Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 681–685

DETERMINATION OF PRIMARY RELAXATION TEMPERATURES AND MELTING POINTS OF ETHYLENE VINYL ACETATE COPOLYMERS

A. Arsac, C. Carrot and J. Guillet

Laboratoire de Rhéologie des Matières Plastiques, Faculté des Sciences et Techniques, Université Jean Monnet, 23, Rue du Docteur Paul Michelon, 42023 Saint-Etienne Cédex 2, France

(Received September 23, 1999)

Abstract

The relationship between copolymer composition and transition temperatures was studied by means of differential scanning calorimetric analysis and dynamic mechanical spectroscopy. Six samples of ethylene vinyl acetate (EVA) copolymers containing from 5 to 40 mass per cent of vinyl acetate (VA) were studied. The differential scanning calorimetric analysis revealed that each EVA copolymer displays two endothermic peaks (T_{m1} and T_{m2}) in the melting zone. Dynamic mechanical spectroscopy was used to determine the primary relaxation temperature (T_α) for EVA copolymers This latter characteristic is relatively insensitive to the level of vinyl acetate contained in the copolymer and is influenced by the pulsation frequency ω, also named the angular frequency.

Keywords: dynamic mechanical spectroscopy, EVA copolymers, primary relaxation temperatures

Introduction

The properties and applications of ethylene vinyl acetate (EVA) copolymers are influenced by their composition. The rubber-like behaviour is emphasized when the level of vinyl acetate (VA) is high. The reactivity ratios of ethylene and VA are both close to one, and thus the copolymers obtained are theoretically statistically random copolymers and their composition is identical to the monomer feed composition [1, 2]. The aim of this work was to investigate the influence of the composition of the EVA copolymers on the melting point and glass transition temperatures, T_m and T_g.

Experimental

EVA copolymers with six different percentage compositions were studied: 5, 9, 14, 18, 28 and 40% VA. Differential scanning calorimetric (DSC) analysis was performed in order to determine T_m and T_g, using a Setaram 141 DSC at a heating rate of 10°C min^{-1} from –110 to 140°C in a nitrogen atmosphere. Each sample was melted

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

and cooled at a cooling rate of 10 min^{-1} before the experimental determination of T_m and T_g, in order to avoid any difference in the thermal history. It was difficult to obtain T_g by DSC analysis. The primary relaxation temperature T_α was measured by use of a Rheometrics Dynamic Analyzer RDA 700. This latter characteristic is in the same temperature range as T_g.

The experiments were performed in nitrogen atmosphere from –140°C to T_m at a heating rate of 5°X min^{-1} for each copolymer at different pulsation frequencies (1, 10, 50, 100 and 500 s^{-1}) in order to establish whether the angular frequency influences the value of T_α. T_α was determined via the maximum in the loss factor tanδ. Samples of EVA copolymers subjected to dynamic mechanical spectroscopy were prepared by compression molding at T_{m_1}+10°C, and had a rectangular shape (length 45 mm, width 10 mm, thickness 2 mm). The temperature was chosen to be low in order to avoid the evolution of acetic acid from the copolymers [3–5].

Results and discussion

Melting point

EVA copolymers are theoretically random copolymers, and thus their T_m should be single and usually fall between those of the corresponding homopolymers [6] (melting point for low-density polyethylene: 110–120°C; softening temperature for poly(vinyl acetate): 35–50°C). In our case, Fig. 1 shows that samples of EVA present two peaks: a large (T_{m_1}) and a secondary, small peak (T_{m_2}) The presence of these two peaks may indicate that EVA copolymers are slightly sequenced. Table 1 gives the values of T_{m_1} and T_{m_2}. T_{m_2} corresponds to the softening temperature of poly(vinyl acetate). The DSC traces in Fig. 1

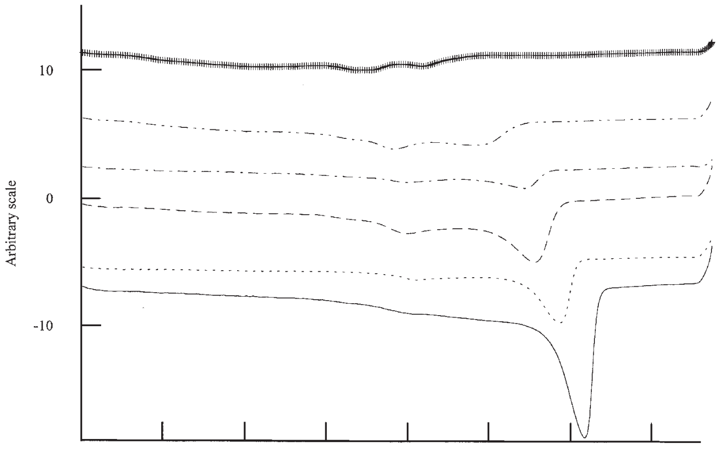

Fig. 1 DSC curves for EVA copolymers (EVA5, EVA9, EVA14, EVA18, EVA28, EVA40%)

suggest that the forms and the areas of the different peaks are functions of the level of VA: increase of the VA content decrease T_{m_1} and T_{m_2} .

Glass transition and primary relaxation temperatures

As for T_m, T_g should have a value between those of the corresponding homopolymers [7] (–110°C for low-density polyethylene; 28–31°C for poly(vinyl acetate). The DSC curves in Fig. 1 shows that for EVA containing a high level of VA (40 or 28%), T_g seems to be near –25°C.

Table 1 Melting points for EVA copolymers

Reference	T_{m_2}/°C	T_{m_1}/°C
EVA5%	104.5	50
EVA9%	97	52.7
EVA14%	90	49
EVA18%	86.5	49
EVA28%	73.5	45.5
EVA40%	55.5	38.4

Table 2 Temperature at the maximum of the loss factor tanδ for EVA copolymers

ω/rad s^{-1}	Temperature/°C					
	EVA5%	EVA9%	EVA14%	EVA18%	EVA28%	EVA40%
1	–24.9	–25	–24.8	–25	–24.9	–25.24
10	–24.1	–23.9	–24	–24	–24.1	–24
50	–22.9	–23.1	–22.9	–23	–23.1	–22.9
100	–21	–20.9	–21.1	–21	–20.9	–20.9
500	–18.7	–18.5	–18.6	–18.5	–18.5	–18.6

However, for other EVA copolymers it was impossible to obtain T_g by DSC analysis, either because of a small change in heat capacity or because the crystalline phase due to the polyethylene contained in the copolymers might hide this phenomenon. Thus, T_α was determined on a Rheometrics Dynamic Analyzer in nitrogen atmosphere. Loss factors at different pulsation frequencies (1, 10, 50, 100 and 500 rad s^{-1}) were obtained for each EVA copolymer. The maximum of the peak in each the tanδ curves increased with the angular frequency and had a value varying between –25 and –18.5°C (Table 2). As can be seen in Fig. 2 (example of EVA 18%), T_α is pulsation frequency-dependent and shifts to higher temperatures as the measurement angular frequency is increased. In addition, the width of the peak increases with the pulsation frequency.

To compare results on different EVA copolymers, therefore, the loss factor was plotted for only one angular frequency, at 1 rad s^{-1}. Figure 3 suggests that T_α is insensitive to the composition of EVA copolymers and has a nearly constant value of

–25°C at 1 rad s^{-1}. In contrast, the composition of the EVA copolymer influences the form and area of the peak of tanδ. Above a VA content of 14%, the loss factor presents an additional peak near 45°C, which can be attributed to the high level of polyethylene in these EVA copolymers. This fact confirms the remark made in connection with the study of T_m, i.e. EVA copolymers are slightly sequenced.

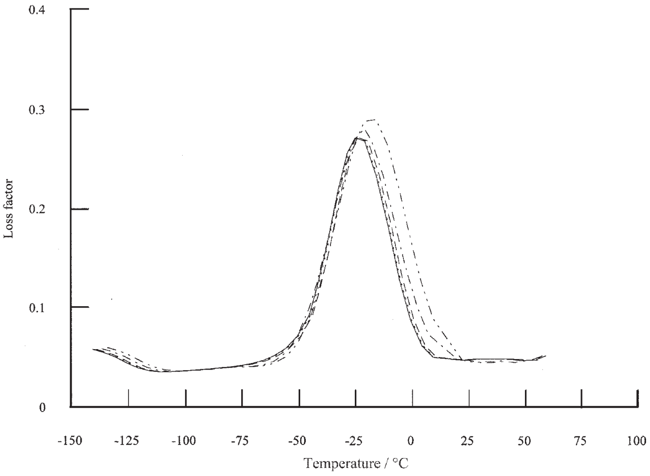

Fig. 2 Loss factors for EVA18% (1 , 10, 50, 100, 500 rad s^{-1})

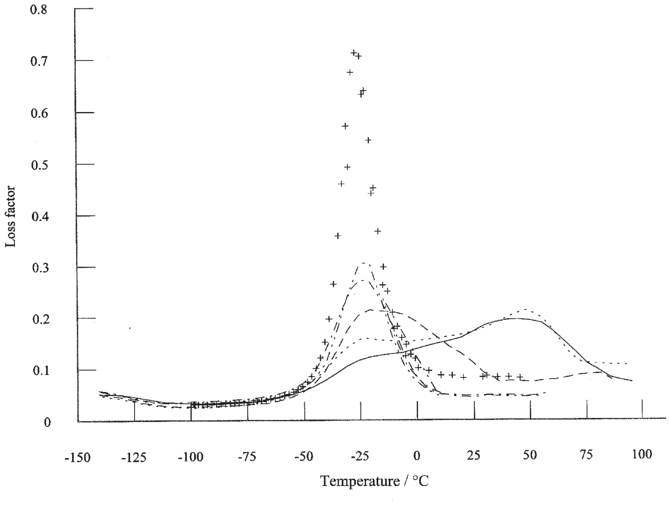

Fig. 3 Loss factors for EVA copolymers at 1 rad s^{-1} (EVA5, EVA9, EVA14, EVA18, EVA28, EVA40%)

In low-density polyethylene (LDPE), there are three transition regions [8, 9]. The intensity of the first relaxation (at low temperatures) increases with a reduction of crystallinity. Thus, this relaxation is associated with the amorphous material and has been tentatively assigned to a glass transition, near –110°C [8, 9]. The second transition is associated with relaxations at the branch-points because this transition disappears in the case of high-density polyethylene, with a value near –8°C [8, 9]. The intensity of the third relaxation decreases as the level of crystallinity is reduced, implying that it is associated with motion within the crystalline regions; the maximum of this third relaxation is near 45°C [8, 9]. The form of the evolution of tanδ for LDPE is very similar to those for EVA 5% and EVA 9%, and particularly the maximum of the second relaxation for LDPE is at the same temperature as that of the additional peak for EVA copolymers containing 14% of EVA.

Conclusions

Transition temperatures were determined by DSC analysis and by dynamic mechanical spectroscopy in order to investigate the influence of the VA content in the EVA copolymers on these characteristics. Two endothermic peaks were obtained in the melting zone for each EVA. The measured T_α was insensitive to the level of VA content, but it was influenced by the pulsation frequency. In addition, at a VA content above 14%, the loss factor presents a secondary peak near 45°C. This latter fact and the presence of two endothermic peaks in the melting zone suggest that these EVA copolymers are not random copolymers, but slightly sequenced copolymers.

References

1 J. P. Mercier and E. Maréchal, Chimie des polymères, Presses Polytechniques et Universitaires Romandes, 1993, chap. 4.
2 D. C. Eagles and A. Rudin, Plastics and Rubber Processing and Applications, 9 (1988) 163.
3 B. A. Sultan and E. Sorvik, J. Appl. Polym. Sci., 43 (1991) 1737.
4 B. A. Sultan and E. Sorvik, J. Appl. Polym. Sci., 43 (1991) 1747.
5 B. A. Sultan and E. Sorvik, J. Appl. Polym. Sci., 43 (1991) 1761.
6 C. Motta, J. Thermal Anal., 49 (1997) 461.
7 J. A. Brydson, Plastics Materials, 5th ed. Butterworth-Heinemann, Munich 1989.
8 R. J. Young, Introduction to polymers, Chapman and Hall, New York 1986.
9 L. E. Nielsen, Mechanical properties of polymers and composites, Dekker, New York 1974.