Crystallinity of Ethylene–Vinyl Acetate Copolymers

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Synopsis

Determination of crystallinity of ethylene–vinyl acetate copolymers according to the usual x-ray diffraction method employed for polyethylene is very much hampered by the fact that these copolymers are usually largely amorphous and the Bragg reflections in their diffraction diagrams which are therefore broad and weak are drowned by the strong and dominant amorphous halo.   As a consequence it is virtually impossible to carry out a realistic resolution of the total diffraction diagram into the individual Bragg reflections in the halo.   In the method described in this paper this difficulty is successfully surmounted by taking advantage of the unique shape and placement of the amorphous halo with respect to the Bragg reflections in the diffraction diagrams of these copolymers. This rather fortunate situation permits a direct determination of amorphous content without having to take recourse to the cumbersome resolution of the Bragg reflections and hence one can obtain crystallinity indirectly.

Introduction

Crystallinity of polyethylene decreases drastically as comonomer units are introduced in the chains via copolymerization, and if the comonomer level is sufficiently high, the copolymer, in fact, becomes totally amorphous. Since properties like stiffness and clarity of these copolymers are to a large extent governed by their crystallinity, accurate estimation of their crystallinities is a primary requirement in any attempt to establish useful structure–properties correlations applicable to them.

Crystallinity of pure polyethylene (both high- and low-density variety) is commonly determined according to the method of Matthews, Peiser, and Richards.[1]   In essence, the method consists of obtaining a suitable x-ray powder diffraction diagram of the polymer first and then resolving the same into its constituent parts comprising two Bragg reflections (110) and (200), stemming from the crystalline regions in the polymer and a halo arising from the amorphous regions.   The crystallinity is calculated from the relative intensities of the amorphous halo and the Bragg reflections after applying appropriate corrections to take into account geometric factors, the angular dependence of polarization, etc.   The crucial step in this method is the resolving of the composite diffraction diagram into its constituent parts in a realistic manner.   If the polymer is largely crystalline this resolving step is relatively simple and straightforward due to the fact that the Bragg reflections in the diffraction diagram of such polymers are quite

intense and appear distinctly over the comparatively diffuse and less intense background of the amorphous halo. However, if the polymer is largely amorphous, which indeed happens to be the case with the copolymers under discussion, the diagram is dominated by the amorphous halo, and consequently the Bragg reflections which tend to be broad appear drowned in the more intense amorphous background. A realistic resolution of the composite diagram into its three separate constituent parts in the usual manner, therefore, becomes almost impossible. This paper is concerned with a new approach for resolving the diffraction diagram.

Discussion

The copolymers used in these investigations were all based on vinyl acetate as the comonomer and were made by the so-called high-pressure process. Figure 1 shows the manner in which their x-ray diffraction traces change in shape, i.e., how the Bragg reflections get progressively drowned in the background of the amorphous halo as the copolymer becomes richer in vinyl acetate. Employing CuKα radiation the two Bragg reflections (110) and (200), occur at 21.65° (2θ) and 24.08° (2θ), respectively, and the amorphous scattering shows its apparent maximum at around 19.75° (2θ). A notable feature of these diffraction traces is that even though their resolution into the two Bragg reflections and amorphous scattering becomes increasingly uncertain as the comonomer content increases, if we examine these traces carefully two observations stand out in a striking fashion. The first is that in all instances in which the resolution of the diffraction diagram into the amorphous scattering and the Bragg reflections can be made with some degree of certainty (Figs. 1a and 1b) the contribution of the (110) Bragg reflection to the diffraction diagram in the angular region below 19.75° (2θ) is virtually zero, and even as this (110) Bragg reflection broadens out with increase in the vinyl acetate content (Figs. 1c, 1d, and 1e) it is apparent that the diffraction diagram in the angular region below 19.75° (2θ) may, for all practical purposes, be considered as entirely due to the amorphous scattering alone. The second striking observation is that in all instances in which the diffraction diagram consists entirely of amorphous halo (Figs. 1f, 1g, and 1h) the shape of the halo, i.e., the relative angular intensity of scattering does not change to any noticeable degree, even as the vinyl acetate content increases from 45 to 60%. In other words, the shape of the amorphous halo seems to be independent of the composition of the amorphous regions. Quantitative substantiation of this last observation is afforded by the fact that when said amorphous halos are corrected by applying the appropriate Lorentz corrections as shown in Figure 2 (see the broken line) wherein for convenience said correction has been carried out relative to 19.75° (2θ) the ordinate at this 2θ position divides the corrected amorphous halos (see the two shaded areas in Fig. 2) in a constant ratio of 1.84:1.00 in all three instances.

An immediate consequence of the above is that since the area of the portion of the diffraction diagram that lies in the region below 19.75° (2θ) and

a: 0% Vinyl Acetate

RELATIVE INTENSITY

28 26 24 22 20 18 16 14

←—2θ

(a)

b: 10% Vinyl Acetate

RELATIVE INTENSITY

28 26 24 22 20 18 16 14

←—2θ

(b)

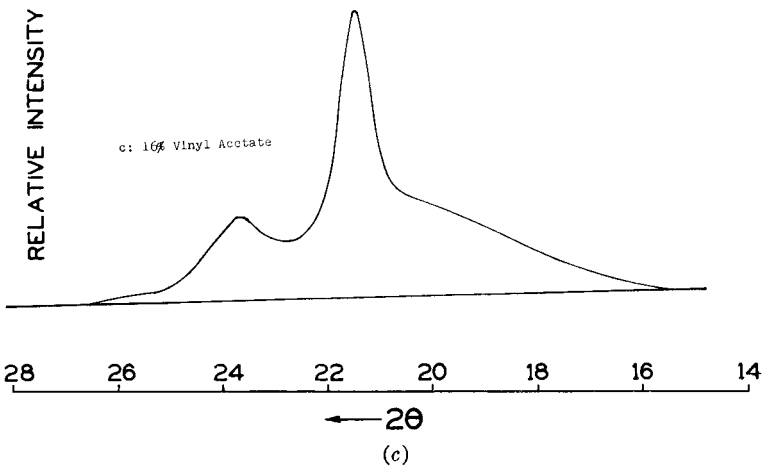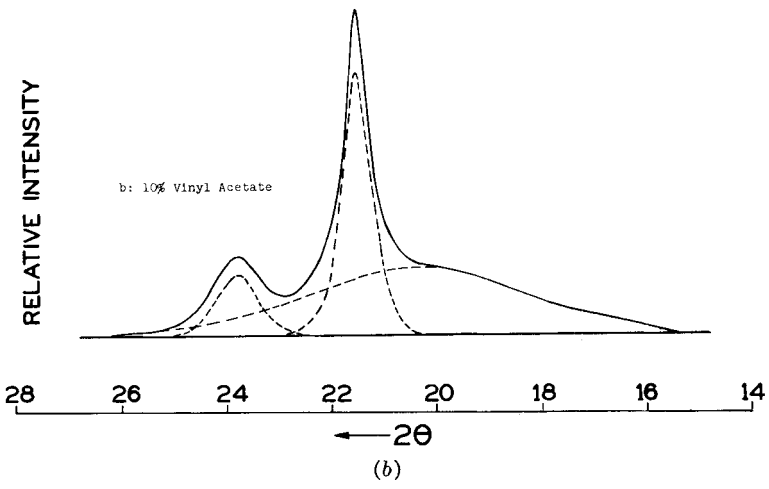c: 16% Vinyl Acetate

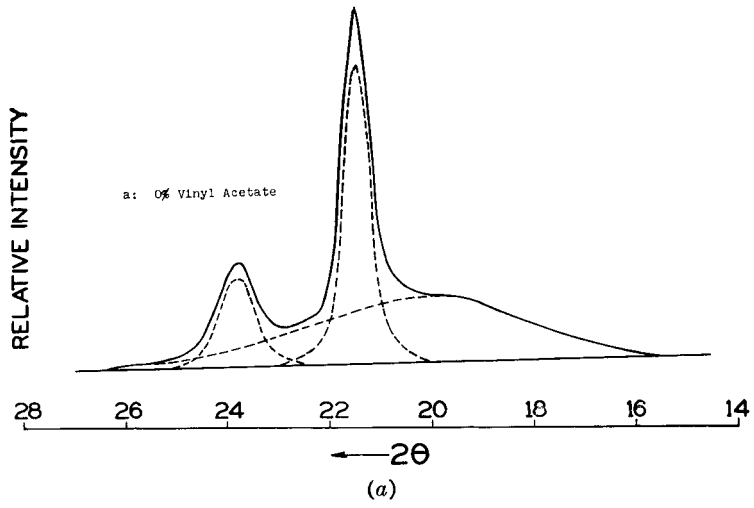RELATIVE INTENSITY

28 26 24 22 20 18 16 14

←—2θ

(c)

Figure 1.   See caption p. 3157.
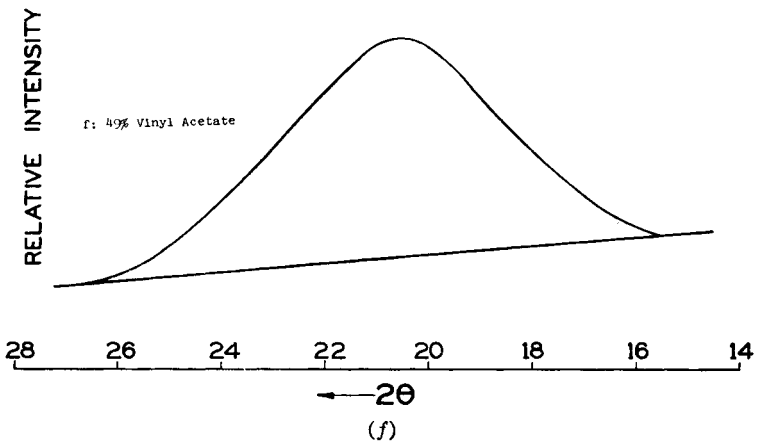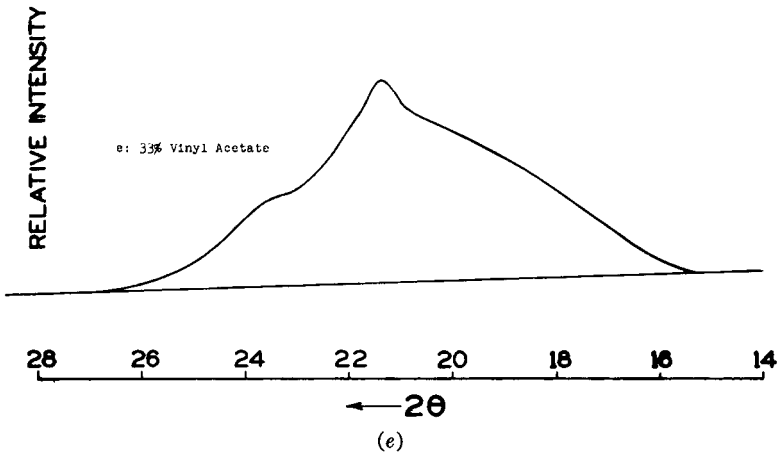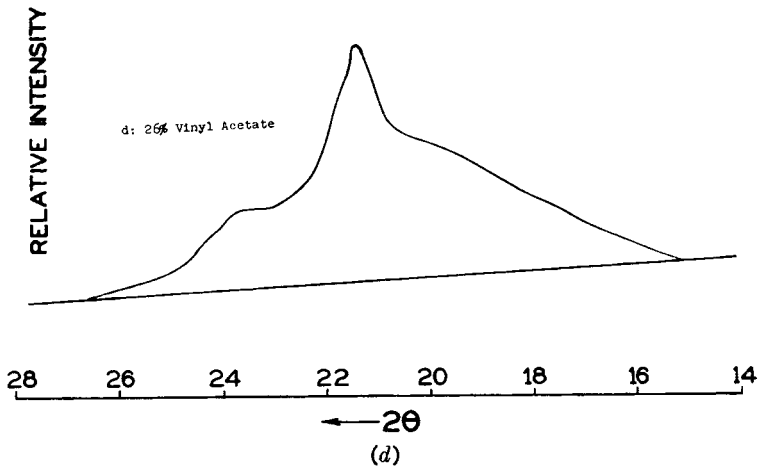
Fig. 1 (*continued*).   See caption p. 3157.

g: 54% Vinyl Acetate

$\longleftarrow 2\theta$

(g)

h: 60% Vinyl Acetate

$\longleftarrow 2\theta$
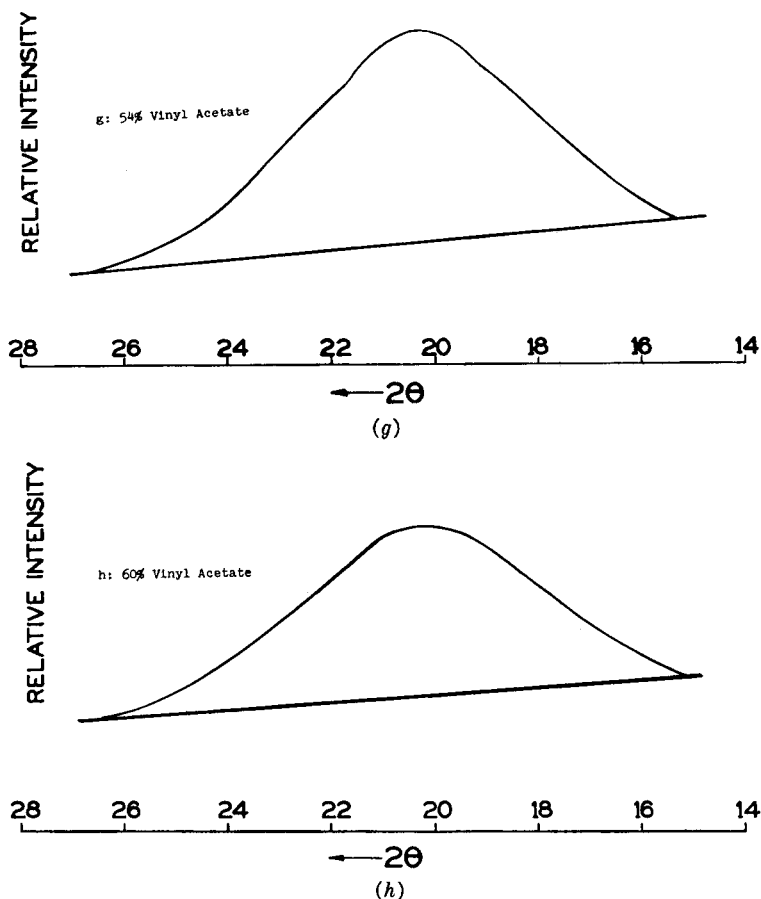
(h)

Fig. 1. Change in shape of x-ray diffraction diagrams of ethylene–vinyl acetate co-polymers with vinyl acetate content: (a) 0%. VA; (b) 10% VA; (c) 16% VA; (d) 26% VA; (e) 33% VA; (f) 49% VA; (g) 54% VA; (h) 60% VA.

which virtually arises from the amorphous scattering alone, is a measurable quantity and this area further represents a constant fraction of the area of the total amorphous scattering irrespective of the comonomer content, one can then readily compute the area of the amorphous scattering in a given diffraction diagram without even attempting to carry out the rather uncertain resolution of the Bragg reflections. In other words, we are in a position to calculate amorphous fraction α of the polymer and hence determine its crystallinity defined as follows:

$$\alpha = K \, A_1 \, 2.84 / A_{\text{Total}} \tag{1}$$

$$\% \text{ Crystallinity} = 100 \, (1 - \alpha) \tag{2}$$

where A_1 is the area of the corrected diffraction diagram in the region below 19.75° (2θ), A_{Total} is the area of the whole corrected diffraction diagram in-
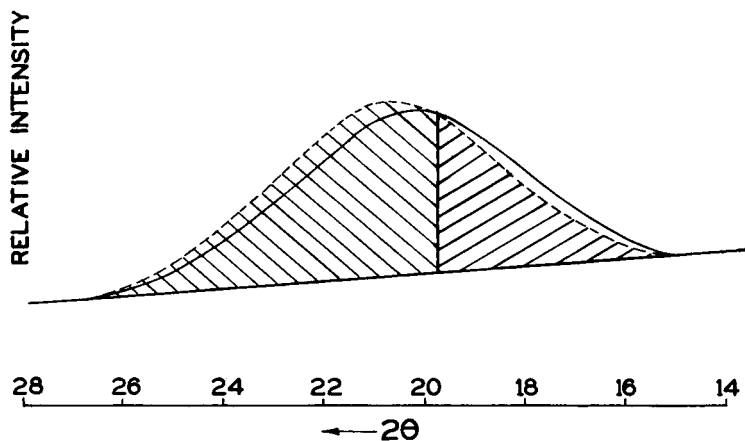
Fig. 2. Resolution of the x-ray diffraction halo according to the new method. ▨ = A_1; ▨ + ▧ = A_{Total}.

cluding the Bragg reflections, and K is a constant that is close to unity. The correction mentioned above refers to Lorentz correction.

The results of analyses carried out in the above manner with four different copolymers representing a fairly wide range of comonomer content are tabulated in Table I and presented graphically in Figure 3. The diffraction diagrams were obtained by using a Norelco diffraction goniometer employing samples approximately 0.8 mm. thick. In these analyses the factor K is assumed to be 1.0. The base lines were drawn following the general procedure of Matthews et al., namely starting from the rather arbitrarily selected point at 15.42° (2θ) position on the diffraction trace and running it tangential to the trace in the 26–27° (2θ) region. An arbitrary choice as above for the starting point of the base lines is necessitated by the fact that the shape of the diffraction trace in the low angle region is such that it is practically impossible to draw a meaningful base line that is tangential at both ends. The areas were measured with a planimeter. The analysis of vinyl acetate in the copolymers was carried out and cross-checked by three independent techniques, namely infrared, NMR, and saponification.

It is clear that the points in Figure 3, even though they are plotted in the simplest way possible, fall on a surprisingly good straight line. It is the

TABLE I
Calculation of Amorphous Fraction in Ethylene–Vinyl Acetate Copolymers

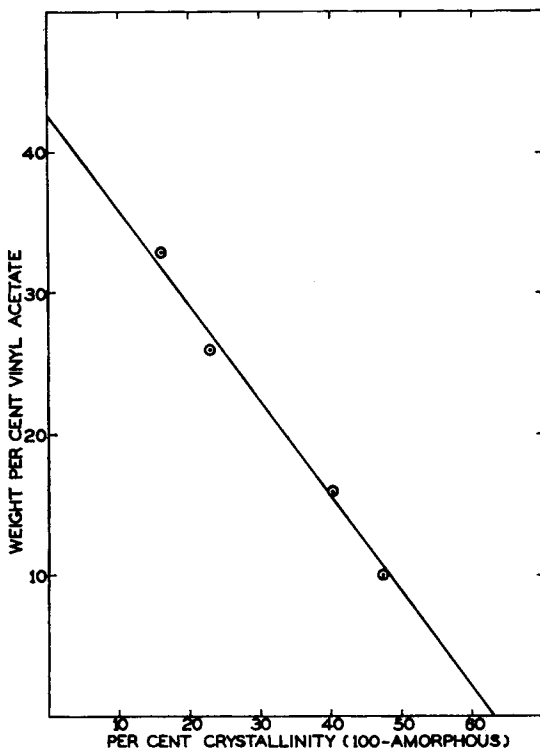| Sample	Vinyl acetate content, wt.-%	A_1, in.^{2}	A_{Total}, in.^{2}	Amorphous fraction
B	10	1.64	8.88	0.53
C	16	3.19	15.07	0.60
D	26	5.30	19.57	0.77
E	33	3.22	10.93	0.84

Fig. 3. Crystallinity vs. vinyl acetate content.

contention of the authors that this observed linearity is not entirely coincidental but that it indeed reflects the soundness of the new approach. The analytical equation corresponding to the line relating crystallinity with vinyl acetate content is:

$$\% \text{ Crystallinity} = 63.0 - 1.47 \times \% \text{ VA} \tag{3}$$

in which $\%$ VA is the weight per cent vinyl acetate in the copolymer. According to eq. (3) the crystallinity of the polymer at zero per cent vinyl acetate content should be 63. The crystallinity of a sample of pure polyethylene made under similar conditions as the copolymers and measured according to the usual method, on the other hand, is 62%, which certainly is excellent agreement. Another interesting prediction of the same equation which may be of some practical value is that the copolymer becomes totally amorphous if vinyl acetate concentration is 43% or over and the observed optical clarities of these copolymers are certainly in good qualitative agreement with this prediction.

Even though the authors have employed this procedure quite successfully to determine the crystallinity of one particular class of copolymers, namely ethylene–vinyl acetate copolymers, there is no reason to believe

that a similar resolution procedure may not prove equally successful in the estimation of crystallinities of other largely amorphous copolymers.

Reference

1. Matthews, J. L., H. S. Peiser, and R. B. Richards, *Acta Cryst.*, **2**, 85 (1949).

Résumé

La détermination de la cristallinité des copolymères éthylèneacétate de vinyle, d'après la méthode de diffraction aux rayons-x, utilisée pour le polyéthylène, est rendue très difficile du fait que ces copolymères sont généralement essentiellement amorphes et les réflecxions de Bragg dans leurs diagram es de diffractions (larges et peu marquées de ce fait) sont noyées dans le halo amorphe, qui lui, est fort et dominant. Par conséquent, il est virtuellement impossible de résoudre les réflexions de Bragg et le halo, dans le diagramme de diffraction. La méthode décrite dans cet article, surmonte cette difficulté grâce à la forme unique et à l'emplacement du halo amorphe par rapport aux réflexions de Bragg dans les diagrammes de diffraction de ces copolymères. Cette situation avantageuse permet la détermination directe du contenu amorphe sans recourir à la résolution fastidieuse des réflexions de Bragg et par conséquent le cristallinité s'obtient indirectement.

Zusammenfassung

Die Bestimmung der Kristallinität von Äthylen-Vinylacetatkopolymeren nach der üblichen, für Polyäthylen verwendeten Röntgenbeugungsmethode wird sehr stark durch die Tatsache behindert, dass diese Kopolymeren gewöhnlich weitgehend amorphs ind und die Braggschen Reflexionen in ihrem Beugungsdiagramm, die aus diesem Grund breit und schwach sind, durch den starken und vorherrschenden amorphen Ring überdeckt werden. Es ist daher praktisch unmöglich, eine realistische Auflösung des Gesamtbeugungsdiagramms in die individuellen Bragg'schen Reflexionen und den Ring durchzuführen. Bei der in der vorliegenden Mittelung beschriebenen Methode wird diese Schwierigkeit dadurch überwunden, dass man sich der besonderen Gestalt und Lage des amorphen Rings in Bezug auf die Bragg'schen Reflexionen im Beugungsdiagramm dieser Kopolymeren bedient. Diese günstige Situation erlaubt eine direkte Bestimmung des Gehalts an Amorphem ohne dass man zur mühsamen Auflösung der Bragg'schen Reflexionen Zuflucht nehmen muss; man kann daher indirekt die Kristallinität erhalten.