Property of Ethylene Vinyl Acetate Copolymer in Melting Processing

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ABSTRACT: The study is focused on the processing behavior of poly(ethylene-*co* vinyl acetate) (EVA) in high temperature, such as 200°C. The specimens are characterized using HAAKE minilab, dynamic mechanical analysis (DMA), and positron annihilation lifetime spectroscopy (PALS) to understand the rheological behavior and microstructure of EVA. It was concluded that in high processing temperature, the viscosity declined first and then increased. The PALS results showed that the free volume of EVA became large at the beginning, and became small afterwards. The glass transition temperature measured with DMA got lower at first and then nearly unchanged with increasing handling time. The results can be explained that the degradation of EVA prevailed, and then degradation was not dominant. A good correlation has been found between the processing time and temperature of the transition point in the viscosity curve. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2022–2026, 2006

Key words: degradation; viscosity; processing; glass transition; rheology

INTRODUCTION

Ethylene-vinyl acetate copolymer (EVA) is widely used for many purposes, such as flexible packaging, footwear, hot melt adhesives, and electrical cable sheathing industry. Many articles have investigated the relation of the property and process of EVA.[1–3] It was found that the values of the viscosity depend not only on the processing conditions of the material. Gianelli et al.[4] found that viscosity is dependent of molecular weight due to the thermomechanical degradation during processing. Attarian et al.[2] reported that the viscosity is expressed in familiar Arrhenius form with constant activation energy, whose value depends on the chemical structure of the polymer blend. Kim et al.[5] studied the correlation between crosslinking behavior and physical properties of foams.

The processing temperature in many articles is mostly in the range of 90–160°C. To improve the properties of the materials, manufacturers usually blend EVA with other polymers, and some of them need a high processing temperature. For instance, the bitumen/EVA blends were maintained at 180°C,[6] and PA/EVA blends were prepared above 200°C.[7] However, there are few articles about the property such as rheological behaviors of EVA in higher temperature range. In this study, the rheological behavior melted in the temperature between 160 and 200°C, and microstructure of EVA processed in 200°C are reported.

EXPERIMENTAL

Materials and sample preparation

The EVA used in this study was supplied by Beijing Organic Chemical Plant, China. Its vinyl acetate content of 14%, melt index is 2 g/10 min, and density is 0.935 g/cm^3. The melt processing of EVA was performed using a HAAKE minilab, which combines key features of batch mixers, twin-screw extruders, and rheometers. A series of specimens with variant processing time (5, 15, 20, 25, 30, and 35 min) were processed at 200°C, 50 rpm in HAAKE minilab. And all samples for dynamic mechanical analysis (DMA) and positron annihilation lifetime spectroscopy (PALS) analysis were obtained on a microinjection molding machine (Thermo Electron Corp.). Injection time is 30 s, injection pressure is 0.55 MPa, injection temperature is 160°C, and mold temperature is 40°C.

Characterization

Rheology

Rheological measurements were performed using a HAAKE minilab with a recycle circuit, which both

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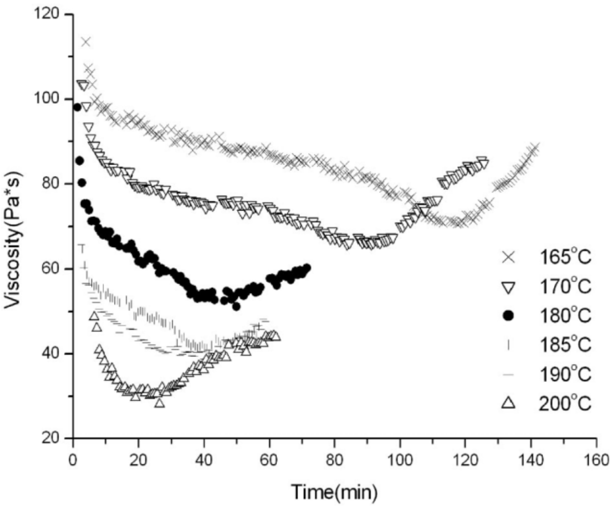

Figure 1 Viscosity of EVA copolymer versus processing time in different temperature.

allowing to recording the viscosity versus time curves. EVA was processed at 50 rpm in different temperature using a counter-rotating screw configuration.

Dynamic mechanical analysis

DMA measurements were performed using a NETZCH DMA 242C. Samples were tested in the temperature range between −70 and 60°C in single-cantilever bending mode. Heating rate of 2°C min^{-1} and a frequency of 1 Hz were used. The glass transition temperature (T_g) of the different samples obtained as the peak maximum of tan δ at 1 Hz.

Positron annihilation lifetime spectroscopy

The positron lifetime measurements were performed using a conventional fast–fast coincident system with a channel width of 48.4 ps. The time resolution of the system was found to be a sum of two Gaussians with FWHM1 = 285 ps (85%) and FWHM2 = 300 ps (15%). A 20 μCi ^{22}Na positron source was sandwiched between two sample disks at room temperature. A million counts were collected for each spectrum. And the spectra were analyzed using the computer program PATFIT.[8]

RESULTS AND DISCUSSION

Rheology

The viscosity versus time curves were shown in Figure 1, the molten EVA behaviors recorded in different temperature.

From Figure 1, it is found that the viscosity value decreases with increasing handling time at the beginning in a fixed processing temperature. When the viscosity value is minimum, we call it transition point. After this transition point, the viscosity increases and reaches a higher lever. Therefore, the process can be divided into two periods. In the first period, the viscosity lowering is because of the degradation of EVA, such as chain scission. At the same time, some free radicals have been produced.[9] In the second period, the dramatic raise of viscosity could be related to crosslinking or grafting reactions due to the free radicals. It can also be concluded that the viscosity value of EVA in the melt is lowering and the degradation rate is accelerating while the processing temperature is increasing.

A linear relationship is found between the processing time and temperature of the transition point in the viscosity curve (Fig. 2), which can be expressed:

$$(T - 155) \times \frac{1}{\tau} = c \tag{1}$$

where T is the processing temperature, τ is processing time of the transition point in the curve, and c is a constant.

Equation (1) also means that, when the EVA processed in 155°C, the transition point would not appear in the viscosity curve. In fact, when EVA was processed in 155°C, the transition point in the curve had not been found until 220 min, which agreed with the eq. (1). And, in many researches, the processing temperature of EVA is about 155°C,[5,10] which should be the perfect temperature to process virgin EVA copolymer.

The flow curves of EVA measured in three different temperatures 160, 180, and 200°C are shown in Figure 3. Compared with the flow curve measured in 160°C, at the higher temperature (180 and 200°C), a slight

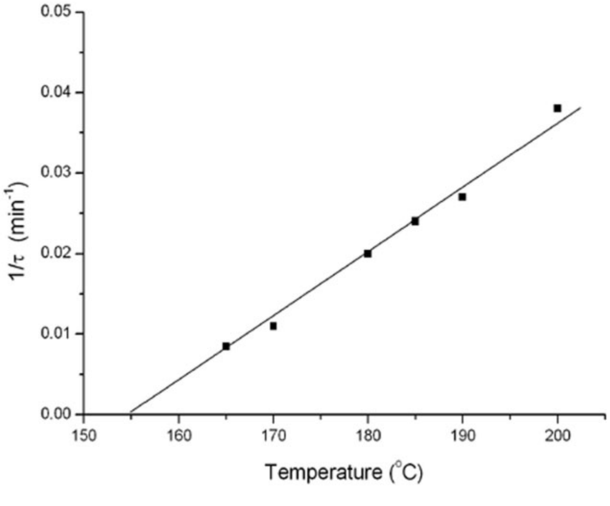

Figure 2 The correlation of time and temperature of the transition point.

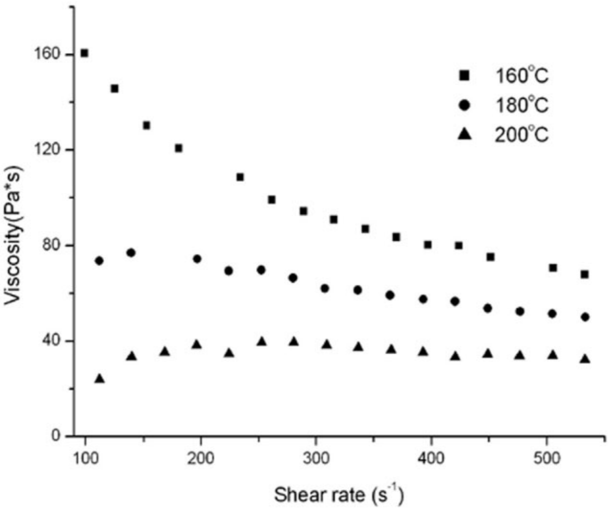

Figure 3 Melt viscosity as a function of shear rate in different temperature.

increase of the viscosity is observed in low shear rate, which could be attributed to crosslinking.

The shear and heat to which the polymer is exposed during extrusion cause thermomechanical degradation. In general terms, if the degradation is preferentially carried out by chain scission, the curve shifts toward the lower molecular weight side. The effect is the opposite if the degradation proceeds through crosslinking.[11] And higher temperature will lead EVA easier to crosslink.

Therefore, EVA processing in high temperature can be divided in two stages. In the first stage, EVA degrades due to the chain scission. In the second stage, the viscosity is an overall function of degradation and crosslinking.

Dynamic mechanical analysis

As shown in Figures 4 and 5, the tan δ peak of each sample (processed in 0, 5, 15, 20, and 25 min) shifts to significantly lower temperature (from 4.4 to −8.3°C) while increasing processing time. Then, there is nearly no change among the peaks of the samples (processed in 25, 30, and 35 min).

The reason may be that at 200°C, EVA degrades in the first 25 min due to high temperature and mechanical chemical mechanics, such as chain scission. And in the following processing time, the degradation does not prevail in the process, so T_g does not shift to the lower temperature. In this period, the glass transition temperature is an overall function of degradation and crosslinking, so it is nearly unchanged. It also agrees with the rheological results.

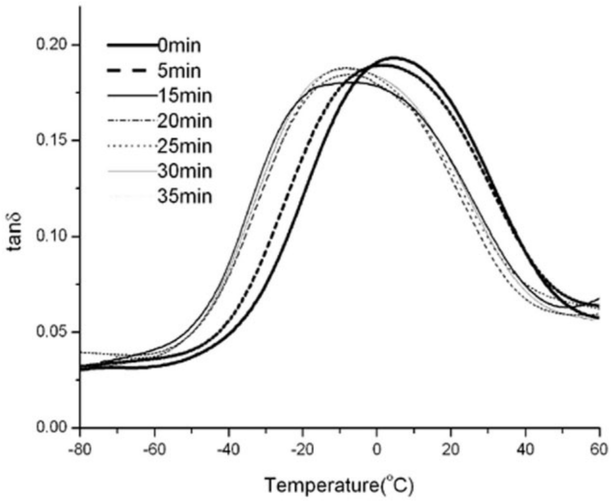

Figure 4 Tan δ curves as a function of temperature for samples processed in different handling time.

Positron annihilation lifetime spectroscopy

Positron annihilation lifetime is an established means to detect the size and concentration of atomic scale free volume holes in polymer.[12] The technique involves using a positron source, to emit positrons into the sample. After the positrons are thermalized, they diffuse at the "free" state or form a bound state, which is known as Positronium (Ps). The typical lifetime of the free positron is in the range of 0.3–0.5 ns, whereas the lifetime of Ps atoms depends on the spin state. The *para*-Positronium(*p*-Ps) with the singlet state annihilates in about 0.1 ns. The *ortho*-Positronium(*o*-Ps) with the triplet state has an intrinsic lifetime of 140 ns in vacuum. However, in polymers the *o*-Ps atoms are preferentially localized in the atomic scale holes and their lifetime is reduced to about 1–5 ns by the pick-off annihilation with an electron from the surrounding method. One can estimate the average volume of the free volume voids in a polymer, which is related to the

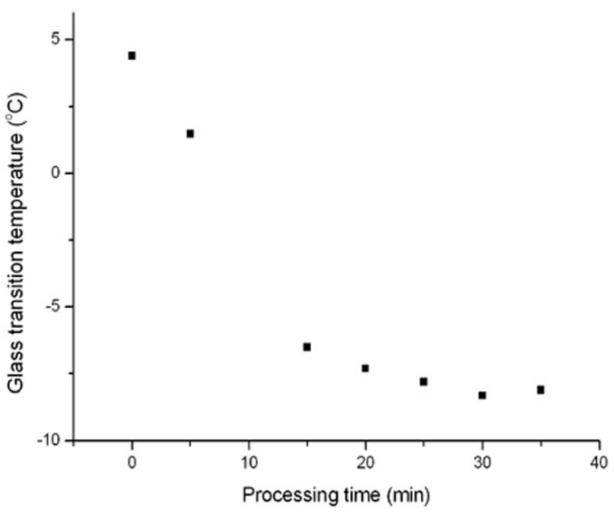

Figure 5 The glass transition temperature T_g versus processing time for EVA.

lifetime τ_3 of the long-lived component. Under the assumption that the hole has a spherical geometry and has an infinite potential for the Ps localizing, the following analytical relation between the *o*-Ps lifetime τ_3 and the average radius R of the free volume voids has been obtained,[13]

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R}{R + \Delta R}\right)^{-1} \quad (2)$$

where $\Delta R = 0.1656$ nm and τ_3 and R are expressed in ns and nm, respectively.

Therefore, the average radius R of the free volume voids in EVA can be calculated from the measured *o*-Ps lifetime τ_3, and the average volume of the free volume voids is $V = (4/3)\pi R^3$.

The measured lifetime spectra have been resolved into three components by using PATFIT and the variance of fits (χ^2) are smaller than 1.2. The longest-lived component is sensitive to the microstructural changes and results from the *o*-Ps annihilation in free volume holes.

From Figure 6, it is clear that the size of the free volume hole increases first, and then decreases, with the increase of processing time. Crosslinking and scission exist in the process of EVA. The former can be considered as leading to a decrease of the free volume, as it hinders the molecular chain mobility. The latter causes decrease of molecular weight and increase of free volume.[14] It implies that with the increase of processing time, at the beginning, the chain scission is dominant in the process, and then the crosslinking is preponderant later, which can reduce the free volume.

The variation of intensity I_2 in EVA is shown in Figure 7. The intermediate component is usually connected with annihilation of positrons in the crystalline regions and the interfacial layers.[15] A slow increase of I_2 is observed with increasing processing time, and then I_2 is nearly unchanged after processed 25 min. Chain scission can increase the interfacial layers in process, which causes I_2 increase, but crosslinking can lead to an opposite effect of I_2.

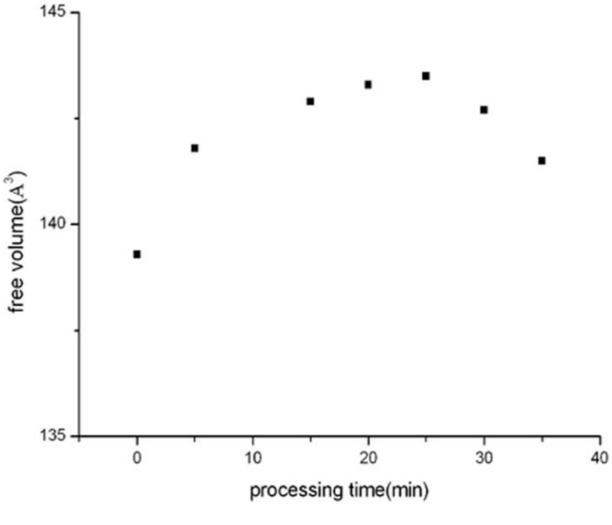

Figure 6 Average free volume as a function of processing time.

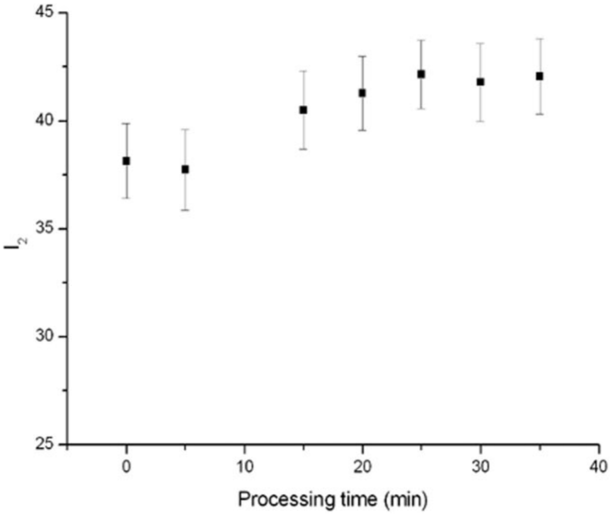

Figure 7 Intensity I_2 in EVA as a function of processing time.

CONCLUSIONS

In this study, we investigated the property of EVA in melt process through HAAKE minilab, DMA, and PALS. The results from various techniques are in agreement each other. The following conclusion can be drawn:

1. The viscosity of EVA was found to decrease with processing time in the first. This shows EVA degrading, which was mainly due to mechanical scission of the polymer chain. Then, the viscosity increased with processing time, which is due to crosslinking caused by peroxide formed in the degradation stage.
2. The processing time and temperature of the transition point in the viscosity curve agree with the eq. (1). But, if the processing temperature is low enough, e.g., 155°C, the transition point in the viscosity curve will not be found in long enough processing time.
3. The glass transition temperature measured with DMA decreased at the beginning, and nearly unchanged afterwards with increasing handling time, which means the degradation prevails first, and then degradation is not dominant.
4. With presenting the results of PALS, the free volume of EVA is formed to increase first, and

decrease next. The free volume of the sample corresponding to the transition point (processed about 25 min) is the largest of all samples.

5. The intermediate component I_2 increased with processing time at the beginning, and then I_2 of the samples processed longer than 25 min is nearly no change.

References

1. Goutille, Y.; Carrot, C.; Majeste, J.-C.; Prochazka, F. Polymer 2003, 44, 3165.
2. Attarian, M.; Taheri-Nassaj, E.; Davami, P. Ceram Int 2002, 28, 507.
3. Arsac, A.; Carrot, C.; Guillet, J. J Appl Polym Sci 1999, 74, 2625.
4. Gianelli, W.; Camino, G.; Dintcheva, N. T.; Verso, S. L.; Mantia, F. P. L. Macromol Mater Eng 2004, 289, 238.
5. Kim, M. S.; Park, C. C.; Chowdhury, S. R.; Kim, G. H. J Appl Polym Sci 2004, 94, 2212.
6. Gonzalez, O.; Nunoz, M. E.; Santamaria, A.; Garcia-Morales, M.; Navarro, F. J.; Partal, P. Eur Polym J 2004, 40, 2365.
7. Wang, X.; Li, H.; Ruckenstein, E. Polymer 2001, 42, 9211.
8. Kirkegard, P.; Eldrup, M.; Mogensen, O.; Petersen, N. J. Computer Phy Commun 1981, 23, 307.
9. Scott, G. Polym Degrad Stab 1995, 48, 315.
10. Zhang, F.; Sundararaj, U. Polym Compos 2004, 25, 535.
11. Canevarolo, S. V. Polym Degrad Stab 2000, 709, 71.
12. Jean, Y.C. Microchem J 1990, 42, 72.
13. Nakanishi, H.; Wang, S. J.; Jean, Y. C. In Positron Annihilation Studies of Fluid; World Scientific: Singapore, 1988; p 292.
14. Misheva, M.; Mihaylova, M.; Djourelov, N.; Kresteva, M.; Kretev, V.; Nedkov, E. Radiat Phys Chem 2000, 58, 39.
15. Wang, S. J.; Zhang, M.; Liu, L. M.; Fang, P. F.; Zhang, S. P.; Wang, B. Mater Sci Forum 2004, 445, 355.