45° sample causes maximum shear stresses in the draw direction and at right angles to this in the plane of the sample. The pattern is thus indicative either of a chain shear process or an interlamellar shear process in a lamellar stack morphology where the inter-lamellar planes are perpendicular to the draw direction. In the case of oriented LDPE, however, the pattern was seen for material in which the lamellae were aligned at approximately 45° to the draw direction and the anisotropy was thus taken to indicate a chain shear process [5]. Assuming a similar morphology for the VAE copolymers then the pattern of anisotropy suggests that the α' relaxation is associated with a chain shear process.

The α and the β processes in the VAE copolymers both exhibit a much reduced anisotropy in tan δ. Since the α process is the glass transition and occurs in the amorphous phase, these processes may be assigned as interlamellar shear processes, similar to the β process in LDPE. Their anisotropy is thus dependent upon the detailed morphology.

Summing up, it can be said that the study of VAE copolymers cut at different directions (parallel, perpendicular and diagonal with respect to the draw direction) has shown the following features.

1. The morphological structure of these VAE copolymers

has been considerably modified due to the drawing process: a strain-induced phase change has occurred in the different VAE copolymers. The transformation is consistent with the loss of lateral ordering judged from the vanishing of the (200) reflection and the broadening of the (100) one. A change from the original undrawn lattice into a disordered crystalline form of mesomorphic character has been suggested.

2. In agreement to this hypothesis, a significant exotherm appears at the lower side of the melting endotherm for stretched specimens. This exothermic peak is ascribed to the reorganization of the mesomorphic phase into the original crystalline one. A first order smectic-to-crystal transition has been proposed [13].
3. Those structural strain-induced phase changes provoked by the deformation process have a very significant effect on the viscoelastic behavior exhibited in the stretched specimens. A remarkable increase in the storage moduli is observed in the direction parallel to the draw direction in detriment to those found in specimens cut transverse and diagonally to the draw direction.
4. Moreover, an additional relaxation mechanism is noted in these stretched VAE copolymers, which has been named as α'. Such a relaxation takes place at temperatures higher than the α relaxation associated with the glass transition of these copolymers. This α' process is attributed to motions within the crystalline regions.
5. The α relaxation significantly decreases its intensity because of the oriented amorphous phase.
6. The β relaxation is moved to higher temperatures for the stretched specimens and its intensity is considerably increased.
7. A clear anisotropy $\tan\delta_{45} > \tan\delta_0 \approx \tan\delta_{90}$ is exhibited for the α' relaxation. Assuming that the lamellae are significantly inclined to the draw direction, as is seen in LDPE, then this process would involve shear in the chain axis direction on planes containing the chain axis of the crystallites.
8. Finally, the α and β processes in the different VAE copolymers show $\tan\delta_0 \approx \tan\delta_{45} > \tan\delta_{90}$. These relaxations have been assigned to interlamellar shear in the lamellar structure mentioned above.

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