

X-Ray Determination of Crystallinity in Poly(ethylene Terephthalate)

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Synopsis

Three recently published x-ray methods for determining the crystallinity of poly(ethylene terephthalate) are discussed and compared with density and infrared methods. The effect of crystallite size is shown to account for most of the disagreement among the several methods. A short method of estimating crystallinity from x-ray diffraction, suitable for counting techniques and requiring only two measurements, is presented and compared with the density method.

The crystallinity of poly(ethylene terephthalate) (PET) has been extensively studied not only because of the outstanding commercial utility of this polymer but also because wide variations in crystallinity are easily accomplished and maintained. The degree of crystallinity can be estimated from x-ray diffraction, density, and infrared-absorption measurements. Intercomparison among these methods often leads to widely different conclusions regarding their relative validity. This paper attempts to account for these differences and offers a simplified alternative method for estimating crystallinity from x-ray diffraction.

Recent Work on the Crystallinity of PET

The disagreement in interpretation of different PET crystallinity measurements can be illustrated by quotations from three recent papers. Statton¹ concludes that using the x-ray ". . . crystallinity index. . ." and comparing results with density the results are scattered greatly. . . . Thus, the density determination of crystallinity is very definitely hazardous." Johnson,² however, finds that "Evidently there is a linear relationship between the specific volume and the x-ray crystallinity within the limits of the data. . . . The reliability, at the 95% confidence level, of estimating the specific volume from a single x-ray crystallinity measurement is ± 0.003 units." Farrow and Preston³ conclude that "There is no correlation between the crystallinity so determined (by x-rays) and that calculated from the density of the yarn." All of these authors imply that the x-ray measurements are inherently superior to density. The three x-ray methods are discussed briefly below.

Statton's method^{1,4} is perhaps the most straightforward, in that esti-

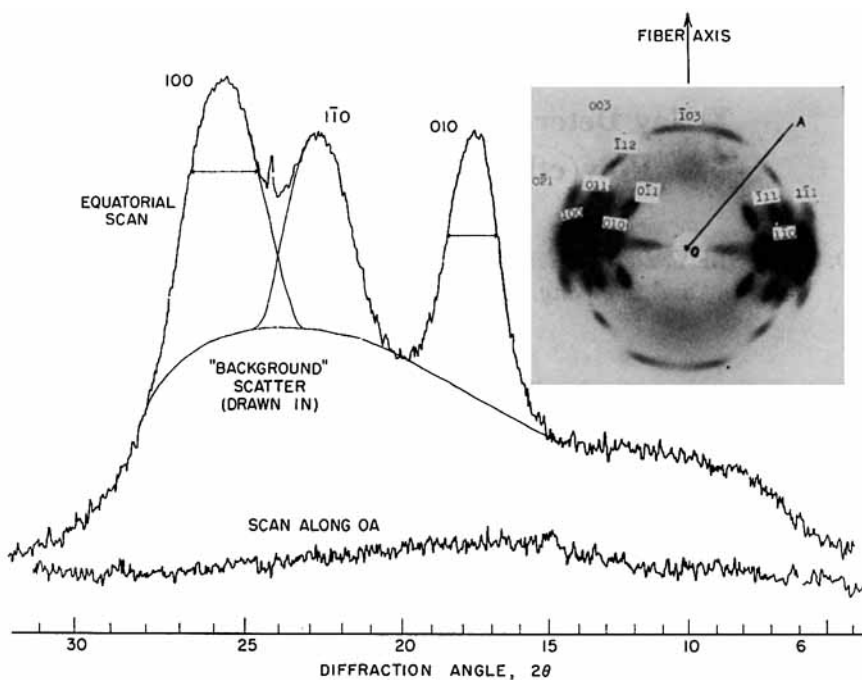


Fig. 1. X-ray diffraction pattern of PET showing principal spots. Indices are located above the corresponding spot. Densitometer traces are along the equator and across the amorphous halo as indicated.

mation of absolute crystallinity is not attempted. X-ray diffraction patterns are recorded on the most "amorphous" and the most "crystalline" samples obtainable, and these are taken as standards of zero and 100 "crystallinity index." The pattern of an "unknown" sample is compared with the standards by measuring the diffracted energy at several angles and interpolating intensity of the unknown between the intensities of the standards. (Implicit in this procedure is that oriented specimens be somehow randomized prior to the diffraction measurement.)

Johnson's procedure² is based on resolution of the radial intensity distribution of scattered x-rays into crystalline and amorphous contributions. His method employs counting rather than photographic techniques. The total area under the diffraction curve is divided, by means of a set of simultaneous equations, into the desired crystalline and amorphous contributions. The details of this method are difficult to describe, because of certain inconsistencies between the analysis and the actual diffraction patterns. The mathematical analysis is based upon the existence of only three diffraction spots, as are observed in the equatorial intensity distribution of scattering from an oriented fiber (Fig. 1). Indices of these spots, in order of increasing diffraction angle, are given as 100, 010, and $1\bar{1}0$, and attributed to the paper of Daubeny and Bunn,⁵ where, however, these reflections are identified as 010, $1\bar{1}0$, and 100. (Johnson's indices are those

of Astbury and Brown's proposed unit cell, which was shown to be incorrect.⁵) A more serious inconsistency in Johnson's method is that by rotating the sample during counting, some seventy reflections contribute to crystalline scattering at different angles.⁵ Apportionment of intensity among three symmetrical peaks and assigning correction factors to these peaks are therefore entirely arbitrary. Although the data are used to calculate a weight-per cent crystallinity, the method can only be regarded as an empirical one whose virtue must derive from its results.

Farrow and Preston³ have described another procedure for calculating percentage x-ray crystallinity. Diffraction of monochromatized x-rays by a mechanically randomized sample is photographed. The densitometer trace of the radial intensity distribution is separated into areas assigned to amorphous and crystalline scattering. The amorphous-scattering curve is constructed by proportionally reducing the scattering curve of a completely amorphous sample until it matches the observed intensity at one or two particular diffraction angles.

Discussion

Examination of some of the assumptions in the above methods will help to clarify the differences in conclusions. The calculation of "per cent crystallinity" implies a division of matter within the polymer into uniquely defined crystalline and noncrystalline phases. Disadvantages of such definition were recognized by Statton by use of the term "index" rather than "per cent." His method, however, defines two phases uniquely by assuming that the radial diffraction intensity distribution of an arbitrary sample is the weighted sum of the intensity distributions from particular amorphous and crystalline standards. A more serious disadvantage of dividing the polymer into crystalline and amorphous phases is the difficulty of establishing an unequivocal demarcation between them. There the x-ray methods, and indeed all methods, break down. The major limitation of x-ray methods is the resolution of small or imperfect crystallites, which leads to line broadening. The diffraction line width increases rapidly with decreasing crystallite size or perfection. Lumping both effects together as effective "size," and with $\text{CuK}\alpha$ radiation (as used by Statton, Johnson, and, presumably, Farrow and Preston), one calculates^{6a} that the half-maximum widths of the principal reflections, for crystallites having linear dimensions of 20–30 Å., are as great as the peak-to-peak separations, excluding instrumental broadening. By the criteria of Farrow and Preston and Johnson, crystallites of this size or smaller (corresponding to four or five repeat units in the h or k direction) would be defined as amorphous. Density, of course, would recognize such material as crystalline, and, as observed by Farrow and Preston, gives a higher value of per cent crystallinity.³ The proportional effect is greatest, as expected, in samples of low crystallinity where small crystallites would be more predominant. Another consequence of assigning small-crystallite scattering to the amorphous phase is that the radial distribution function will

probably be altered so that proportional reduction of unresolved background to a pure-amorphous scattering curve would be questionable. Furthermore, the radial intensity distribution from noncrystalline material has been shown to depend on interatomic spacing^{6b} so that the assumption of a constant amorphous-scattering contour is not consistent with the postulated variations in noncrystalline density.³

The magnitude of the small-crystallite effect can be appreciated by analyzing the intensity distribution of an x-ray diffraction pattern (Fig. 1). Two densitometer traces, along the equator and about 40° off the equator, are shown. (The pattern in Fig. 1 is not the one scanned; it was selected to show a greater number of reflections.) Scattering from noncrystalline material is not oriented, as pointed out by Statton¹ and as any good pattern of stretched rubber will show. An x-ray pattern showing orientation not resolved into discrete spots (oriented halo) is sometimes attributed to oriented amorphous material. However, moderate orientation, without crystallization, does not orient the amorphous halo,⁷ and sufficiently small crystallites would necessarily give an "oriented halo" pattern. Therefore, it seems preferable to assign oriented x-ray scattering to crystallites and regard an "oriented halo" as an extreme consequence of small-crystallite line broadening. With such a definition, the trace along OA represents true amorphous scattering. The background drawn in beneath the discrete equatorial scattering is substantially greater than this, and, although it is caused by a truly crystalline phase, it is the overwhelming contribution to what has been regarded as amorphous scattering in the procedures discussed above. Randomization or rotation of the sample will add somewhat to the resolved crystalline intensity, but a major contribution from unresolved-crystallite scattering will remain, which qualitatively accounts for density versus x-ray discrepancies.

In addition to x-rays and density methods, infrared absorption has been used to estimate crystallinity of PET. The infrared methods are based on absorption bands assigned to *trans* or *gauche* conformations of the glycol linkage.⁸⁻¹⁰ The crystalline conformation has been shown to be *trans*.⁵ Therefore, infrared methods would recognize a single *trans* repeat unit as being crystalline. A single repeat unit is the smallest "crystallite" that can be imagined, and one would expect infrared crystallinity estimates to be quite high, even higher than density estimates, and particularly for oriented fibers. This is observed,⁹ although a good correlation can be obtained with unoriented PET films.⁸ Density and infrared estimates of crystallinity tend to converge as orientation decreases.⁹

The distinction as to what is crystalline is highly arbitrary, although the concept is qualitatively well understood. There has been a tendency to compare any measurement with x-ray methods since x-ray diffraction is the *sine qua non* of polymer crystallinity; however, severe difficulties of interpretation arise in deciding how crystalline crystallinity must be. The philosophy of Statton seems most reasonable and requires only that the method be operationally precise and give larger numbers when the property

qualitatively understood as crystallinity increases. His insistence on the term "crystallinity index" is well grounded.

Much argument, both interesting and useful, is possible over the relative merits of different methods of estimating polymer crystallinity. However, no unique division of phases exists within the polymer, and crystallinity values derived from a particular procedure signify only the response of the polymer to the imposed conditions. Rather than say that one method is "better" than another, one should say it is "different." The most that can be expected of a crystallinity determination is that it show changes associated with treatments that change other properties associated with crystallinity (opacity, shrinkage, etc.). Other desirable features would be convenience and precision. For PET, density satisfies these requirements outstandingly. Johnson's results show that density agrees with a particular x-ray method; the disagreement observed by Farrow and Preston results from the obvious reasons pointed out above. Because of our close association with Statton's laboratory, we have had occasion to use his crystallinity-index method, and have never observed significant reproducible disagreement with density determinations, except in well understood cases as those mentioned in the next paragraph. Quite apart from the fact that it correlates with x-ray crystallinity, density has the great advantage of being a primary measurement that can be easily reproduced in different laboratories with a precision of about 1% (of the maximum observed range) using inexpensive, and thus widely available apparatus. It is doubtful if different x-ray diffractometers could be set up to give comparable agreement using any of the methods so far described.

For some purposes, an x-ray method of determining crystallinity of PET is desirable, e.g., where obvious inaccessible voids exist within the polymer or in the presence of significant amounts of copolymers, delusterants, or other additives whose effects on density have not been established. Recognizing that any measurement is more-or-less arbitrary, a simple x-ray procedure can be developed consistent with the primary assumption of present methods.

Simplified X-Ray Crystallinity Method

A basic postulate of all x-ray methods is that the scattering efficiencies to x-rays of the crystalline and amorphous regions are the same. This statement should be further qualified by stipulating that the orientation of crystalline material present must be sufficiently randomized that all diffractions are equally probable. Experimentally, such a condition may be difficult to attain. Diffraction from a single crystal can vary widely depending on its orientation relative to the incident beam; for this reason (planar) oriented films of PET are unsuitable for x-ray crystallinity determinations, as some reflections are completely absent. Other, more fundamental theoretical objections to this assumption have been raised.¹¹ Nevertheless, the assumption is usually made, and probably can be adequately satisfied by good randomization of the sample. A second postulate

is that the polymer exists as two definite phases, crystalline and amorphous, each scattering in its characteristic pattern. Statton's method assumes that scattering from any sample can be described as a weighted sum of the two. Johnson's and Farrow and Preston's methods assume that amorphous scattering is invariant but would allow variations in line profiles (except asymmetry in Johnson's) of crystalline scattering. If these two assumptions were true, the total radial intensity distribution of scattered radiation from a fixed weight of any sample would have a constant value, while the function, i.e., the shape or profile of the scattering curve, would vary with the degree of crystallinity. Curves representing different degrees of crystallinity, when superimposed, would therefore cross, and would cross at the same points. In other words, at any diffraction angle where scattering intensities from amorphous and crystalline material are equal, the intensity diffracted by a fixed amount of material would not vary with the degree of crystallinity.

Ideally, at any diffraction angle the intensity will vary linearly with crystallinity. Once calibrated, a single such measurement could be converted to crystallinity. In practice, variations in experimental conditions prohibit this simplicity; and in the methods described above, the entire curves are integrated in one way or another to allow for inter- or intra-comparison. Once the total diffracted intensity is established, then the adjusted intensity at any angle would be expected to vary simply with crystallinity. This is the essence of Statton's method, except that results obtained at a number of points are averaged. A similar method for determining the crystalline fraction in isotactic polystyrene has been proposed that is based, in its simplest form, on the diffraction intensity at a single angle. The experimental procedure requires, however, that the sample thickness and beam intensity be normalized by separate measurements.¹²

Now the basic postulates cited above are not true, and in general the scattering cannot be attributed to two distinct phases. Fortunately, however, the required conditions happen to be closely fulfilled for PET at one diffraction angle: in working with Statton's crystallinity index method, we have found that diffraction at 2θ of about 28.5° is nearly independent of the crystallinity of the sample. Intensity at this point can be used as a reference measure of amount of diffracting material, primary beam intensity, etc., analogous to a "thickness band" in infrared. As a crystallinity measurement, the scattering at $2\theta = 25.6^\circ$, the 100 diffraction peak, can be used. This is equivalent to selecting the point that, in Statton's method, carries the most weight in determining the slope of his index line. Additional advantages of using this point are that it depends on a structure that almost everybody would agree is crystalline, and, being located at a peak, would be less affected by crystallite-size differences.

The possibility of using such a two-point index was discovered with photographic methods; however, the difference in intensity between the two points is usually too great to be accommodated on one film. The

method is ideally suited to counter techniques, and it was investigated as described below.

PET as unoriented film and drawn fiber was subjected to various heat treatments in order to develop different degrees of crystallinity. The samples were mounted in a holder designed to cover a 0.5-in. circular open space with about 0.020 in. thickness of sample and which could be fitted into a rotating mount. Nickel-filtered copper radiation was provided by a Norelco x-ray diffractometer, collimated with 1° slits and detected by a scintillation counter. Samples were rotated at 47 rpm. The diffracted energy was scanned at $1^\circ/\text{min.}$ from $2\theta = 10^\circ$ to 36° for purposes of normalization, and measured by fixed count at 26° (the observed location of the 100 maximum) 28° , 28.5° , and 29° . Scanned curves, normalized to equal integrated intensity to account for differences in scattering material, were replotted. The normalized intensities of all curves were nearly equal at $2\theta = 28.6^\circ$. Fixed-count measurements in the region $28\text{--}29^\circ$ were then plotted and the expected values at 28.6 interpolated. Routinely, only fixed counts at 28.6° and 26° (with this instrument) would be needed.

A crystallinity index was calculated from the fixed-count measurements at 28.6° and 26° following the ideas of Statton. The intensity ratio $I_{26}/I_{28.6}$ was calculated for each sample. This normalizes the 26° scattering for experimental variations. The value of this ratio was assigned indices zero and 100 for the most amorphous and most crystalline samples available. For samples of intermediate crystallinity, indices were calculated proportionately. Results are given in Table I and plotted in Figure 2. A reasonable correlation exists between this index and density, both measurements increasing with temperature of heat treatment as expected. Only single x-ray measurements were made with each item, and the scatter can be taken as an indication of the probable accuracy of the method (assuming perfect linearity with density). Counting rates were not corrected for background scatter.

A significant deviation from linearity is apparent at low crystallinity. This is the deviation expected from small crystallites present in oriented

TABLE I
Two-Point Crystallinity Index

Sample	Heat treatment	$100 \left(\frac{I_{26}}{I_{28.6}} \right)$	Index	Density
Film	None	140.2	0	1.3380
Film	245°	269.5	100	1.4339
Film	240°	252.5	86.8	—
Yarn	None	159.8	15.1	1.3660
Yarn	83	155.8	12.0	1.3615
Yarn	95°	167.2	20.9	1.3699
Yarn	160°	189.2	37.9	1.3925
Yarn	180°	203.0	48.5	1.3964
Yarn	194°	185.8	35.2	1.3859
Yarn	200°	213.3	56.5	1.4000

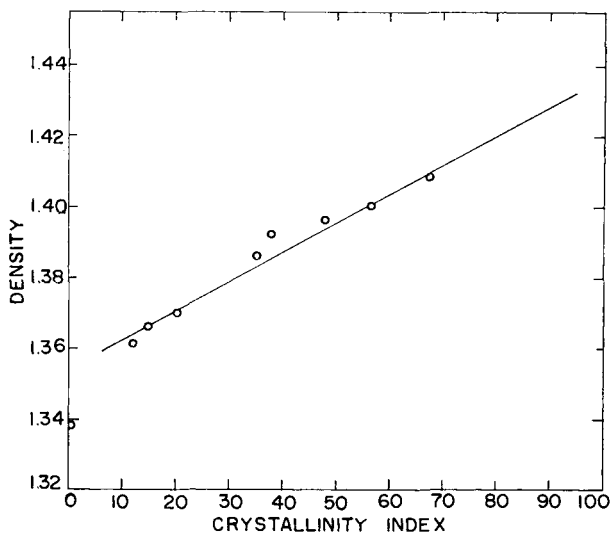


Fig. 2. Relationship between density of PET and crystallinity index derived from x-ray diffraction at two angles.

fibers, which are detectable by density effects but not by x-ray diffraction. There is, in addition a difference in x-ray scattering behavior of the un-oriented film and oriented fibers, together with a slight effect of delusterant. All fibers lay perpendicular to the primary beam; rotation in this plane is substantially equivalent to randomization.

This two-point index method of estimating crystallinity of PET by x-ray diffraction is probably the ultimate in simplicity, containing only the minimum requirements of a randomizing operation, normalizing measurement, and a crystallinity measurement. Calculations are easily made with a slide rule. Although the numbers reported here are based on "standard" samples, this is purely arbitrary, and all necessary data can be obtained from a single sample. The scale could be adjusted to give closer agreement with per cent crystallinity from density if desired.

Conclusions

Crystallinity of high polymers is not a well-defined property, and no method can logically claim superiority. Desirable features of any method are precision, convenience, and correlation with polymer properties associated with the concept of crystallinity. Among methods proposed for PET, density satisfies these requirements best. Estimation of crystallinity by x-rays can be made by a simplified procedure requiring only two measurements, and which is consistent with the assumptions required for any x-ray measurement. Elaborate experimental refinements and calculations, while of great value in measuring specific details of polymer crystalline structure, cannot be justified on the basis of accuracy in determining an absolute per cent crystallinity.

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Résumé

On discute trois méthodes aux rayons-X publiées récemment pour la détermination de la cristallinité du poly-(éthylène téréphthalate) et on les compare avec les méthodes de densité et les méthodes à l'infra-rouge. On a montré que les effets de la grandeur du cristal sont responsables des écarts entre les différentes méthodes. On décrit une méthode rapide pour l'estimation de la cristallinité par diffraction des rayons X utilisant la technique des comptages et exigeant seulement deux mesures. Cette méthode est comparée à celle des densités.

Zusammenfassung

Drei kürzlich veröffentlichte Röntgenstrahlenmethoden zur Bestimmung der Kristallinität von Poly(äthylen-terephthalat) werden diskutiert und mit Dichte- und Infrarotmethoden verglichen. Der Einfluss der Kristallitgröße kann für die meisten Unstimmigkeiten zwischen den einzelnen Methoden verantwortlich gemacht werden. Ein Kurzverfahren zur Bestimmung der Kristallinität aus der Röntgenbeugung, das für Zählverfahren geeignet ist und nur zwei Messungen erfordert, wird angegeben und mit der Dichtemethode verglichen.

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