Correlation Study between the Rheological Property and the Free Volume for Ethylene Vinyl Acetate Copolymer under Melt Extrusion

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The rheological behavior of ethylene vinyl acetate copolymers (EVA) with different vinyl acetate (VA) contents during the extrusion process was investigated by means of viscosity and positron lifetime measurements. The viscosity of EVAs in the liquid state under shearing stress initially decreased with processing time before passing through a minimum at the transition point. The variation of processing time at this transition point with extrusion temperature showed that higher extrusion temperature leads to lower viscosity and faster degradation. The relationship between the inverse of the processing time for the transition point and the corresponding process temperature suggested that the VA content is a key factor for the degradation process of EVA. The positron results indicated that the free-volume size exhibits a corresponding variation to the rheological behavior.

1. Introduction

Ethylene-vinyl acetate (EVA) is a random copolymer synthesized from ethylene and vinyl acetate (VA) monomers. Polar VA groups randomly introduced into the copolymer backbone act as intervals of the ethylene chain segments with various lengths. This copolymer has good transparency, flexibility and oxygen barrier properties [1], therefore, it has been widely applied to flexible packaging, footwear, hot melt adhesives, and electrical cable sheathing in industry.

EVA products are generally formed via melt extrusion. In this process, the thermal stability and the rheological properties of the polymers are important. For instance, high extrusion temperatures lower the viscosity for the polymer material which leads to a higher extrusion efficiency for the process, however, higher temperatures also result in the thermal degradation of the polymer backbone [2]. For a pure EVA product, the process temperature is mostly in the range between 90 °C and 160 °C. In order to improve the mechanical-thermal property as well as the flame retardancy, EVA needs to be mixed with either fillers (clay or nanotube) or different polymers. In this case, a high temperature is conventionally chosen during the extrusion process. For instance, bitumen/EVA blends are compounded at 180 °C [3], EVA/rectorite composites are prepared at 200 °C [4], and polyamide6/EVA blends are processed above 200 °C [5], respectively. For optimizing the process temperature, better knowledge, concerning the rheological behavior and the thermal stability of EVA at temperatures higher than 160 °C, is of importance to both theoretical research and industrial manufacturing. In a previous study, we reported the rheological behavior for EVA with a VA content of 14 % during the extrusion process and showed both the extrusion temperature and the processing time are responsible for EVA degradation during the extrusion process. [2]

Various properties such as crystallinity and adhesive force for EVA are dependent on the VA

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content [6], because the VA group plays an important role in the intermolecular interaction for EVA. However, there have been few previous studies on the relationship between VA content and thermal degradation in the melt extrusion. In this work, two kinds of EVA with different VA contents are examined, and the effect of the VA groups on the degradation of EVA in the extrusion process is discussed.

2.   Experiments

Two kinds of EVA with different VA contents, adopted for the present work, were purchased from Beijing Organic Chemical Plant, China. The polymers with VA contents of 14 % and 18 % are hereafter referred to as EVA14–2 and EVA18–3, respectively. The melt extrusion for the EVA materials was performed using a micro compounder, built in a HAAKE minilab (Thermo Scientific, USA), that combines key features of batch mixers, twin-screw extruder, and rheometers.

The rheological properties for the polymers were measured using the HAAKE minilab with a recycle circuit, which allows the viscosity versus time curves to be recorded. All the samples were processed at 50 rpm using a counter-rotating screw configuration.

A series of specimens for the positron measurement were prepared as follows. EVA14–2 materials were prepared at 200 °C, 50 rpm in the HAAKE minilab with different processing times (0, 5, 10, 15, 20, 25, 30 and 35 min). The obtained materials were molded by using a microinjection molding machine (Thermo Electron Corp., Germany). The injection time was 30 seconds, the injection pressure was 0.55 MPa, the injection temperature was 160 °C, and the molding temperature was 40 °C, respectively. The prepared samples, with the dimensions 10 mm × 10 mm × 2 mm, were cut out from the molded polymer for the positron lifetime measurements. The lifetime measurements were performed at room temperature using a conventional fast-fast coincidence system with a channel width of 48.4 ps. A 0.74 MBq ^{22}Na positron source was sandwiched between two sample sheets. One million counts were collected for each spectrum. The obtained spectra were analyzed using the computer program PATFIT [7] to deduce the *ortho*-positronium (*o*-Ps) lifetime and subsequently to quantify the free-volume size.

3.   Results and Discussion

Figures 1a and 1b show the variation of the viscosity at different extrusion temperatures for EVA18–3 and EVA14–2, respectively, as a function of processing time. Both EVA samples show a similar relationship between viscosity and processing time. For each EVA sample, higher extrusion temperature results in lower viscosity, while at each extrusion temperature, the viscosity displays a V-shaped variation with processing time. In this study, for each extrusion temperature, a transition point is defined as the processing time corresponding to the minimum measured viscosity for each EVA. For example, the viscosity for EVA14–2 at 200 °C, monotonically decreases with increasing processing time, and it approaches the minimum value of around 28 Pa·s at a processing time of 25 min. The viscosity then increases with further increasing the time above 25 min.

Several parameters, such as the molecular weight, the chain branch, and the chain entanglement, influence the viscosity in the extrusion process. In general, enhanced entanglement of polymer chains increases the polymer viscosity, while lower molecular weight after chain scission decreases the polymer viscosity. In the present extrusion process, the EVA chains are sheared with the high temperature, possibly giving rise to the chain scission, that is, lowering the molecular weight. This thermodynamical degradation due to the shear and heat treatment may cause a reduction of chain entanglement. On the other hand, free radicals may be generated simultaneously with the chain scission during the heat treatment. These free radicals react with each other to form crosslinking between the main chains. This crosslinking process leads to enhancement of the molecular weight, resulting in the increased viscosity. [8] It is suggested that the observed reduction in viscosity in the first stage of the process-

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ing in Fig. 1 is ascribed to the predominant effect of chain scission under shearing treatment at high temperature, while the increase in viscosity in the second stage below the transition point is ascribed to the increased molecular weight of EVA due to the crosslinking.
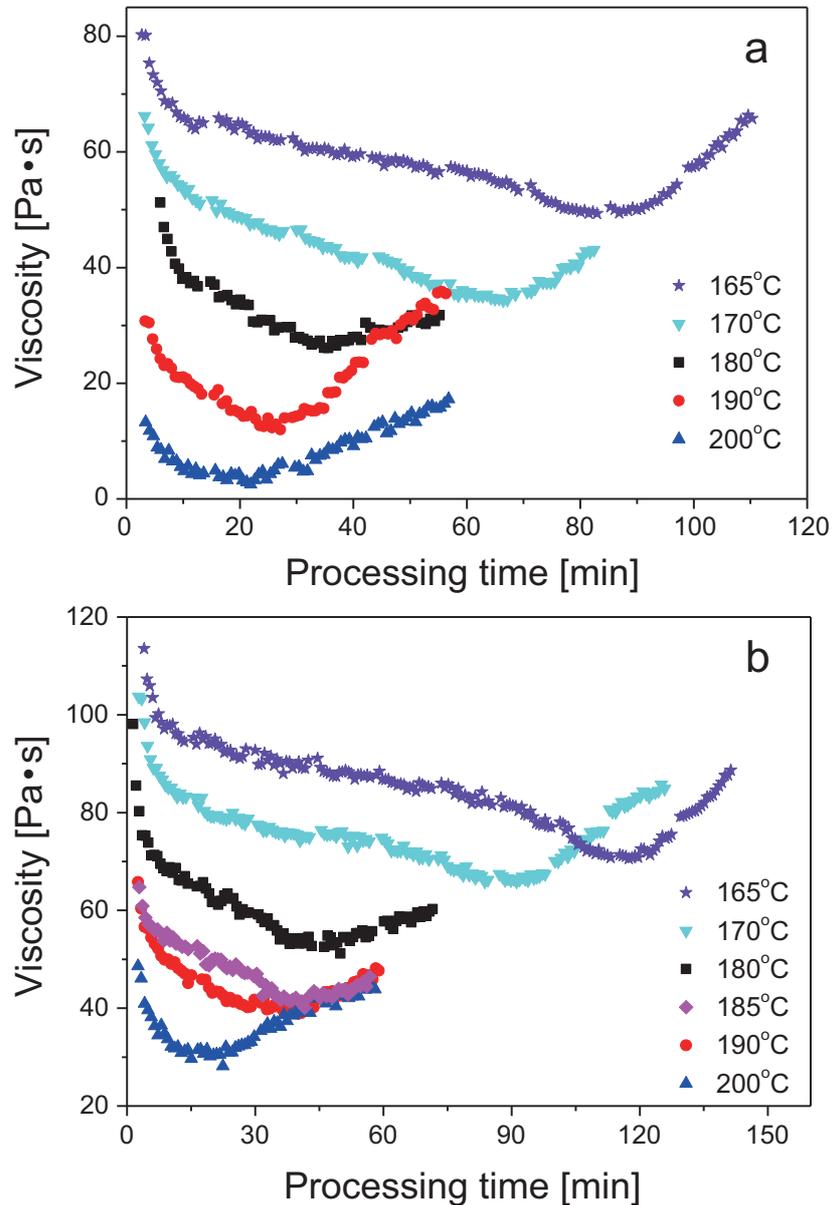

Fig. 1. Variation of the viscosity at different temperature as a function of processing time (a) for EVA18–3 and (b) for EVA14–2.

The result of Fig. 1 indicates that the transition from decreasing to increasing viscosity is related to the extrusion temperature, as well as the processing time. In order to investigate details of the extrusion process, the inverse of the handling time at the transition point $1/\tau$ is plotted versus the extrusion temperature T, with the result is shown in Fig. 2. As seen in the figure, a linear correlation is obtained between T and $1/\tau$ for each EVA. The correlations can be described by the following

equations:

$$1/\tau \quad = \quad (T - 155) \times c_{18-3} \tag{1}$$
$$1/\tau \quad = \quad (T - 155) \times c_{14-2} \tag{2}$$

where c is a constant specific to the respective polymers denoted by the subscripts, 18–3 and 14–2. Eqs. (1) and (2) indicate that extruding the present EVA below 155 °C leads to infinite or negative τ, meaning that the disappearance of the V-shaped change in viscosity. In other words, it is expected that EVA will not degrade at temperatures below 155 °C in the extrusion process. In a subsequent experiment, we checked this expectation: at a temperature of 155 °C and a shearing rate of 50 rpm, both EVA18–3 and EVA14–2 maintained nearly constant values of their viscosity for longer than three hours. In fact, in several previous studies, the processing temperature of EVA has been chosen to be about 155 °C [9, 10], signifying that 155 °C is the optimal temperature of the extrusion process for a virgin EVA.
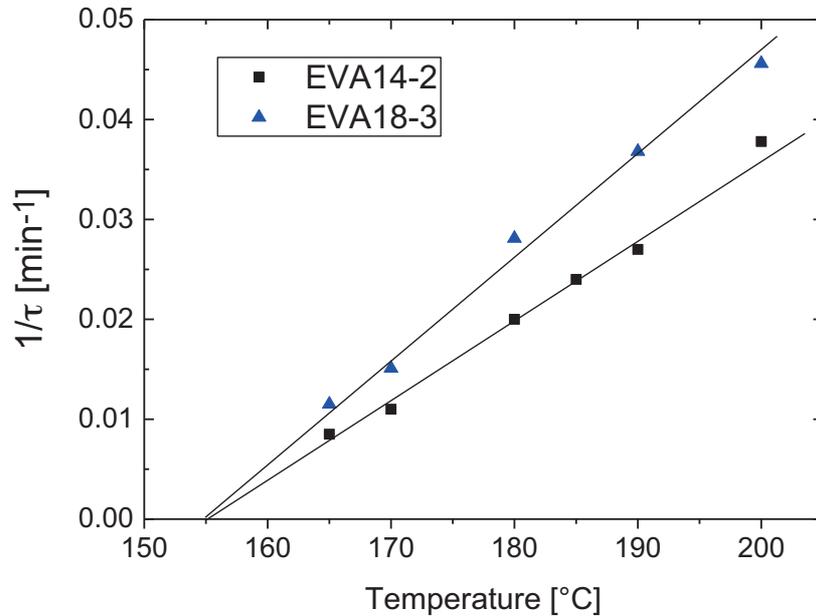

Fig. 2. Correlation of the inverse of processing time at the transition point and the corresponding temperature.

Based on the experimental data of Fig. 2, the ratio of c_{18-3} and c_{14-2} is calculated as:

$$\frac{c_{18-3}}{c_{14-2}} = \frac{18}{14} \tag{3}$$

The value of the ratio suggests that degradation during the extrusion process is related to the VA content for the two copolymers and furthermore it is essentially consistent with the VA content ratio. In comparison with the other atoms, the tertiary carbon of the VA group is easily attacked by the radicals generated by the thermal scission during extrusion [11], followed by the crosslinking of the EVA chains through the mutual termination of EVA macroradicals to form a network structure. As a result, higher VA content leads to faster chain scission under the thermomechanical effect, and the transition point for the present polymers is relevant to the VA content.
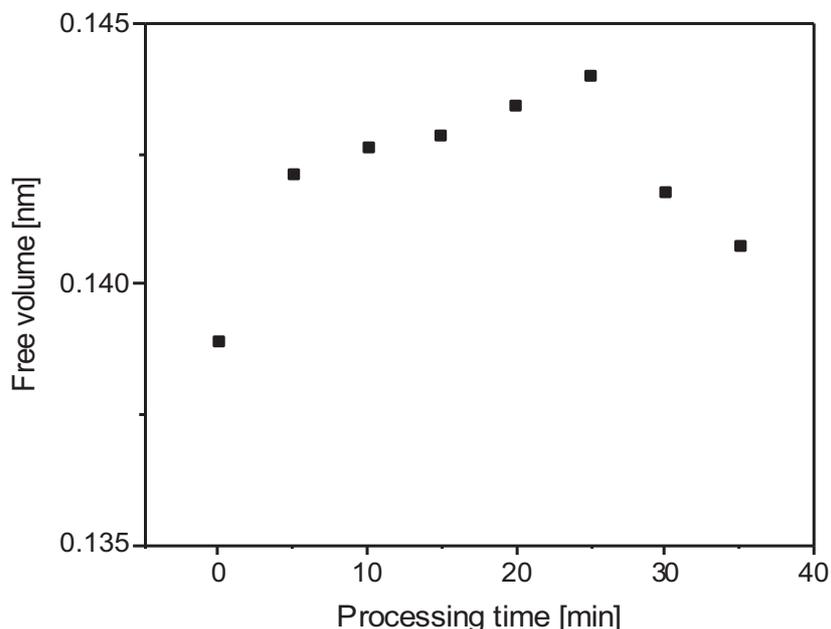
Fig. 3. Variation of the average free-volume size for EVA14–2 extruded at 200 °C as a function of processing time.

The positron annihilation lifetime technique was employed to study the microstructure of EVA14–2 under thermomechanical degradation. Figure 3 shows the variation of the free-volume size, evaluated from the o-Ps lifetime, for EVA14–2 extruded at 200 °C as a function of processing time. The free-volume size increases with increasing processing time from 0 to 25 min, and then decreases with further increasing the time above 25 min. Chain scission leads to an increase in branched chains, possibly followed by an enlargement of the free-volume size, whereas chain crosslinking hinders the polymer-mainchain mobility, resulting in a reduction of the free-volume size. The transition results signifies that as the processing time increases the dominant factor on the free-volume size changes from chain scission the chain crosslinking, and the processing time corresponding to the maximum free-volume size is in good agreement with the transition point in the viscosity during extrusion at 200 °C.

4. Conclusion

The rheological behavior of EVA with different VA content has been investigated during the extrusion process. At extrusion temperatures higher than 160 °C, the viscosity showed a V-shaped variation with the processing time, characterized by a transition point at the minimum viscosity. It is suggested that the decreasing viscosity in the first stage below the transition point is due to chain scission of EVA during the extrusion, while the increased viscosity in the second stage above the transition point may be due to crosslinking, caused by the free radicals formed on the main chains. The relationship between the inverse of the processing time at the transition point and extrusion temperature signified that higher VA content leads to faster degradation in the extrusion process and that the optimal temperature of the process for a pure EVA is estimated as 155 °C. The positron results indicated that the variation of free-volume size exhibits a similar transition point to the corresponding rheological behavior.

Acknowledgment

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