

Procedure for Calculating the Crystallinity of Ethylene-Vinyl Acetate Copolymers and Low-Density Polyethylene as a Function of Temperature

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Synopsis

A method is described for determining the x-ray crystallinity of ethylene-vinyl acetate copolymers at differing temperatures. An equation is derived for the symmetrical curves of crystallinity versus temperature thus obtained, from which the crystallinity at any temperature can be calculated. In order to determine the constants of the equation for a particular polymer, it is only necessary to determine the melting point and per cent crystallinity of the resin at a known temperature. The equation can also be applied to conventional polyethylenes, but not to linear polyethylenes. It is suggested that this is due to the former resins having a broad crystallite size distribution compared with the narrow distribution present in high-density polyethylene.

INTRODUCTION

Several methods are available for determining the degree of crystallinity of semicrystalline polymers as a function of temperature. Charlesby and Callaghan¹ and Reding² measured the density dilatometrically, and Ke³ has made use of thermal analysis to achieve the same objective. In this work, the crystallinity of ethylene-vinyl acetate copolymers and low-density polyethylenes has been measured directly by x-ray diffraction analysis at differing temperatures. The symmetry of the crystallinity-versus-temperature curves obtained suggested a simple mathematical relationship between the per cent crystallinity and temperature. An empirical equation was derived which fits the curves. Using this equation, it is only necessary to determine the melting point and per cent crystallinity at room temperature in order to determine the constants of the equation for a given polymer.

EXPERIMENTAL

Samples

The copolymers and low-density polyethylenes used in this work were commercial and experimental resins manufactured by U.S. Industrial Chemicals Co.

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Apparatus

The x-ray diffraction patterns were obtained with a Phillips Electronic Instrument Company x-ray diffraction unit equipped with a wide-range goniometer. The sample holder was modified so that the sample could be maintained at temperatures up to 70°C. The temperature of the sample was measured with a thermocouple which was imbedded in the specimen.

The melting points of the polymers and copolymers used in these studies were determined using a du Pont Instrument Company DTA 900 employing a programmed heating rate of 10°C/min. Materials for x-ray analysis and melting point determinations were exposed to the same thermal history prior to analysis, i.e., they were all cooled slowly from the melt.

Calculation of Results

Figure 1 shows a typical ethylene-vinyl acetate copolymer x-ray diffraction pattern obtained at 24°C. The amorphous peak is area *A* plus

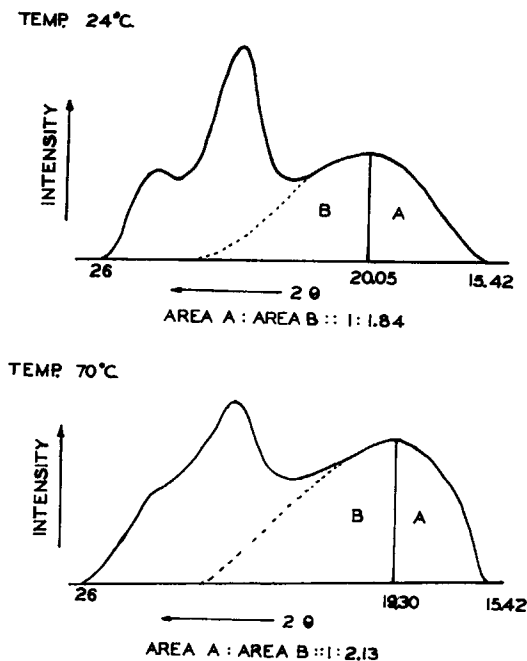


Fig. 1. Typical x-ray diffraction of an ethylene-vinyl acetate copolymer at 24° and 70°C.

area *B*; Kamath and Wakefield⁴ found that the ratio of area *A* to area *B* was constant (1:1.84), irrespective of the vinyl acetate content of the copolymer. Since there are no contributions from the crystalline peaks to segment *A* of the amorphous peak area, Kamath and Wakefield calculated the percentage of amorphous material in the copolymer from the x-ray diagram as follows:

$$\text{per cent amorphous material} = \frac{K \times A}{D} \times 100$$

where K = constant = ratio area A + ratio area B , or $1 + 1.84$ at room temperature; A = area under amorphous peak from $2\theta = 15.42^\circ$ to the peak maximum $2\theta = 20.05^\circ$ (at room temperature); and D = total area under the x-ray curve.

At elevated temperatures, the equation still applies; however, the value of K is changed due to a change in the asymmetry of the amorphous peak and its translation to lower diffraction angles (see Fig. 1). In order to determine the value of K at elevated temperatures, three copolymers containing more than 40% vinyl acetate (i.e., copolymers 100% amorphous at room temperature) were used. The peak positions and ratios of area A to area B were found for each resin at increasing temperatures. These data were then used in determining the percentage of amorphous material present in various copolymers at elevated temperatures, employing the above equation.

Calculation of the crystalline content of polyethylene at elevated temperatures was accomplished without difficulty, employing the method of Matthews et al.⁵

RESULTS AND DISCUSSION

Employing the above techniques, three ethylene-vinyl acetate copolymers of differing comonomer content and melting point were subjected to x-ray analysis over a broad temperature range. The results were plotted directly as per cent crystallinity versus temperature, as shown in Figure 2. At the melting point of the material, its crystallinity by definition is zero. It was observed from Figure 2 that, as the temperature was lowered, the crystallinity asymptotically approached a maximum and, by extrapolating the curve to 0°C , it appears that the crystallinity is very close to its maximum at this temperature.

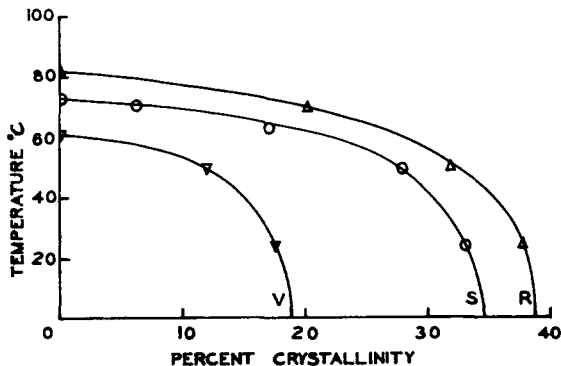


Fig. 2. Variation of x-ray crystallinity with temperature for the three ethylene-vinyl acetate copolymers (∇) V; (○) S; (Δ) R.

It can be seen that the curve for each resin is similar in shape; this suggested that there was a mathematical relationship between the temperature and crystallinity of these resins. The following equation was derived empirically and describes the variation of per cent crystallinity with temperature:

$$C_T = C_0 (1 - Fe^x)$$

where $x = BT/T_m$ or

$$\ln \left(1 - \frac{C_T}{C_0} \right) = \frac{BT}{T_m} + \ln F$$

where C_T = per cent crystallinity at temperature $T^\circ\text{C}$, C_0 = maximum crystallinity attainable, and T_m = melt point of polymer at temperature $T^\circ\text{C}$.

It is assumed that the samples which are annealed have attained 99% of their maximum crystallinity at 0°C . In other words, at $T = 0^\circ\text{C}$, $(1 - C_T/C_0) = 0.01$ and therefore $F = 0.01$ and at $T = T_m^\circ\text{C}$, $(1 - C_T/C_0) = 1.00$ and therefore $B = 4.606$. It was decided for convenience, and also because this is an empirical method, to use the centigrade temperature scale, since this simplifies plotting the data.

In order to check the validity of the assumptions for the values of B and F , the experimental data given in Table I for the crystallinity of sample R at 24°C , 70°C , and 82.5°C , where C_T is zero, were used to calculate the values of C_0 , F , and B for this copolymer. The values obtained were $B = 4.787$ and $F = 0.0085$. It is thought that these values are sufficiently close to the assumed values to support the hypothesis that this is a valid equation. The value of C_0 was also calculated at this time and was found to be

TABLE I
Comparison of Calculated and Experimental
Crystallinities for Ethylene-Vinyl Acetate Copolymers

Copolymer	Temp, $^\circ\text{C}$	Crystallinity, %	
		x-ray $\pm 2\%$	calculated
Sample R (18.5% vinyl acetate, mp/82.5 $^\circ\text{C}$)	0	38.7*	39.1
	24	37.6	—
	50	31.9	32.7
	70	20.1	19.6
Sample S (26.4% vinyl acetate, mp/73.0 $^\circ\text{C}$)	0	34.3*	34.7
	24	33.1	—
	50	28.0	26.6
	60	17.0	19.4
	70	6.3	5.9
Sample V (33.0% vinyl acetate, mp/60.7 $^\circ\text{C}$)	0	18.4*	18.8
	24	17.6	—
	50	12.1	10.9

* Extrapolated from Figure 2.

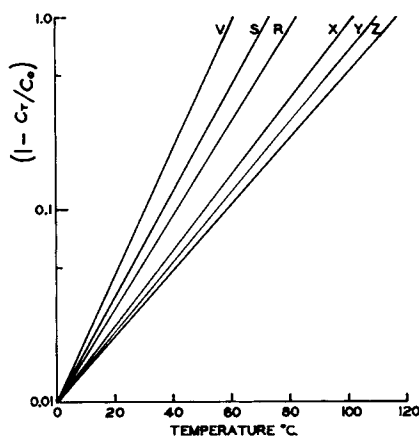


Fig. 3. Empirical relationship between per cent crystallinity and temperature for ethylene-vinyl acetate copolymers and low-density polyethylene.

38.9%, which is also in good agreement with the value of 39.1% obtained from Figure 3.

Employing the experimentally determined melting points, the curves for the three copolymers were plotted as shown in Figure 3. Employing the value of the crystallinity C_T , determined experimentally at room temperature (24°C), and the corresponding value of $(1 - C_T/C_0)$, obtained from the graphs, the value of C_0 for each of the three copolymers was calculated. In order to determine the crystallinity at an elevated temperature, the value of $(1 - C_T/C_0)$ is read from the graph at the particular temperature, and since C_0 is known, the value of C_T is easily calculated.

It is readily apparent from these results that there is a good correlation between the calculated and experimentally determined values. It was thought that polyethylene would behave in a similar manner, and indeed the observed and calculated values for three low-density resins, examined in this manner, show quite good correlations (see Table II). In addition, some results of Charlesby and Callaghan¹ and Reding,² who used dilatometric methods to examine the crystallinity-temperature relationship, were also analyzed in this fashion and show good agreement with their experimentally determined data. It was not possible to apply this method to crystallinity-temperature relationships determined by means of thermal analysis since it is practically impossible to extrapolate the baseline in such experiments to a zero point at, for example, 0°C; in fact, meaningful results are not generally obtained below 70°C.

An attempt was made to apply this procedure to linear polyethylene and ethylene- α -olefin copolymers; however, it was unsuccessful.

The broad melting range of low-density polyethylene has been shown to be a direct result of a wide distribution in crystallite size (1 and 3); thus, as the temperature increases, the less perfect crystals containing the more highly branched species are preferentially melted, followed by the more

TABLE II
Comparison of Calculated and Measured Crystallinities of
Conventional Polyethylenes at Various Temperatures

Polymer	Temp, °C	Crystallinity, %	
		x-ray $\pm 2\%$	calculated
Sample X (mp/102°C)	0	—	70
	24	68	—
	50	59	62
	70	54	52
Sample Y (mp/110°C)	0	—	76
	24	74	—
	50	71	70
	70	65	62
Sample Z (mp/117°C)	0	—	77
	24	75	—
	50	74	72
	70	68	65
Sample 7 ^a (mp/ 113°C)	0	—	49
	25	48	—
	50	45	46
	80	37	37
	110	5.5	5.7
Sample a ^b (mp/108°C)	0	—	52.3
	40	48	—
	60	44	45
	80	36	36
	100	17	15

^a Sample 7 of Reding.²

^b Sample "a" of Charlesby and Callaghan.¹

ordered crystals. Consequently, as the crystals melt, the crystallinity decreases, and it is thought that the wide crystallinity distribution accounts for the exponential decrease of crystallinity as the temperature approaches the melting point. This also explains why this method cannot be applied to high-density polyethylenes which, owing to their linear structure, are capable of crystallizing in a highly ordered fashion that gives rise to materials having a narrow crystallinity distribution and therefore a narrow melting range.

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