Rheological Characterization of Ethylene Vinyl Acetate Copolymers

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ABSTRACT: A series of ethylene vinyl acetate (EVA) copolymers was studied by dynamic mechanical spectroscopy to understand the relative influence of composition, structure, and molecular weight distribution on their rheological behavior in the melt. The examination of their viscoelastic properties in a large temperature range showed that the glass transition temperature is nearly independent on their composition because of the statistical nature of the copolymers, though some long sequence of polyethylene homopolymer may exist at low vinyl acetate (VA) content. The successful use of the time temperature superposition for oscillatory experiments in the melt confirmed the previous remarks, because the application of the Williams Landel Ferry (WLF) equation leads to a unique set of WLF coefficient, whatever the composition of the EVA. This enables the comparison of the rheological behavior in the melt at the same temperature, in the same free volume condition, and at last it was shown that in the terminal zone, the molecular weight distribution is more influent on the behavior of EVA copolymers than their composition. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2625–2630, 1999

Key words: copolymers; rheological behavior

INTRODUCTION

Ethylene vinyl acetate (EVA) copolymers generally contain from 1 to 50% weight percent of vinyl acetate (VA) and consequently show different properties. Indeed, because of the similar reactivity ratios of ethylene and VA, the monomers can polymerize over a wide range of compositions. In addition, these reactivity ratios are both close to one, thus the obtained EVA copolymers are expected to be statistically random copolymers and the copolymer composition is identical to the monomer feed composition.[1,2] They are synthesized by a high pressure, high temperature, bulk polymerization process just like low density polyethylene.

In addition, these copolymers may contain branches, but the branching degree decreases with increasing VA content. This effect arises because the VA residues inhibit the formation of cyclic intermediates that are involved in the occurrence of the short branches.[3]

The purpose of this paper was to understand the relative influence of the structure, composition, and molecular weight distribution on the rheological behavior of EVA in the melt. However, to perform a reliable comparison of such materials for these properties, attention must be focused on the iso-free volume condition which defines the segmental friction factor. For this reason, a deeper study of the glass transition of the copolymers has been performed by means of dynamic mechanical spectroscopy at low temperature. In addition, this helps to understand the detailed structure of the copolymers.
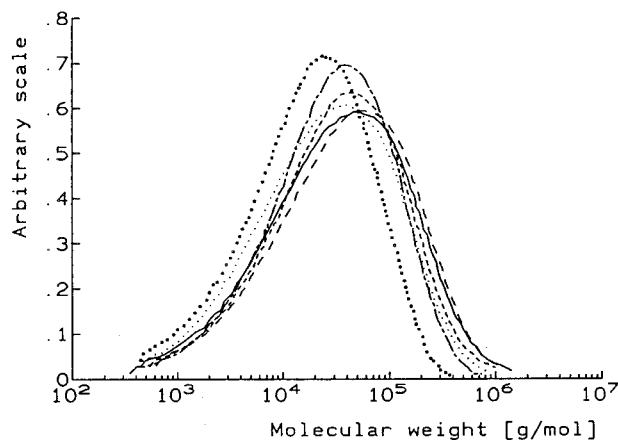
Figure 1 Molecular weight distribution for EVA copolymers (_ EVA5%, … EVA9%, - - - EVA14%, – – – EVA18%, – · – EVA28%, . . . EVA40%).

Figure 2 Thermogram for EVA copolymers (_ EVA5%, … EVA9%, - - - EVA14%, – – – EVA18%, – · – EVA28%, . . . EVA40%).

For this condition to be fulfilled, the rheological behavior in the melt should thus be considered at an iso-(T-T_g) temperature.

EXPERIMENTAL

Materials

Six samples of EVA copolymers containing from 5 to 40 weight percent of VA were studied. The behavior of these copolymers is dependent on the level of VA, the rubber-like behavior being emphasized when this level is high.

The molecular weight distribution of these materials, named EVA5%, EVA9%, EVA14%, EVA18%, EVA28%, and EVA40%, has been determined by size exclusion chromatography (SEC). Figure 1 shows the molecular weight distribution of the six samples. Values of average molecular weights and polydispersity indices are summarized in Table I.
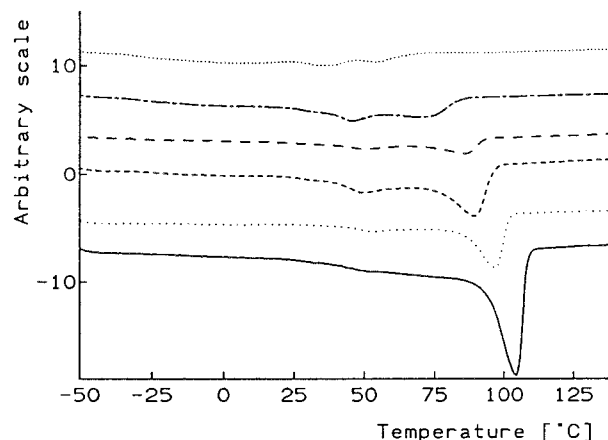
Differential scanning calorimetry analysis was performed to determine the melting point temperature and the glass transition temperature (T_g) using a Setaram 141 DSC at a rate of 10°C/min from −60°C to 140°C. To avoid any difference in the thermal history, each sample was melted and cooled before the determination of the melting point temperature and of the T_g. Figure 2 shows the thermogram of the EVA copolymers.

All the EVA copolymers display a large endothermic peak (T_{m1}) in the thermogram and a secondary endothermic peak (T_{m2}) between 38 and 50°C. Values of T_{m1} and T_{m2} are given in Table I. The temperature of the second peak corresponds to the melting point of polyvinylacetate (between 35 and 50°C) which may indicate that EVA copolymers are slightly sequenced. The form and the magnitude of these two peaks are dependent on the composition of the EVA copolymers. Increasing the ethylene content increases T_{m1} and T_{m2}.

It was impossible to obtain the glass transition by differential scanning calorimetry (DSC) anal-

Table I   Molecular Weight Distribution and Melting Points for EVA Copolymers

Reference	M_w (g/mol)	Ip	M_n (g/mol)	T_{m_1} (°C)	T_{m_2} (°C)
EVA5%	86,200	9.1	9500	104.5	50
EVA9%	60,100	7.7	7800	97	49
EVA14%	61,000	8.0	7650	90	49
EVA18%	72,600	8.7	8350	86.5	49
EVA28%	58,300	6.2	9350	73.5	45.5
EVA40%	34,800	5.2	6675	55.5	38.4

ysis, either because of a small change of heat capacity or because the crystalline phase might hide this phenomena. However, for EVA containing 40 and 28% of VA, the T_g can be estimated to be nearly −25°C. More accurate determination of the glass transition has been performed using dynamic mechanical spectroscopy at low temperature.

SAMPLE PREPARATION

The preparation of samples of EVA copolymers for use in dynamic mechanical spectroscopy at low temperature and in oscillatory shear flow in the melt has been performed by compression molding at T_{m1} + 10°C. The temperature must be kept in this range because EVA copolymers evolve acetic acid at high temperature. Indeed, Sultan and Sorvik[4−6] have already found significant acid acetic evolution at 150°C. Fast initial acid acetic release followed by a slower constant deacetylation rate was found. These authors have also shown that acid acetic evolution increases with temperature and VA content.

Dynamic Mechanical Spectroscopy Below the Melting Point

The dynamic moduli and loss factor were determined at 1 rad s^{-1} from −140°C up to the melting point for the EVA copolymers using a rectangular torsion device on a Rheometrics Dynamic Analyzer RDA 700 in nitrogen atmosphere.

Oscillatory Shear Flow in the Melt

Rheological measurements in the melt were obtained in oscillatory mode using disk and plate geometry in a Rheometrics Dynamic Spectrometer RDA 700. The storage modulus G' and loss modulus G'' were measured at different temperatures from T_{m1} − 5°C to high temperature from 0.01 to 500 rad s^{-1} after checking the linear domain.

The lowest temperature (T_{m1} − 5°C) used is just below the melting point T_{m1} of the copolymers. To perform this measurement, the sample was heated at a temperature greater than T_{m1} and then cooled to the experimental temperature hindering any rapid growth of the crystallites. Nitrogen atmosphere was used to prevent any polymer degradation.
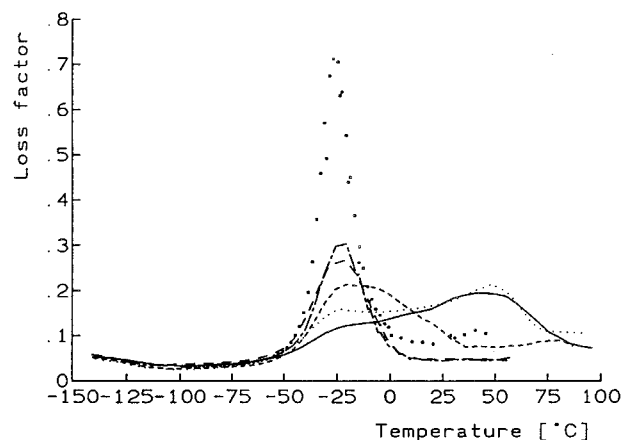

Figure 3 Loss factor for EVA copolymers (_ EVA5%, ... EVA9%, - - - EVA14%, − − − EVA18%, − · − EVA28%, . . . EVA40%).

RESULTS AND DISCUSSION

Glass Transition

The comparative curve of Figure 3 shows that the variation of the loss factor with temperature at content frequency displays one major relaxation for all the samples. The temperature of this relaxation is relatively insensitive to the level of VA in the copolymer and has a nearly constant value of −25°C at 1 rad s^{-1}. The form and the magnitude of the peak of loss factor is dependent on the VA content and increases with it. For these reasons it can be attributed to the glass transition of the VA sequences. This is in agreement with Ray and Khastgir[7] who have studied the covulcanized blends of ethylene vinyl acetate/ethlene propylene diene monomer (EVA/EPDM), with EVA containing 28% of VA. Dynamic mechanical analysis was used to determine the glass transition at −18°C.

As can be seen from Figure 3, for VA content above 14%, the loss factor exhibits the beginning of a weak additional relaxation at very low temperature. The increase of the damping at −135°C might be attributed to the movement of methylene groups in a crankshaft mechanism for a few monomeric units of ethylene. Unfortunately, because of the very local motion of these groups, the temperature of this relaxation is too low for the whole relaxation to be observed.

For low VA content (EVA9% and EVA5%), one more maximum can be observed at 45°C; this type of absorption process is often attributed to the branching points in polyethylene (PE). It should be noted that a maximum in this range of tem-
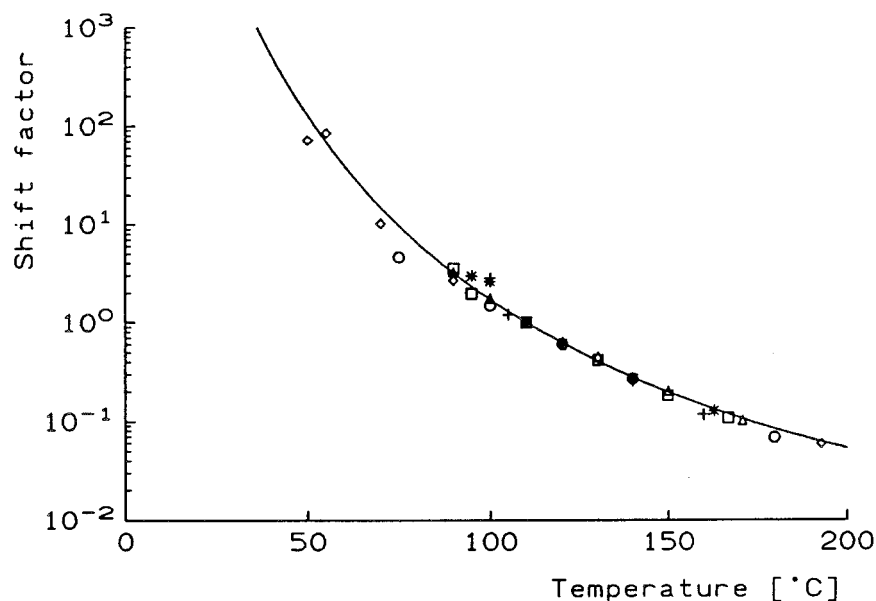
Figure 4 Shift factors for EVA copolymers (+ EVA5%, * EVA9%, □ EVA14%, ▷ EVA18%, ○ EVA28%, ◇ EVA40%).

peratures is also observed for EVA40%. However, in this particular case no firm conclusion can be drawn because of the low value of the melting point (55.5°C; see Table I).

The difference of behavior between these two EVA and the others that do not display such a relaxation can be explained by the fact that at high VA level, the number of long chains of polyethylene is low and there are few homosequences so that the probability of branching is low. On the opposite, when the VA content is low, longer chains of polyethylene may exist together with a high probability of branching point. In addition, these copolymers should be slightly sequenced in this case. The pure statistical random copolymers show only one glass transition whose value lies between those of the homopolymer polyvinyl acetate (PVA) and PE. The peak is broad because of the variety of random structure that are generated at low VA content.

The experimental constant value −25°C of the glass transition obtained does not agree with any prediction of the classical equations for the glass transition of the copolymers.

Shift Factors and Time Temperature Superposition

Measurements in dynamic oscillatory shear flow in the melt were performed at different temperatures ranging from $T_{m1} - 5$°C to high temperature.

The determination of shift factors has been made to obtain master curves at 110°C. As can be seen from Figure 4, the plot of the shift factors vs. temperature gives a single curve regardless of the composition of the VA copolymers.[8]

This enables the determination of the WLF parameters at 110°C, $C_1^{110°C} = 3.54$ and $C_2^{110°C} = 160.8$°C.

Because the T_g and WLF shift factors of the various copolymers remain the same whatever their composition is, it is relevant to compare the rheological behavior in the melt of the sample at the same temperature that may be a sufficient condition to obtain the iso-free volume condition which is necessary to understand the influence of the various structural parameters.

Flow Curves and Newtonian Viscosity

Figure 5 shows the plots of the complex viscosity η^* vs. the frequency ω for the samples at 110°C in the molten state. Quite similar evolution of the complex dynamic viscosity is observed for EVA9%, EVA14%, and EVA28%, although the Newtonian viscosity is slightly higher for EVA9%. Despite the fact that their compositions are different, these three EVA have nearly the same molecular weight distribution and this factor seems to be more important than the chemical composition of the copolymers. For EVA18%, the value of the Newtonian viscosity is higher due to
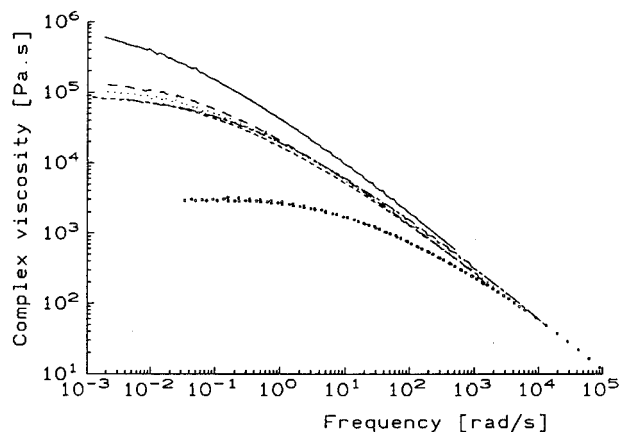
Figure 5 Complex dynamic viscosity for EVA copolymers (_ EVA5%, … EVA9%, - - - EVA14%, – – – EVA18%, – · – EVA28%, . . . EVA40%).

Figure 6 Storage modulus for EVA copolymers (_ EVA5%, … EVA9%, - - - EVA14%, – – – EVA18%, – · – EVA28%, . . . EVA40%).

a higher molecular weight. On the opposite, because of its low molecular weight, EVA40% shows a completely different behavior—a large plateau of the Newtonian viscosity and a lower value of η_o is noticed. For EVA5%, the Newtonian viscosity could hardly be obtained in the available frequency domain but due to the large molecular weight, its value is much higher. The Newtonian viscosities η_o at 110°C are given in Table II.

Gupta et al.[9] have also studied the properties of molten PP/EVA blends and measured the variation of the melt viscosity as a function of shear stress at constant EVA content with varying VA% of EVA (9, 12, and 19%). They attributed the difference of behavior to a difference of origin or to a difference of molecular weights rather than to a variation of VA content in EVA,[9] in agreement with our results.

The scaling law for variation of the Newtonian viscosity η_o as a function the molecular weight M_w gives a good correlation coefficient, but the value (5.63) of the scaling exponent is high.

This value could be due to broadness of the molecular weight distribution[10,11] but it is also known that for low density polyethylenes, high exponent have been reported.[12] Kraus and Gruver[13] have also noted that high slope is obtained when the branch length is above the critical length for entanglement in polybutadienes.

Kraus and Gruver[13] have suggested that entanglements of the branches may contribute to a much more rapid increase in η_o than what is experienced with unbranched polymers or with branched polymers wherein the branch length is lower than the critical value for entanglement. Following these authors, one can expect that the long branches of low density polyethylenes contained in EVA copolymers, especially at low VA content (EVA5%), are above the critical molecular weight for entanglement and may increase the scaling law exponent. This could also explain the slight difference of EVA9% compared with EVA14% and EVA28%, which has been shown previously to be slightly sequenced and contains points some branch points.

Plateau Modulus

The plateau modulus has been determined thought the highest value of the storage modulus G' (Table II). Alternatively, some authors[14–18] propose the value of the storage modulus G' at the minimum of the loss factor tan δ in the plateau zone as a simple way to estimate G_N°. In the present case, the minimum of tan δ corresponds to the greatest value of G'.

However, as can be seen on Figure 6, the pla-

Table II   Newtonian Limit Viscosity and Plateau Modulus for EVA Copolymers

Reference	η_o (Pa · s)	G_N° (Pa)
EVA5%	6.20 10^5	2.69 10^5
EVA9%	1.02 10^5	3.14 10^5
EVA14%	8.79 10^4	2.53 10^5
EVA18%	1.29 10^5	2.64 10^5
EVA28%	7.56 10^4	5.81 10^5
EVA40%	3.03 10^3	10.18 10^5

teau modulus is difficult to obtain, especially because of the broadness of the molecular weight distribution of the samples.

At high frequency, a single curve is obtained whatever the molecular weight distribution and the composition of the sample. It is well known that the molecular weight does not have any influence on the plateau modulus, but in the present case, the independence of the plateau modulus with the VA content confirms the previous results.

CONCLUSION

The viscoelastic behavior in the melt of EVA copolymers was obtained by dynamic mechanical spectroscopy to investigate the influence of the VA content. However, for comparison purposes it was necessary to estimate the influence of the VA content on the free volume. This implies the determination of the T_g, which unfortunately was not visible on DSC thermograms. Mechanical spectroscopy below and just above was found to be suitable for this purpose and has shown that the T_g is independent of the VA content of the copolymer which is nearly a random copolymer of VA and ethylene. However, for very low VA content, some long branched PE sequences might exist as indicated by the existence of a secondary relaxation at 45°C.

Time temperature superposition has shown that a single set of WLF parameters can be found independently of the VA content.

These two conclusions indicate that the samples can be compared in the molten state at the same temperature without difference in the free volume.

The comparison of the flow curves has shown that the molecular weight distribution together with branching remain the major parameter that influences the rheological behavior in the molten state and that the chemical composition has only a secondary effect.

Moreover, the value of the plateau modulus remains the same for all samples independently of the molecular weight distribution (MWD) or VA content. The scaling law for the newtonian viscosity displays a large exponent which is probably due to the broad distribution of the sample but also to the occurrence of long branches in the PE sequences for low VA contents.

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