

Dynamic–Mechanical Properties of Modified Poly(ethylene-co-vinyl Acetate)

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ABSTRACT: To study the relationship among relaxation peaks observed in dynamic mechanical experiments and the structure of poly(ethylene-co-vinyl acetate) (EVA), EVA copolymers with different substitution in the carbonyl group were synthesized. EVA was hydrolyzed to obtain poly(ethylene-co-vinyl alcohol) and was subsequently reacted with formic, hexanoic, and octanoic acids. The copolymers synthesized were characterized by infrared spectroscopy. Analysis of the DMA spectra of the copolymers showed that their

relaxation behavior depends on the vinyl acetate concentration. The α - and β -transitions were observed in EVA copolymers with 8 and 18 wt % of functional groups, and the relationship among relaxation process with the structure of polymer was investigated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1371–1376, 2005

Key words: DMA; EVA; EVAL; relaxation process

INTRODUCTION

Semicrystalline polymers such as ethylene/vinyl acetate copolymers (EVA) have a complex morphological structure that depends on the amount of side branches and on the way they are distributed along the polymeric chain. A three-phase model extensively used to describe the morphological structure of semicrystalline polymers comprises a crystalline phase, an interfacial region, and an amorphous phase.¹ In EVA copolymers, the vinyl acetate groups are not included in the crystals and their melting temperatures do not depend directly on their composition but depend on the sequence distribution of monomer units along the polymeric chain.² Therefore, the amount of vinyl acetate groups in the copolymer alters the relative composition of the amorphous and interfacial regions.

Although the influence of the polymer structure and composition on the dynamic mechanical properties of ethylene copolymers has been the subject of many studies,^{3–10} some aspects regarding the relation between the segmental motions and the specific relaxation observed are still neither well defined nor under general agreement.

Similar to other ethylene copolymers, EVA exhibits three main relaxations called α -, β -, and γ -transitions

in order of decreasing temperature.^{6,9} The α -transition is related to the motions of chain units within the crystals and their surrounding areas, and its intensity decreases with the decrease of polymer crystallinity.^{6,10–12} Although α -transition requires the presence of a crystalline phase to occur, according to the literature, both the amorphous and the crystalline phases contribute to the α -relaxation process.^{12–14} The α -transition temperature depends mainly on the crystallite thickness and on the method of crystallization and recrystallization.

The β -transition is controversially discussed in the literature. Some authors attribute β -transition to the segmental chain motions that occur within the crystal–amorphous interfacial region,^{6,7,15} while others associate it to the glass transition.^{10,14,16} An increment in the number of side chain branches increases the β -transition intensity. The temperature of β -transition depends on the chemical nature and concentration of the unit.¹

The γ -transition is attributed to a restricted motion of disordered chain segments in amorphous and crystalline polymers, which requires at least three methylenic units in succession^{9,10,17} and can be modeled in terms of crankshaft mechanism.

Because of their interesting structures with flexible ester side groups, vinyl acetate polymers as well as methyl acrylate polymers have been used as models to study the subglass relaxation processes associated with flexible side-group motions in polymers through dielectric experiments.^{18,19} Thermal dynamic mechanical experiments have also been used to study the

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phase transitions of vinyl acetate homopolymers and copolymers and to evaluate the compatibility of their blends with other polymers.^{20–24} The thermal dynamic mechanical behavior of EVA copolymers in comparison with other ethylene copolymers, mainly ethylene/ α -olefin copolymers, has been analyzed by some authors.^{6,25}

Yamaki et al.²⁶ have studied the phase transitions and relaxation processes of several random EVA copolymers and their respective homopolymers (low-density polyethylene, LDPE, and poly(vinyl acetate)) by fluorescence spectroscopy. The phase transition temperatures were assigned to the following:

(a) T_g : 27 to 37°C—glass transition of poly(vinyl acetate);

(b) T_{α} : -3 to 27°C— α -relaxation processes of the ethylene units present in LDPE and EVA;

(c) T_g : -53 to -23°C—glass transition of the LDPE and EVA;

(d) T_{γ} or T_{β} : -113 to -83°C—relaxation process of interfacial defects of methylenic chains of LDPE and rotation of the acetate group of the poly(vinyl acetate) and EVA;

(e) T_{γ} : -183 to -143°C—relaxation processes of small sequences of methylene units in LDPE and end groups of poly(vinyl acetate).

The major difficulty in defining the dependence of the EVA relaxations on the vinyl acetate content seems to be related to knowledge of the relative compositions of the amorphous phase and of the interface between the crystalline and amorphous phases. It is not clear whether the relaxation processes and the temperature shown by Yamaki et al.²⁶ are amorphous or crystalline contribution.

In the present work, a series of copolymers (EVA, EVF, EVH, EVO, and EVAL) with different cunit types and two cunit contents (8 and 18 wt %) were studied by DMA to evaluate the influence of the cunit type and content on the relaxation processes.

EXPERIMENTAL

EVA copolymers with 8 and 18 mol % of vinyl acetate (EVA-8 and EVA-18, respectively) were supplied by Petroquímica Triunfo SA. The copolymers were hydrolyzed to obtain ethylene/vinyl alcohol copolymers (EVAL), with 8 mol % (EVAL-8) and 18 mol % (EVAL-18) of vinyl alcohol as described in previous works.¹¹ The poly(ethylene-*co*-vinyl formic) (EVF), poly(ethylene-*co*-vinyl hexanoic) (EVH), and poly(ethylene-*co*-vinyl octanoic) (EVO) copolymers, with 8 and 18 mol % of counits, were obtained through the esterification of EVAL-8 and EVAL-18 with formic, hexanoic, and octanoic acids in toluene and extraction of water during 48 h. The reaction was carried out in nitrogen atmosphere, and the polymers were purified through precipitation in ethanol. The esterification reaction

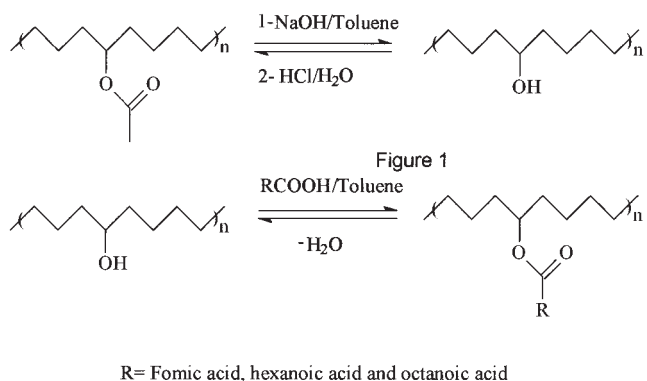


Figure 1 Scheme of the copolymers synthesis (PVF, PVH, and PVO).

was followed by infrared spectrometry. Figure 1 shows the schematic reaction of the copolymer synthesis.

Differential scanning calorimetry (DSC) measurements were performed by a Polymer Laboratories DSC instrument under nitrogen. The samples were heated from 0 to 180°C, cooled down to 0°C at a cooling rate of 10°C/min, and subsequently heated to 180°C. The melting temperature (T_m) and the heat of fusion (ΔH_f) values were taken from the second heating curve.

For the DMA measurements, the samples were melt pressed at 180°C to obtain thin films and were allowed to cool at room temperature. Rectangular films averaging 5 mm wide, 12 mm long, and 0.2–0.3 mm thick were used. The dynamic-mechanical experiments were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer MK II Instrument in the tensile mode. The measurements were carried out at 1 Hz. The temperature ranged from -125°C to next to the melting point of each copolymer (100°C, depending on the sample used), and the heating rate used was 2°C/min.

Some samples were submitted to a thermal treatment before being analyzed in the DMA equipment. The samples were melt pressed at 180°C to obtain thin films and allowed to cool in liquid nitrogen for 15 min. Rectangular films averaging 5 mm wide, 12 mm long, and 0.2–0.3 mm thick were used.

RESULTS AND DISCUSSION

Figure 2a and b shows the loss tangent ($\tan \delta$) versus temperature curves for EVA-8/EVAL-8 and EVA-18/EVAL-18, respectively. The EVA-8 presents the α -transition with the maximum at 68°C and the β -transition as a shoulder at -10°C. After the hydrolysis of the acetate group (EVAL-8), the α -peak maximum changed to a higher temperature (80°C) and the β -peak decreased in intensity.

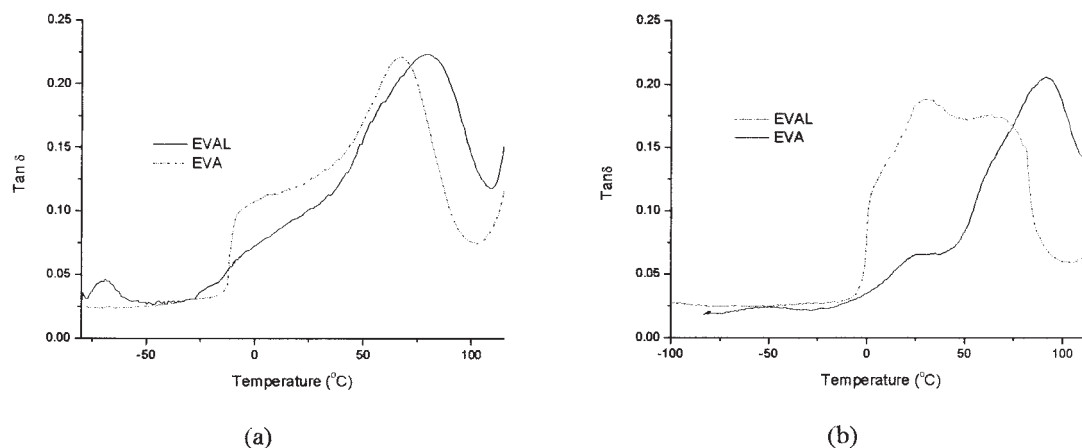


Figure 2 Tan δ versus temperature curves of EVA-8 and EVAL-8 (a) and EVA-18 and EVAL-18 (b).

The same behavior is observed with EVA-18/EVAL-18. The β -transition is much more intense than for the EVA-8, indicating that the acetate group has a high contribution to this transition. When the acetate group is changed to “-OH” the β -peak decreases considerably. The residual peak of both EVAL is probably due to the alkyl branch formed during the radical polymerization of ethylene.

Observing the crystallization behavior of the copolymers (Table I) it is possible to visualize the difference in structure organization of EVA-8 and EVA-18. The increase in acetate groups decreases the crystallinity and the T_m . When the EVA was hydrolyzed, the T_m of both copolymers increases and they are the same. Also, observed an increase in the heat of fusion (ΔH) is observed and this is more pronounced for the EVA-18, since the -OH may participate in the crystal structure. The format of the tan δ curve shows a displacement of the peaks to high temperature. This transition is associated with the movements of chains within the crystalline regions or in the crystal-amorphous interface and it is generally observed at temperatures 20–30°C lower than their melting temperatures.

The transition at -70 and -50°C for the EVAL-8 and EVAL-18, respectively, can be associate with hydrogen bonds of the hydroxyl groups in the main

chain. The high temperature to EVAL-18 is due to the high concentration of hydroxyl groups.

To verify the influence of acetate group in the β -transition of EVA-8 and EVA-18, a series of copolymers with different branches EVF-8/EVF-18 (formic group), EVH-8/EVH-18 (hexanoic group), and EVO-8/EVO-18 (octanoic group) was synthesized.

In Figure 3a and b, it is possible to observe the FTIR of these copolymers with 8 and 18 mol % of comonomer, respectively. The FTIR shows that the EVA was completely hydrolyzed to EVAL. The carboxylic ester group peak at 1780 cm^{-1} disappears and a hydroxyl group band appears at 3200–3700 cm^{-1} in the EVAL-8 and EVAL-18. The esterification reaction of EVAL with formic, hexanoic, and octanoic acid was complete, as observed in the FTIR with the disappearance of the hydroxyl band at 3200–3700 cm^{-1} and the appearance of the carboxylic peak at 1780 cm^{-1} .

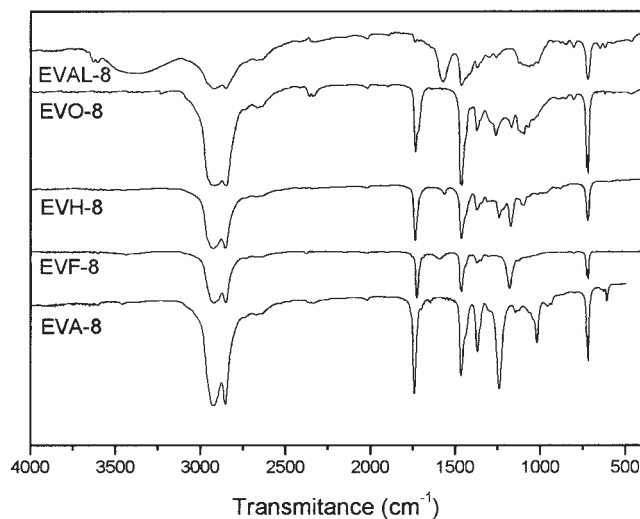
Figure 4 shows loss tangent (tan δ) versus temperature obtained for EVA-8/EVF-8, EVA-8/EVH-8, and EVA-8/EVO-8 copolymers with 8 mol % of vinyl acetate, respectively. The EVF-8 and EVO-8 show similar behavior and transitions with similar shapes and at the same temperature range. However, the EVH-8 shows a displacement of the α - and β -transition to lower temperatures.

When the acetic group in EVA-8 was substituted by the formic group (EVF-8) a small shift of the α -transition to lower temperatures ($\sim 2^\circ\text{C}$) was observed. This copolymer also shows a sharp peak at higher temperature that can be associated with the α -transition.

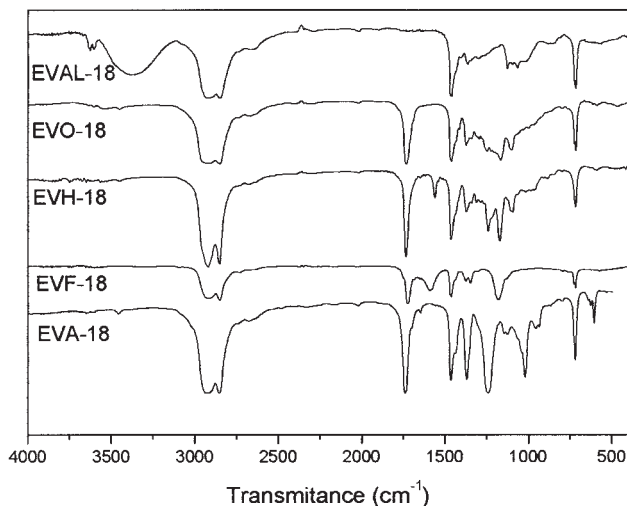
Although a significant displacement of the transition to lower temperature is observed with the change to the hexanoic group, when the acetic group is changed to the octanoic group, which is longer than the hexanoic group, the displacement to lower temperature is much smaller.

TABLE I
Determination of T_m and ΔH of Polymers by
Differential Scanning Calorimetry

Polymer	T_m (°C)		ΔH (J/g)	
	8%	18%	8%	18%
EVA	98	88	80	64
EVAL	110	110	89	110
EVF	99	87	93	69
EVH	98	81	47	50
EVO	103	82	91	47



(a)



(b)

Figure 3 FTIR of EVA-8, EVF-8, EVH-8, and EVOc-8 (a) and EVA-18, EVF-18, EVH-18, and EVOc-18 (b).

The displacement toward lower temperature indicates an increase in the molecular (or chain) mobility due to a plastificant effect of the branch and the differences in behavior presented by EVOc-8 and EVH-8 may be attributed to differences in mobility and crystallinity along the polymeric chain. The crystallinity of the EVOc-8 copolymer is higher than of the EVH-8 as shown in Table I. Also, since the octanoic group is longer than the hexanoic, interchain interactions may occur, restricting the movements and, by consequence, contributing to the increase in temperature.

In all three cases, the copolymers show transitions with similar shapes and there is evidence of the development of a new peak at higher temperature (above 90°C), probably due to a small population of more organized crystalline structure.

Figure 5 shows loss tangent ($\tan \delta$) versus temperature for EVA-18/EVF-18, EVA-18/EVH-18, and

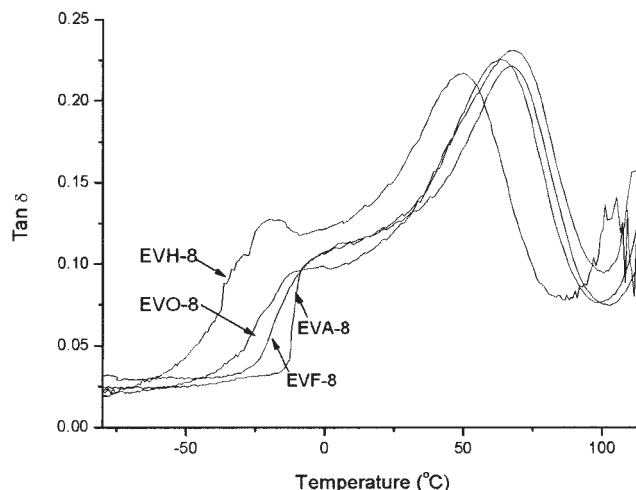


Figure 4 $\tan \delta$ versus temperature curves of EVA-8, EVF-8, EVH-8, and EVOc-8.

EVA-18/EVO-18 with 18 mol % of vinyl acetate, respectively. Comparing these curves with the ones obtained for the copolymers with 8 mol % of comonomer, it is possible to observe a pronounced displacement to lower temperatures. This displacement is similar to the one observed for ethylene/ α -olefin copolymers,³ where there is a decrease in the temperature of α - and β -transitions when the amount of comonomer (or branches) increases. The differences in the shape of the peaks can also be related to the fact that these copolymers have a higher content of comonomer.

Copolymers with higher branch content are more affected by the size of the branch and the α - and β -transitions have almost the same intensity. The differences in the shapes of the curves when comparing with the copolymers with 8 mol % is probably due to

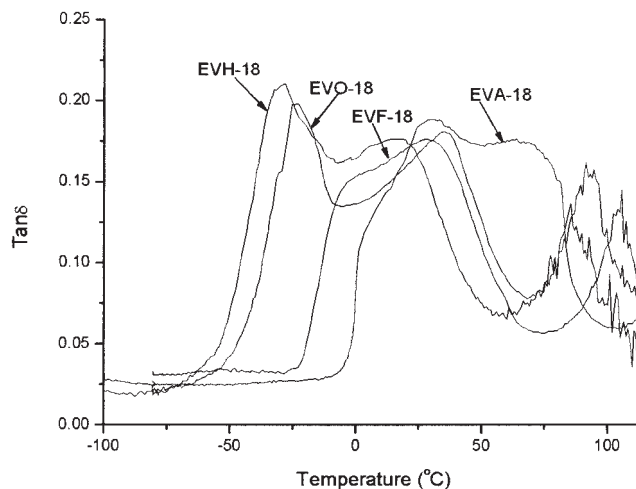


Figure 5 $\tan \delta$ versus temperature curves of EVA-18, EVF-18, EVH-18, and EVOc-18.

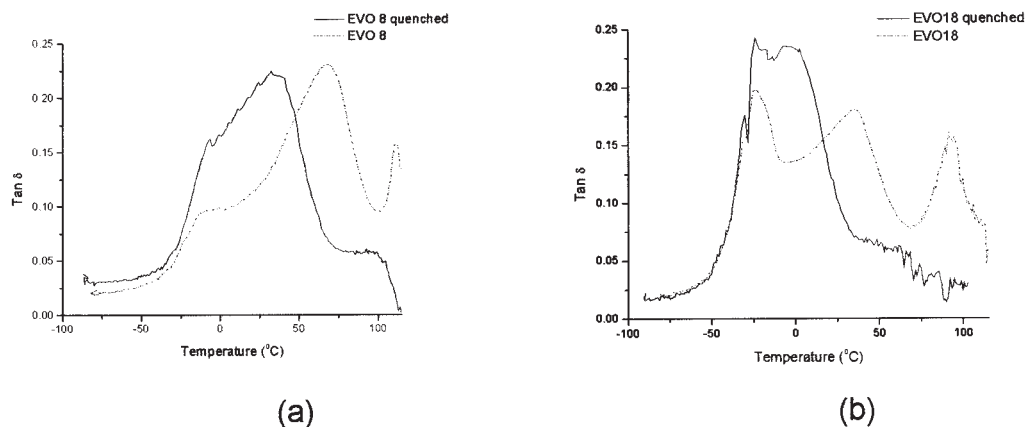


Figure 6 Tan δ versus temperature curves of EVA-8/EVOc-8 (a) and EVA-18/EVOc-18 (b).

the higher comonomer content where the groups interact with each other. Then, the intensity of the transition at low temperature may be increased because the internal movement within the side group is affected by the presence of other side groups in a close position in the polymeric chain and perhaps may interact also with the side groups of the other chains.

The EVH-18 and EVOc-18 copolymers show a very well-defined β -transition at -30°C (EVH-18) and -25°C (EVOc-18). All peaks including the α -transition were shifted to lower temperature region because of the plastificant effect of group in the polymer. The copolymer EVF-18 (T_m $93,7^{\circ}\text{C}$) had shifted to low temperature and the α - and β -transition is not well separated due to the small size of the branch. Both EVH-18 and EVOc-18 were capable of disorganizing the crystalline structure and show the best definition to the β -transition. The T_m and the crystallinity of EVF-18 are quite similar to that of EVA-18 (Table I), but when the side group increases in size, both decrease. So, the branching or pendant group affects the β -transition since the group is not kept inside the crystal and is dependant on concentration of the vinyl acetate. The concentration of the pendant group also affects the lamellar thickness, decreasing the crystallinity.³

EVAF-18, EVAH-18, and EVAOc-18 also present a peak at higher temperature at 104, 85, and 92°C , respectively. This peak seems to be more intense than that for EVAF-8, EVAH-8, and EVAOc-8.

In fact, the behavior of the DMA spectra is related to the group introduced in the polymer chain, and this relationship is associated with the amorphous and crystalline phase of the polymer structure. In EVA-8 the peak from -25 to 95°C and in EVA-18 the peak from -25 to 95°C have contribution of both α - and β -transition. In EVA-8 the contribution of α -transition is higher than the β -transition, because the ethylene group in the main chain controls the morphology of the polymer. In the case of EVA-18 the contribution of

crystalline phase is lower than in EVA-8; then both transitions are more evident.

Simanke at al.,³ working with ethylene/ α -olefin, obtained a loss tangent (tan δ) versus temperature curves of ethylene homopolymer and copolymer with 2 mol % of 1-octadecene. The DMA spectra of this copolymer show a peak that starts from -50 to 110°C , like to the EVA-8 and EVAL-8 curve. They called this transition an α -transition, associated with the crystalline structure of polymer, which is in agreement with the results shown. When the copolymers has 4.8 mol % of 1-octadecene, the curve showed two peaks and the authors called that α and α' -transitions.

Lower temperature transition in the EVA and copolymers with 18 mol % of comonomers has a relationship with the movement of the vinyl group and with the β -transition. To confirm that the transitions observed in the EVA spectra are involved with α - and β -transitions, a sample after quenching to minimize the crystallization effect was analyzed. The samples were melt pressed at 180°C to obtain thin films and allowed to cool in nitrogen liquid for 15 min. Figure 6a and b shows the spectra of tan δ for the EVA-8/EVAOc-8 quenched and EVA-18/EVAOc-18 quenched, respectively. The contribution of the transition at higher temperature decreases with quenching of the polymer in both polymers (EVA-8 and EVA-18), indicating that this transition is associated with the crystallization behavior or the α -transition.

CONCLUSIONS

EVA-8 and the EVA-18 show two transitions in the DMA spectra; the α -transition, at high temperature, is associated with the crystalline behavior and the β -transition, at low temperature, is associated with the carboxylic branch. The β -transition is more affected by the concentration of the vinyl acetate than by the size of the pendant group, although the type of branch may cause some displacement of this peak.

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