

Viscoelastic processes in vinyl alcohol–ethylene copolymers. Influence of composition and thermal treatment

M.L. Cerrada*, J.M. Pereña, R. Benavente, E. Pérez

Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

Received 16 April 1999; received in revised form 29 October 1999; accepted 17 November 1999

Abstract

Viscoelastic relaxations of three samples of vinyl alcohol–ethylene copolymers, richer in the former comonomer, were studied in a wide range of temperature. The temperature location, intensity and apparent activation energy of the distinct relaxations found are discussed and compared with those of the homopolymers, poly(vinyl alcohol) and polyethylene. Differential scanning calorimetry and X-ray diffraction results of the specimens are also discussed in the frame of the dynamic mechanical analysis, showing that the polymorphism exhibited in some copolymers is a result of the thermal treatment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Vinyl alcohol–ethylene copolymers; Dynamic mechanical analysis; Thermal treatment

1. Introduction

The relationship between composition and properties of vinyl alcohol–ethylene (VAE) copolymers is a topic of increasing interest, owing to the great potential of those copolymers as barrier materials used in foods and pharmaceuticals packaging. The gas barrier properties of VAE copolymers are enhanced in samples with composition rich in vinyl alcohol, around 60–80 molar fraction, as occurred in the samples studied by Séguelá et al. [1] and in the present work.

The composition peculiarities of VAE copolymers can be adequately studied by dynamic mechanical analysis. This technique allows to elucidate the different motions taking place in the macromolecular chain, which are affected by the possible presence of sorbed water tied by hydrogen bonds to the vinyl alcohol moieties. Taking into account the three mechanical relaxations exhibited in both “parent” homopolymers—poly(vinyl alcohol) and low-density polyethylene—the study of viscoelastic relaxations of VAE copolymers in comparison to those of homopolymers seems to be an adequate route to assess the influence of composition in the mechanical properties of VAE copolymers. This type of study has been only partially undertaken in a recent paper [1].

The present paper scans the dynamic mechanical behavior of three samples of VAE copolymers and two of

the “parent” homopolymers, relating the results to those obtained either by differential scanning calorimetry (DSC) or X-ray diffraction (XRD). The latter technique is very useful to detect the polymorphism shown by these copolymers, reported extensively by us elsewhere [2].

2. Experimental

Three commercially available 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 ^1H and ^{13}C NMR spectroscopies as well as the other characteristics of the samples supplied by the manufacturers. Sheet specimens were obtained as films by compression molding in a Collin press between hot plates (210°C) at a pressure of 2.5 MPa for 15 min.

Each one of the VAE samples was crystallized under two different conditions (Q and S). The first treatment, Q, consisted of fast cooling between plates cooled with water after melting in the press. The S specimens were slowly cooled from the melt at the inherent rate of the press. The corresponding cooling rates were, approximately, 100 and 2.5°C min⁻¹ for the Q and S specimens, respectively.

The “parent” homopolymers, poly(vinyl alcohol), (PVAL), and polyethylene, (LDPE), were commercial grades and, for LDPE, the manufacturing conditions (pressure and temperature) were similar to those used for the production of the VAE copolymers studied. The PVAL

* Corresponding author.

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

Copolymer	Composition (f_{VAL})			Density (g cm^{-3})	Melt flow index (g 10 min^{-1})
	Nominal	$^1\text{H NMR}$	$^{13}\text{C NMR}$		
VAE1	0.71	0.76	0.77	1.196	2.8
VAE2	0.68	0.73	0.72	1.190	3.1
VAE3	0.56	0.61	0.62	1.150	16

homopolymer samples were obtained by melt compression under the same conditions than those of VAE copolymers. On the other hand, LDPE films were obtained by melt compression at 140°C .

The molded homopolymers and copolymers were characterized by DSC and XRD. The thermal properties were carried out in a Perkin–Elmer DSC7 calorimeter, connected to a cooling system and calibrated with different standards. To avoid differences in the glass transition and melting temperatures caused by variations in sample weight, the mass of the sample was fixed at approximately 6 mg in all the experiments. The heating rate used was $10^\circ\text{C min}^{-1}$. The values of the glass transition and melting temperatures gathered together to the melting enthalpy are shown in Table 2. On the other hand, X-ray patterns at wide angles were recorded at room temperature with an X-ray diffractometer from Philips Co. equipped with a Geiger counter detector, using nickel-filtered CuK_α radiation.

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 ($\tan \delta$) and of each sample were determined at 3, 10, 30 Hz over a temperature range from -150 to 150°C at a heating rate of 2°C min^{-1} . The specimens used were rectangular strips 2.2 mm wide, around 0.18 mm thick and over 13 mm long. The apparent activation energy values were calculated according to an Arrhenius-type equation, employing an accuracy of 0.5°C in the temperature assignment of $\tan \delta$ maxima.

3. Results and discussion

The DSC melting curves of the different VAE copoly-

Table 2

Thermal properties: glass transition temperatures (T_g), melting temperatures (T_m) and enthalpies of melting (ΔH) of Q and S VAE copolymers specimens (estimated errors: temperatures $\pm 1^\circ\text{C}$; enthalpies $\pm 4 \text{ J g}^{-1}$)

Sample	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH (J g^{-1})
VAE1-Q	57	188	75
VAE1-S	–	188	75
VAE2-Q	57	183	76
VAE2-S	–	183	75
VAE3-Q	52	166	72
VAE3-S	–	166	74

mers and the two homopolymers are displayed in Fig. 1 for the quenching treatment. The glass transition temperature in PVAL is observed around 72°C while those of copolymers are ranging within 50 – 60°C , depending on composition (Table 2). The melting temperatures, T_m , of the crystalline phase are clearly affected by vinyl alcohol content increasing as such a comonomer in the copolymers does. However, T_m is not influenced by the thermal treatment [2–4].

The X-ray patterns of specimens slowly cooled from the melt are shown in Fig. 2. PVAL-S exhibits a monoclinic crystal lattice while LDPE-S is presenting an orthorhombic one. Copolymers with higher vinyl alcohol content, VAE1-S and VAE2-S (see Table 1), crystallize in the same type of lattice than PVAL-S homopolymer under the conditions of this particular thermal treatment. Since ethylene comonomer units are increased in VAE3, the cocrystallization of

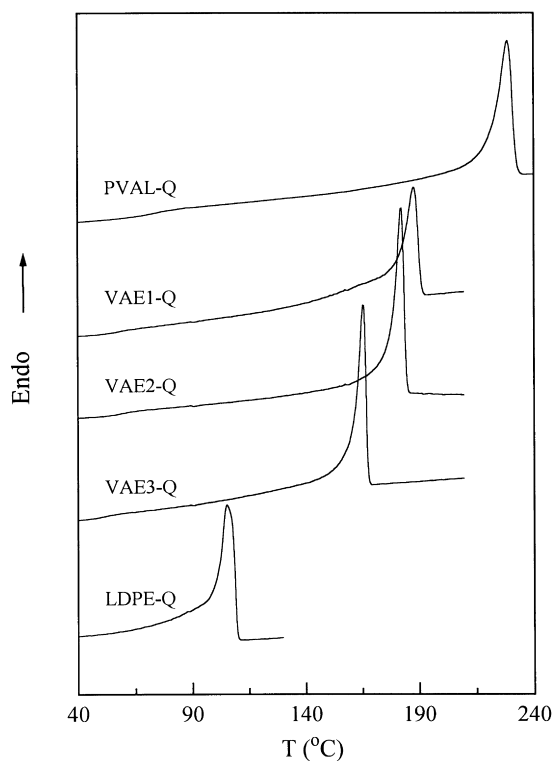


Fig. 1. DSC curves corresponding to the two homopolymers and the three copolymer specimens quenched from the melt. From the top to the bottom: poly(vinyl alcohol) (PVAL-Q); vinyl alcohol–ethylene copolymers (VAE1-Q, VAE2-Q, VAE3-Q); and low-density polyethylene (LDPE-Q). Q stands for “fast cooling”.

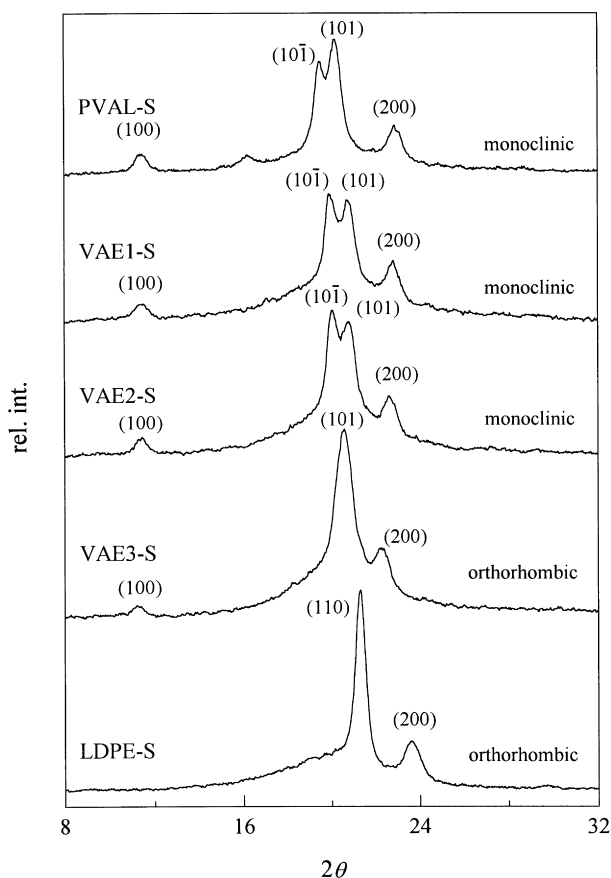


Fig. 2. X-ray diffraction patterns of the different samples slowly cooled from the melt. From the top to the bottom: poly(vinyl alcohol) (PVAL-S); vinyl alcohol–ethylene copolymers (VAE1-S, VAE2-S, VAE3-S); and low-density polyethylene (LDPE-S). S stands for “slow cooling”.

both comonomers does not take place into a monoclinic lattice but an orthorhombic crystalline cell [2,3,5]. On the other hand, the three VAE copolymers quenched from the melt display an orthorhombic crystal lattice, as depicted in Fig. 3. There is a change in crystal lattice depending upon composition, just mentioned, in addition to a change in crystal lattice upon thermal treatment. 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 [2].

Some important data representing the dynamic mechanical behavior of the investigated materials are listed in Tables 3 and 4. Temperature location, intensity, apparent activation energy and storage modulus of the distinct relaxation processes are gathered together to storage modulus at low temperature, where no viscoelastic mechanism is taking place, and at high temperature after the glass transition. Fig. 4 shows storage and loss moduli and loss tangent for one of the parent homopolymers, PVAL-Q, at the different experimental frequencies used while Fig. 5 is displaying the same parameters in LDPE for both thermal treatments. On the one

hand, PVAL-Q shows three relaxation mechanisms at -53 , 82 and 113°C ($\tan \delta$ results at 3 Hz), being named as β , α and α' in order of increasing temperatures. On the other hand, other three viscoelastic relaxations (on loss tangent basis) are found for LDPE at approximately -120 , -10 and 37°C , though the two latter processes are overlapped, mainly in specimens that slowly cooled from the melt. In this case, the relaxations have been labeled γ , β and α , respectively. Fig. 6 depicts the two viscoelastic mechanisms exhibited in the three VAE copolymers, at approximately -25 and 50°C (3 Hz) also considering loss tangent results. These peaks are termed β and α , as referred in our preliminary results [6]. Moreover, VAE3 for both thermal treatments, as represented in Fig. 7, displays an additional relaxation at lower temperatures, around -125°C , being named γ . In Figs. 4–7, it can be seen that the evolution of the storage modulus is in accordance with that of the loss modulus and $\tan \delta$, showing inflexions at temperatures approximately similar to those of the corresponding relaxation loss peaks. The different observed relaxation processes are analyzed separately as follows.

3.1. γ relaxation

The relaxation at the lowest temperature takes place exclusively in LDPE and VAE3, as mentioned above and depicted in Figs. 5–7. γ relaxation in LDPE has been attributed to crankshaft movements of polymethylene chains [7]. Despite the vast amount of work which has now been published concerning the γ relaxation in polyethylene, there is no clear consensus concerning the details of the underlying motional process [8,9]. There is, however, a body of opinion which support one or more of the various model for restricted *conformational* transitions such as kink inversion and formation, and crankshaft motions involving either three or five chain bonds [10–13]. The position of the γ loss peak and the calculated low activation energy suggest for VAE3 copolymer the same molecular origin. This type of motion requires chains containing sequences of, at least, three or more methylenic units. Due to this requirement, the γ relaxation is only displayed in the sample with the highest ethylene content, VAE3, and its magnitude is very weak. There is not significant effect of thermal treatment on this relaxation process, as seen in Table 3 and Fig. 7. No mention of such γ relaxation has been made in a recent study on this type of copolymers within a similar composition range [1]. In addition, this γ process has been also found in polyesters containing oxyethylene spacers, where the oxygen atom plays an equivalent role than methylenic groups [14,15], and it has been associated with kink formation, inversion and migration in amorphous regions [16].

3.2. β relaxation

The β relaxation is very broad in all the samples analyzed. A different origin of this relaxation process has to be noted in PVAL and in both LDPE and the three VAE

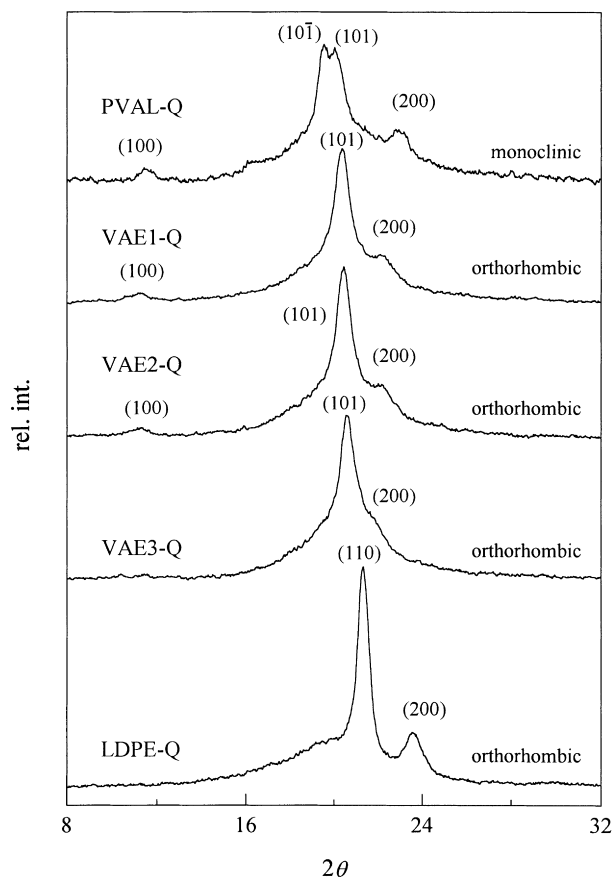


Fig. 3. X-ray diffraction patterns of the different samples quenched from the melt. From the top to the bottom: poly(vinyl alcohol) (PVAL-Q); vinyl alcohol–ethylene copolymers (VAE1-Q, VAE2-Q, VAE3-Q); and low-density polyethylene (LDPE-Q). Q stands for “fast cooling”.

copolymers. 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 [17,18] or to local torsion movements around main chain bonds [19]. On the other hand, the β relaxation has been universally detected in branched polyethylenes at tempera-

tures 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 [20,21]. The temperature location of the β peak and a higher value of the apparent activation energy suggest a mechanism for the VAE copolymers similar to that found in LDPE.

Any conclusive tendency cannot be established with the composition and thermal treatment. As detailed in Table 3, VAE1 and VAE2 show close values for both thermal treatments. As vinyl alcohol content is decreased, in the case of VAE3, this β relaxation is located at lower temperature. For VAE3-S specimen, this relaxation appears at slightly lower temperature, such as in LDPE case. It suggests a higher mobility in the interfacial phase of the most perfect crystalline samples than that found as the sample was quenched from melt. This feature is not exhibited by VAE1 and VAE2, being possible that the different crystalline lattice developed for these copolymers by changing the cooling procedure [2] is responsible for the difference.

3.3. α relaxation

The α relaxation is considered as the glass transition of the three copolymers and PVAL sample, due to its sharpness, to the correspondingly strong decrease of the storage moduli at the relaxation maximum, as observed in Figs. 4, 6 and 7, and to the high value of the apparent activation energy, as listed in Table 3. Nevertheless, the mechanism associated to this relaxation in LDPE is different and it involves motions within crystalline regions [22].

The temperature of the α relaxation increases with the vinyl alcohol content, approaching the glass transition temperature of PVAL. This feature is due to the major rigidity of vinyl alcohol as consequence of the intra and intermolecular hydrogen bonds. As the ethylene content is diminished the flexibility in the chains is reduced, so as the mobility.

Table 3

Relaxation temperatures, intensities ($\tan \delta$ basis, at 3 Hz) and activation energies for the different relaxation processes in the homopolymers and the three VAE copolymers. The numbers in parentheses refer to the relative values of $\tan \delta$

Sample	f_{VAL}	T ($^\circ\text{C}$)				$\tan \delta$				ΔH (kJ mol^{-1})			
		γ	β	α	α'	γ	β	α	α'	γ	β	α	α'
PVAL-Q	1.00	–	–53.0	82.0	113.0	–	0.022 (2.41)	0.36 (40.0)	0.32 (35.9)	–	50	> 400	– ^a
VAE1-Q	0.77	–	–22.5	48.0	–	–	0.046 (2.98)	0.18 (11.4)	–	–	110	> 400	–
VAE1-S	0.77	–	–18.0	59.5	–	–	0.037 (3.36)	0.12 (10.9)	–	–	80	> 400	–
VAE2-Q	0.72	–	–20.5	48.0	–	–	0.045 (2.99)	0.18 (11.8)	–	–	110	> 400	–
VAE2-S	0.72	–	–17.0	55.0	–	–	0.048 (4.00)	0.13 (11.1)	–	–	105	> 400	–
VAE3-Q	0.62	–125.0	–28.5	45.5	–	0.020 (1.02)	0.050 (2.59)	0.18 (9.3)	–	25	95	> 400	–
VAE3-S	0.62	–125.0	–31.0	49.5	–	0.020 (1.21)	0.040 (2.50)	0.12 (7.4)	–	25	90	> 400	–
LDPE-Q	0.00	–122.0	–8.0 ^b	37.5	–	0.046 (1.40)	0.133 (4.02) ^b	0.25 (7.5)	–	60	230	105	–
LDPE-S	0.00	–121.5	–12.5	37.5 ^b	–	0.044 (1.22)	0.081 (2.26)	0.16 (4.4) ^b	–	60	240	–	–

^a $\tan \delta$ maximum values are not observed at the three frequencies.

^b Tentative assignment in the inflection point.

Table 4

Storage modulus values at different temperatures (at 3 Hz): those at which the distinct relaxation processes occurred, in the minimum value of E'' , at -100°C (where no relaxation mechanism is taking place) and at 80°C (after the glass transition process)

Sample	f_{VAL}	E' (MPa)				E' (MPa) (in E''_{min})	$E'_{-100^{\circ}\text{C}}$ (MPa)	$E'_{80^{\circ}\text{C}}$ (MPa)
		γ	β	α	α'			
PVAL-Q	1.00	–	6500	610	90	5300	7400	780
VAE-1-Q	0.77	–	5650	1060	–	3800	7650	500
VAE-1-S	0.77	–	5150	1240	–	3850	6900	710
VAE-2-Q	0.72	–	5250	830	–	3600	6950	330
VAE-2-S	0.72	–	4850	1380	–	3700	6300	620
VAE-3-Q	0.62	7050	4500	740	–	2700	6500	280
VAE-3-S	0.62	7750	4950	1150	–	3350	7100	600
PE-Q	0.00	3350	560	90	–	–	2600	25 ^a
PE-S	0.00	3850	920	200	–	–	3000	30 ^b

^a 62°C is the last temperature measured.

^b 75°C is the last temperature measured.

The α relaxation is also sensitive to the thermal treatment, as seen in Fig. 7. The slowly cooled from the melt copolymers present a higher crystallinity [2,23] and larger and more perfect crystallites [2,4] than those quenched. Consequently, the glass transition temperature is shifted towards higher temperatures in these slowly cooled specimens because of their higher crystallinity, their large crystallites and the major motion constraints imposed to the amorphous phase, where the relaxation process takes place. In addition,

the difference in the temperature location of the α process for S and Q samples increases as the vinyl alcohol content does (see Table 3). It has been attributed to the crystal lattice change occurring under the experimental thermal treatments imposed for obtaining the Q and S specimens. The monoclinic cells seem to cause greater restrictions in the amorphous phase than the orthorhombic ones. These mobility reductions also provoke a broadening in the relaxation times distribution and, consequently, the α relaxation process becomes broader, as it can be observed in Fig. 7. Moreover, the intensity of the α peak, considering $\tan \delta$ values, increases in the rapidly cooled samples, Q, due to its major content in amorphous phase.

The modulus drop between the glass and the rubbery states ranges from two to three decades. This remarkable reduction of modulus is due to the initiation of micro Brownian motions of the molecular chains from the frozen state when increasing temperature. Thus the storage modulus decreases rapidly, and the loss modulus and $\tan \delta$ exhibit maxima at the glass transition temperature depending on structure and flexibility of the molecular chain.

Table 4 shows an anomaly from the theoretical expectations in VAE1 and VAE2 at the lowest temperatures. Thermal treatment and composition are not the two exclusive factors determining the storage modulus behavior. Quenched specimens display higher storage moduli than slowly cooled VAE1 and VAE2. This feature points out as responsible for the change in crystalline lattice with thermal treatment, being tougher the quenched copolymers at such low temperatures. Related to copolymer composition is the fact that VAE3-S (which presents an orthorhombic crystal cell, see Fig. 2) exhibits a higher value at -100°C than VAE1 and VAE2 (crystallizing both of them in a monoclinic system), as depicted in Fig. 4. Nevertheless, the expected tendency is shown as no polymorphism occurs. Therefore, storage modulus is higher in VAE3-S than in VAE3-Q, as observed in Fig. 7. Composition has been found to be an important parameter in the three quenched

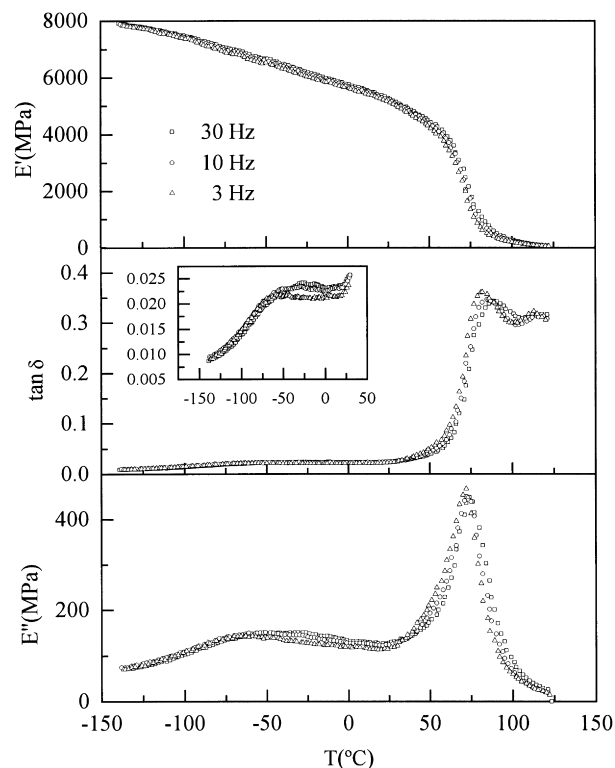


Fig. 4. Temperature dependence of the complex modulus and loss tangent of poly(vinyl alcohol) (PVAL-Q) at the three different frequencies. Q stands for “fast cooling”.

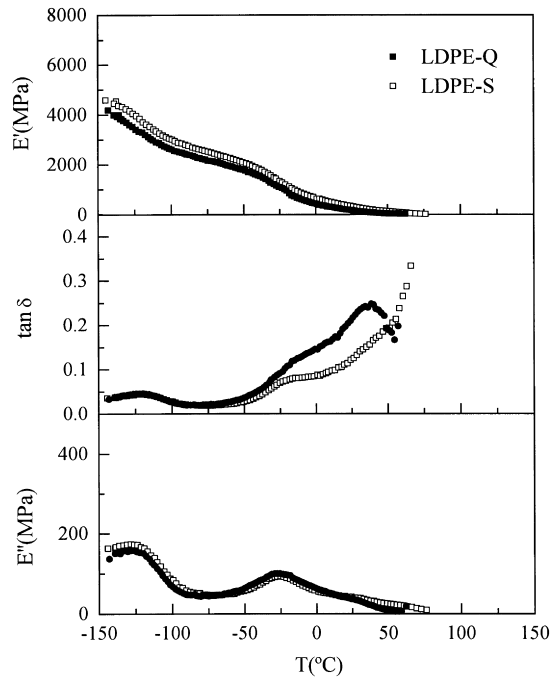


Fig. 5. Temperature dependence of the complex modulus and loss tangent of low-density polyethylene LDPE, for the two thermal treatments, Q and S, fast and slow cooling, respectively.

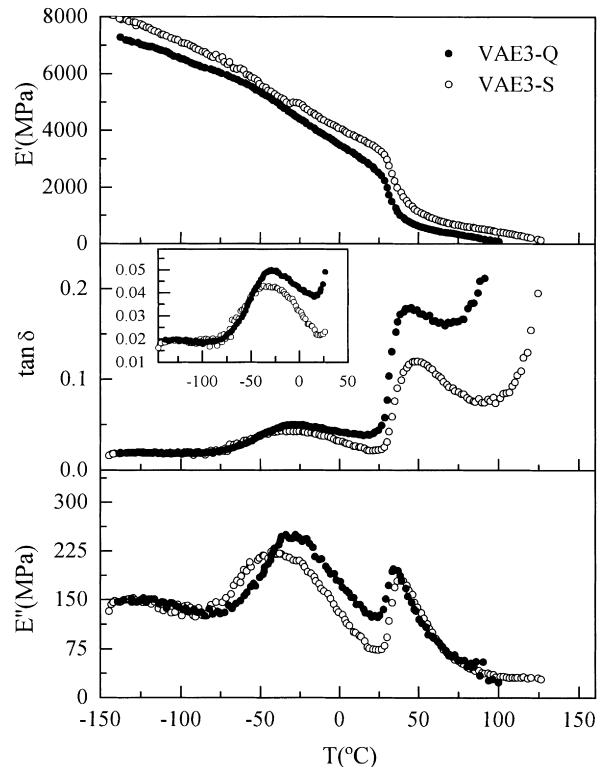


Fig. 7. Temperature dependence of the complex modulus and loss tangent of vinyl alcohol-ethylene (VAE3) copolymer for the two thermal treatments, Q and S, fast and slow cooling, respectively.

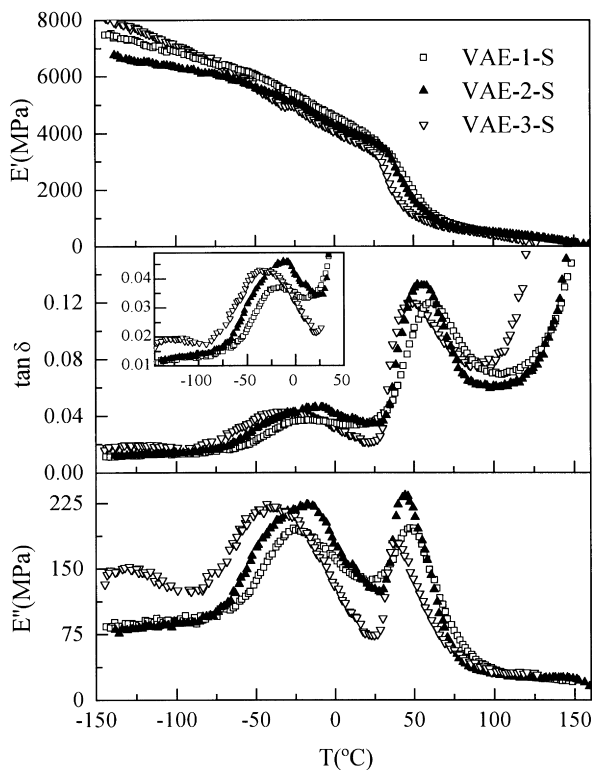


Fig. 6. Temperature dependence of the complex modulus and loss tangent of the three vinyl alcohol-ethylene copolymers (VAE1-S, VAE2-S, VAE3-S). S stands for “slow cooling”.

VAE copolymers (all of them crystallize in an orthorhombic lattice as seen in Fig. 3), and consequently, storage modulus value increases as the vinyl alcohol content increases. At higher temperatures, as mobility is larger, the storage moduli exhibit the expected behavior. E' increases as vinyl alcohol content does and, in addition, its value raises in specimens slowly cooled.

3.4. α' relaxation

The relaxation at the highest temperature is only observed in PVAL. It has been assigned to motions within the crystalline phase being caused either by the relaxation of hydrogen bonds between the hydroxylic groups in this phase [24,25] or to movements close to the crystal lamellae surface [26]. When studying the copolymers after the glass transition, $\tan \delta$ values start to increase but no other relaxation takes places under these particular experimental conditions.

4. Conclusions

Two relaxation mechanisms have been found in the three VAE copolymers investigated: β and α in increasing order of temperatures. The former relaxation is attributed to motions in the interfacial phase while the latter is associated to the glass transition process of such copolymers. An additional relaxation at very low temperature (around

–125°C) is observed in VAE3, the copolymer with the highest ethylene content. This process is only occurring in VAE3 because sequences of, at least, three methylenic units in the amorphous region are more probable in this copolymer.

The α process is dependent upon composition and thermal treatment. The α relaxation is shifted to higher temperatures as vinyl alcohol content increases in the copolymer because this is the taut comonomer unit. Temperature at which the maximum is located is higher in a slowly cooled than in a quenched specimen, for a particular copolymer, because of a major constraint on the amorphous phase since a larger crystallinity and crystal size is found in such specimens. A higher temperature difference has been observed between S and Q specimens in VAE1 and VAE2 than in VAE3, being attributed to the polymorphism exhibited in the two first copolymers with the thermal treatment. The intensity of the α relaxation is also influenced by thermal treatment. The slowly cooled specimens present a lower intensity since this mechanism, associated to the amorphous phase, is larger in Q than in S specimens. Some anomalies found in storage modulus values at the lowest temperatures are also attributed to the polymorphism exhibited in these VAE copolymers.

Acknowledgements

The financial support of the CAM and the CICYT (Projects 07N/0051/1998 and MAT98-0961-C02-01) is gratefully acknowledged.

References

- [1] Djezzar K, Penel L, Lefebvre J-M, Séguelá R, Germain Y. Tensile drawing of ethylene/vinyl alcohol copolymers. Part I. Influence of draw temperature on the mechanical behaviour. *Polymer* 1998;39(17):3945–53.
- [2] Cerrada ML, Pérez E, Pereña JM, Benavente R. Wide angle X-ray diffraction study of the phase behavior of vinyl alcohol–ethylene copolymers. *Macromolecules* 1998;31(8):2559–64.
- [3] Cerrada ML. PhD thesis. Mechanical properties, viscoelastic behavior and anisotropy of vinyl alcohol–ethylene copolymers. Universidad Complutense, Madrid, 1995.
- [4] Fonseca C, Pereña JM, Benavente R, Cerrada ML, Bello A, Pérez E. Microhardness and thermal study of the annealing effects in vinyl alcohol–ethylene copolymers. *Polymer* 1995;36(9):1887–92.
- [5] Nakamae K, Kameyama M, Matsumoto T. Elastic moduli of the crystalline regions in the direction perpendicular to the chain axis of ethylene–vinyl alcohol copolymers. *Polym Engng Sci* 1979;19(8):572–8.
- [6] Cerrada ML, Benavente R, Pereña JM, Pérez E, Bello A. Dynamic mechanical behavior of vinyl alcohol–ethylene copolymers. In: Conde A, Conde CF, Millan M, editors. *Trends in non-crystalline solids*, Singapore: World Scientific, 1992. p. 321–4.
- [7] McCrum NG, Read BE, Williams G. *An elastic and dielectric effects in solid polymers*. New York: Dover, 1991. chap. 10.
- [8] Arridge RGC. The low temperature (γ)-relaxation in polyethylene. *Rev Deform Behav Mater* 1981;3:249–97.
- [9] Boyd RH. Relaxation processes in crystalline polymers: molecular interpretation—a review. *Polymer* 1985;26:1123–33.
- [10] Shatzki TF. Glass transition in ethylene copolymers and vinyl homopolymers and copolymers. *J Polym Sci* 1962;57:496.
- [11] Boyer RF. The relation of transition temperatures to chemical structure in high polymers. *Rubber Chem Technol* 1963;36(5):1303–421.
- [12] Boyd RH, Breitling RS. The conformational analysis of crankshaft motions in polyethylene. *Macromolecules* 1974;7(6):855–62.
- [13] Boyd RH. The energetics of kinks in polyethylene. *J Polym Sci: Polym Phys* 1975;13:2345–55.
- [14] Benavente R, Pereña JM, Pérez E, Bello A. Relaxation processes in thermotropic polydibenzoates with oxyethylene spacers in the main chain. *Polymer* 1993;34(11):2344–7.
- [15] Benavente R, Pereña JM, Pérez E, Bello A. Influence of annealing on the thermal and viscoelastic behavior of poly(triethylene glycol *p,p'*-dibenzoate). *Polymer* 1994;35(17):3686–90.
- [16] Heaton NJ, Benavente R, Pérez E, Bello A, Pereña JM. The γ relaxation in polymers containing ether linkages: conformational dynamics in the amorphous phases for a series of polybibenzoates containing oxyethylene spacers. *Polymer* 1996;37(17):3791–8.
- [17] Illers KH. Dynamic-mechanical behaviour and chemical transformations of polymer systems. *Eur Polym J* 1969;Suppl.:133–47.
- [18] Macknight WJ, Tetreault RJ. Dynamic mechanical behavior of partially hydrolyzed ethylene–vinyl acetate copolymers. *J Polym Sci Part C* 1971;35:117–27.
- [19] Fujiki T, Saito M, Uenura M, Kosaka Y. On the secondary dispersion due to motion of chain branches in ethylene polymers. *J Polym Sci A2* 1970;8(1):153–9.
- [20] Popli R, Mandelkern L. The transition in ethylene copolymers—the beta transition. *Polym Bull* 1983;9(6/7):260–7.
- [21] Popli R, Glotin M, Mandelkern L, Benson RS. Dynamic mechanical studies of alpha-relaxations and beta-relaxations of polyethylenes. *J Polym Sci: Polym Phys Ed* 1984;22(3):407–48.
- [22] Ward IM. *Mechanical properties of solids polymers*. Chichester: Wiley, 1985. chap. 8.
- [23] Pérez E, Cerrada ML, VanderHart DL. Rapid determination of comonomer content, crystallinity and long spacing by multiple-pulse proton NMR in ethylene–vinyl alcohol copolymers. *J Polym Sci: Polym Phys* 1998;36(12):2103–9.
- [24] Nagura M, Matsuzawa S, Yamaura K, Ishikawa H. Tacticity dependence of molecular motion in crystal of poly(vinyl alcohol). *Polym J* 1982;14(1):69–72.
- [25] Garrett PD, Grubb DT. Effect of drawing on the α relaxation of poly(vinyl alcohol). *J Polym Sci: Polym Phys Ed* 1988;26(12):2509–23.
- [26] Hong PO, Myasaka K. Drawing of poly(vinyl alcohol) gel films. *Polymer* 1991;32(17):3140–6.