

Kinetics and Extent of Low-Temperature Crystallization of Ethylene–Vinyl Acetate Copolymers

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SYNOPSIS

The enthalpies of fusion of two types of EVA copolymers containing 9 and 16% of vinyl acetate, respectively, were investigated by DSC. After melting, the samples were cooled down and held at 10, 15, 20, and 25°C for different periods of time from 15 min to 2.5 months (only at 20°C). The enthalpy of fusion increased over the 2.5-month period for 9.3 and 11.3 J/g, respectively. There was a new small melting peak on the endotherm of the aged sample whose position and size depended on aging temperature and aging time. During 2.5 months, the peak shifted toward higher temperature for 8°C. The enthalpy of fusion and corresponding degree of crystallinity changed linearly with the logarithm of time, as is the case in high-temperature annealing or secondary crystallization at high temperatures. The rate and the extent of low-temperature crystallization of ethylene copolymers depend on the comonomer content, sequence length distribution, and temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Physical and chemical properties of semicrystalline polymers and copolymers depend on the chemical structure, molecular weight, molecular weight distribution, degree of crystallinity, and crystallization conditions. Crystallization conditions influence the structure, the size of the crystallites, and the degree of crystallinity. Crystallization proceeds at temperatures (T_c) well below the melting temperature. The early stage of crystallization is known as primary and the later as secondary crystallization.

A variety of *n*-alkanes,^{1–4} polyethylenes,^{5–17} ethylene copolymers,^{18–22} and other polymers have been studied from the point of view of the kinetics and morphology. The changes in crystallinity at relatively small undercooling were studied and the development of crystallization and crystallization kinetics, both primary and secondary, are quite well known.

The changes during the annealing of fully crystallized polymer at the temperatures below the melting point were studied as well. DSC curves of

annealed materials show two or more melting peaks. These observations suggest separate crystallization of various types of copolymer crystallites according to the size differences of crystallizable polyethylene sequences. Some efforts were made to determine the copolymer structure from the position of the annealing melting peaks. Since the position and the enthalpy of peaks change with time, the results are questionable. The changes in the degree of crystallinity are proportional to the logarithm of time and are higher at higher annealing temperatures.

Little is known about the low (room) temperature annealing or aging, which also increases density and alters mechanical properties.²⁶ The physical aging process below the glass transition temperature has been studied in detail for amorphous polymers. Semicrystalline polymers age above T_g , and there could be at least two mechanisms involved: physical aging, as in case of amorphous polymers, and secondary crystallization. Secondary crystallization as a possible cause for aging has been known for some time, but there is no information on the increase of crystallinity or on the kinetics.^{5,23,27,28} The crystallization at “room” temperature and lower was the aim of the present work.

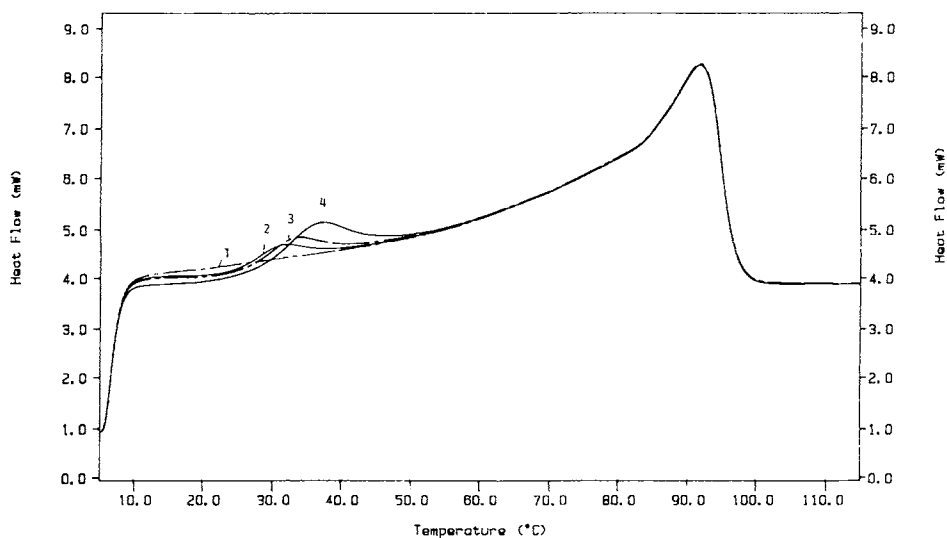


Figure 1 The changes in DSC curves of EVA 16 when aged at 20°C for different periods of time: (1) unaged; (2) aged for 2 h; (3) aged for 10 h; (4) aged for 2.5 months.

EXPERIMENTAL

Materials

Ethylene–vinyl acetate copolymers with 9% (EVA 9) and 16% (EVA 16) of vinyl acetate, with a random monomer sequence distribution, HIPTEN 27016 (EVA 9), and HIPTEN 33004 (EVA 16), HIP Pančevo, were used.

Methods

Thermal analyses were performed using a Perkin-Elmer DSC-7. Samples (≈ 10 mg) were annealed at 10, 15, 20, and 25°C from 15 min to 2.5 months (only at 20°C) and then heated and cooled twice from 0°C (samples aged at 10°C only) or at 5–115°C at a constant rate of 10°C/min. The enthalpies of fusion were calculated from both cycles in the temperature range from annealing temperature to 108°C for EVA 9 and to 103°C for EVA 16. The enthalpy of low-temperature crystallization was obtained from the difference between the first and the second heating cycles. Two cycles were also necessary to minimize the effect of the baseline instability. Enthalpies of fusion were converted to degrees of crystallinity by using the enthalpy of fusion of perfect polyethylene crystal, 293 J/g.²⁹ Calculated values of crystallinity might be slightly inaccurate, because it is impossible to determine the specific heat differences in the melting range. Since the work is based on the measurements of the difference in melting enthalpy, this inaccuracy is of minor importance.

RESULTS

For the melting of random ethylene copolymers, a broad fusion curve is characteristic. Therefore, a DSC scan starting at room temperature will not yield an accurate value of the enthalpy of fusion, since a portion of the melting endotherm would not be taken into account.^{5,20}

In Figure 1, the changes in DSC curves of EVA 16 when aged at 20°C for different periods of time are shown. Curve 1 represents the second melting, which is used to determine the degree of crystallinity (X_0) according to the standard method (ASTM D3418). A small endotherm peak between 20 and 50°C can be seen on curves 2 (2 h of aging), 3 (10 h of aging), and 4 (2.5 months of aging). The peak increases with aging time and shifts to a higher temperature for 8°C.

Due to the low-temperature crystallization, the enthalpy of fusion increased over the 2.5 month period of aging for 9.3 J/g (9%) for EVA 9 and for 11.3 J/g (15%) for EVA 16 (Fig. 2). The main reason for the difference is a higher content of small polyethylene sequences, melting in the range of 20–50°C in EVA 16.

Indeed, there are two processes going on simultaneously: One is the nucleation and the growth of new small crystals and the second is the growth of crystals already formed at higher temperatures. Crystallization of ethylene–propylene and ethylene–octene copolymers of similar composition as EVA 16 proceed even at temperatures as low as -70°C .³⁰ The crystallites are apparently too small or too im-

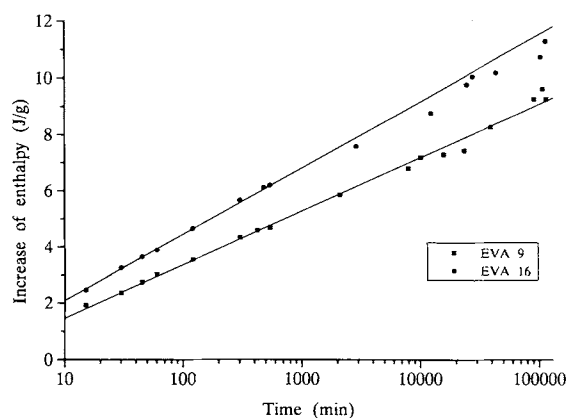


Figure 2 The increase of the melting enthalpy for both copolymers at 20°C during a 2.5 month period.

perfect to give constructive interference with WACS, while the crystallization process can be followed with both SAXS and DSC.

In Figure 3, the changes in DSC curves of EVA 16 aged at different temperatures are shown. Curves 2 and 3 represent melting after holding the sample for 2 h at 15 and 25°C, respectively. Small endotherm peaks appear at 27.8 and 36.7°C. The increase of melting enthalpies and its thermal dependence during the first 1000 min of aging for EVA 9 are shown in Figure 4. The increase is linear with logarithm of time, being higher at higher temperature.

From the curve 1 in Figures 1 and 2, it can be seen that melting proceeds in the entire temperature range from 5 to 103°C. By lowering the temperature, some new crystals appear and the degree of crys-

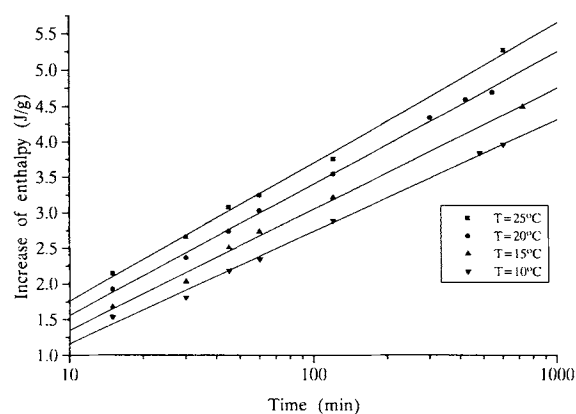


Figure 4 The increase of the melting enthalpy of EVA 9 at different temperatures.

tallinity (X_0) is higher. Besides, the degree of crystallinity (X) increases linearly with the logarithm of time as in case of high-temperature annealing (Fig. 5). Any increase of temperature causes melting of some small crystals and faster growth of bigger ones.

The enthalpy of fusion and the corresponding degree of crystallinity can be calculated by equations also valid for secondary crystallization or high-temperature annealing:

$$\Delta H = \Delta H_0 + K \ln(t) \quad (1)$$

$$X = X_0 + k \ln(t) \quad (2)$$

The equations are not valid for the time range of 0–1 min. “ k ” and “ K ” are the slopes of the straight

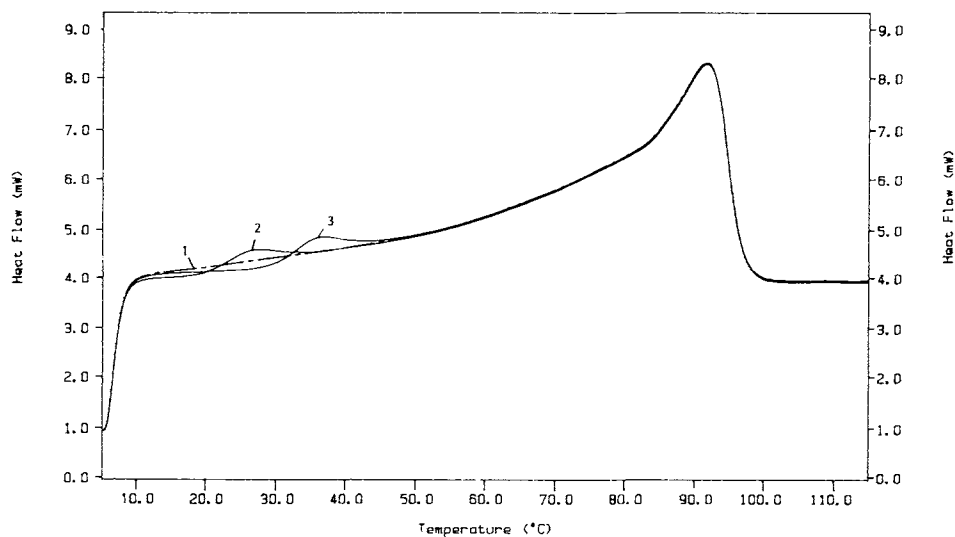


Figure 3 The changes in DSC curves of EVA 16 aged for 2 h at different temperature: (1) unaged; (2) 15°C; (3) 25°C.

lines and represent the rate constants of crystallization.

The values of measured enthalpies, corresponding degree of crystallinity, and the rate constants are shown in Table I. Samples were aged at 20°C in two ways: Samples aged up to 1000 min were held in the DSC, while for a longer time, aged samples (up to 2.5 months) were held in a thermostat. The melting enthalpies of the samples aged in a thermostat were lower than expected, especially for EVA 16. There may be two reasons for this: First, the temperature in the thermostat was slightly lower than 20°C, since its accuracy was $\pm 0.1^\circ\text{C}$. Second, the melting of small crystals occurred during the transfer of the sample from the thermostat to the DSC, since the room temperature was usually higher than 20°C. Deviations are bigger for EVA 16 with its higher thermal sensitivity. Rate constants were calculated from the samples aged in the DSC only.

Monitoring Figure 5 precisely, it can be seen that the first points (X_0) do not lay exactly on the straight lines but are slightly higher. Therefore, using X_0 and the experimentally determined rate constants, higher crystallinity (0.2–0.3%) than calculated from the measured enthalpies is obtained. The reason for this difference lies in the fact that the measured crystallinity X_0 is slightly higher than is the crystallinity of the sample at the time it reaches the aging temperature; namely, to measure the enthalpy of fusion, the sample was cooled from the aging temperature to 5°C or to 0°C. While cooling the sample to this temperature, some crystallization proceeded and increased the measured enthalpy. The

Table I The Enthalpies of Fusion of Unaged Sample, Corresponding Degree of Crystallinity, and Rate Constants for Eqs. 1 and 2

Temperature (°C)	ΔH_0 (J/g)	K	X_0 (%)	k
EVA 9				
10	107.9	0.684	36.8	0.233
15	105.4	0.739	36.0	0.252
20	103.0	0.801	35.2	0.273
25	100.3	0.843	34.2	0.288
EVA 16				
10	79.8	0.878	27.2	0.300
15	77.0	0.930	26.3	0.317
20	74.4	1.004	25.4	0.343
25	71.2	1.074	24.3	0.367

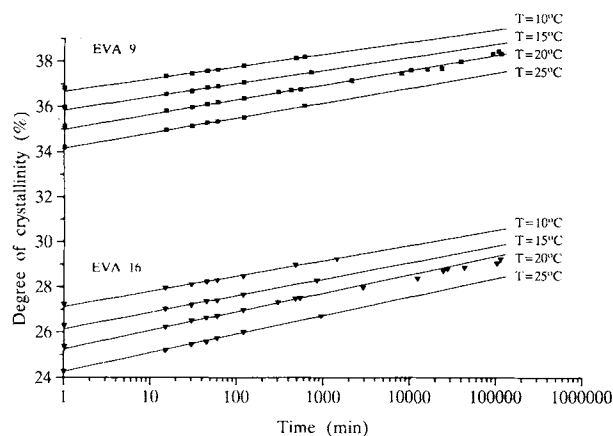


Figure 5 The dependence of the degree of crystallinity on time for both copolymers at different temperatures.

increase in enthalpy is higher for the unaged sample than for the aged ones, while the part of all units which crystallize in this temperature range have already crystallized. This can be seen well from the first part of the melting curves in Figures 1 and 3. Curve 1 is the melting curve of an unaged sample. It slowly increases with temperature from 5°C to the melting peak. The melting curves of the aged samples are almost leveled off to the aging temperature and they all lie below curve 1. In Figure 1 it can be seen that with longer aging time the first part of the melting curve lies lower, because in aged samples, fewer polyethylene segments have crystallized during cooling to 5°C.

CONCLUSION

EVA copolymers slowly crystallize at room or lower temperature for at least 2.5 months. The rate and the extent of crystallization depend on the comonomer content, sequence length distribution, and temperature. The degree of crystallinity increases linearly with the logarithm of time as in case of high-temperature annealing. The differences in degree of crystallinity during a 2.5 month period at 20°C are 3.1% for EVA 9 and 3.8% for EVA 16, which represents 9 and 15%, respectively, of all at that conditions crystallizable units. We can assume that ethylene copolymers at room and lower temperature tend to reach a thermodynamic equilibrium between crystalline and amorphous phase. Any increase of the temperature causes melting of some small crystals and further growth of bigger ones, while a decrease of the temperature causes the formation of new crystals and their growth.

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