

Contribution to the Problem of Crystallinity Determination in Poly(ethylene Terephthalate)

Interlayer Spacings

The d spacings of two major diffraction peaks, 100 and $\bar{1}10$ (assignments of Daubeny et al.¹), have been determined for a series of poly(ethylene terephthalate) (PET) specimens of varying crystallinities. The specimens were prepared by isothermally annealing melt-quenched PET for extended periods of time in the range 80–245°C. in a vacuum oven.² This determination was prompted by the observation of an apparent trend toward higher angles of the 100 maxima of the diffractograms of these specimens with increasing annealing temperature. Bosley³ seems to have made a similar observation since he had routinely taken the fixed counts of his two-point crystallinity index, which is based upon the 100 maximum of PET, at 26.0° (2θ) rather than the 25.7° angle one would expect from the unit cell of Daubeny et al. The variation of these spacings with annealing temperature is shown in Figure 1. (The measured 100 spacing of a specimen of commercial fiber compares favorably with that calculated from the unit cell, while the measurement of the same spacing of specimens of commercial biaxially oriented film, which had been annealed at 100 and 200°C. for 72 hr., matches the unoriented data of Figure 1 at the respective temperatures.)

The interplanar spacings were determined by the fit of a parabola to three points (time for 100,000 counts) method used on the broad martensite diffraction peak for the measurement of residual stress.⁴ The Lorentz and polarization corrections used are those of the Debye-Scherrer method as given by Klug and Alexander.⁵ Nickel-filtered copper radiation was used in a standard diffractometric flat (powder) sample procedure. The calibrating standard was reagent-grade sodium chloride,⁶ $400 < \text{mesh} \leq 325$.

While measured interplanar spacings (especially those taken at low angles and for a triclinic crystal) are not directly comparable with those calculated from lattice constants the differences shown in Figure 1 are of such a magnitude as to cast doubt upon the appli-

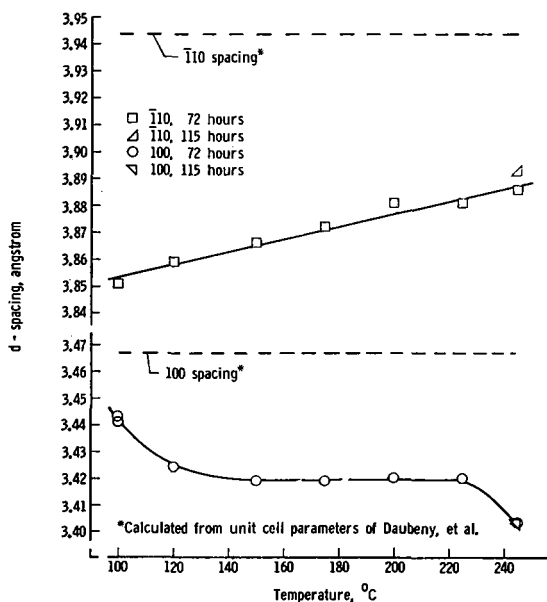


Fig. 1. Change of spacing with isothermal annealing temperature.

capability of a unit cell derived from oriented fiber to the unoriented bulk material. The postulation of a more dense ideal crystal for the bulk polymer would result in changes in the right direction for bringing Farrow and Ward's⁷ crystallinity by density (for unoriented film) data into better agreement with their crystallinity by x-ray data. Kilian et al.,⁸ have, in fact, calculated a crystalline density of 1.495 g./cm.³ for bulk PET. The measurement of the 100 spacing of Figure 1 extrapolates smoothly to the value (3.40 Å.) reported by Kilian et al.,⁸ for a specimen of PET heated at 253°C. for 8 hr. These workers, however, obtain a different value (3.46 Å.) for temperatures up to 200°C., presumably due to shorter annealing times. The higher the temperature above 200°C. the closer the two data sets. The $\bar{1}10$ and 100 spacings of Figure 1 approach the calculated spacings of Astbury and Brown's⁹ unit cell (010 and $\bar{1}10$, respectively) at the higher temperatures.

X-Ray Crystallinity Indices

Due to the difficulties involved in the absolute separation of x-ray scatter into crystalline and amorphous contributions, various index procedures, in which certain measurements are interpolated between the same measurements for amorphous and crystalline standards, have evolved.^{3,10,11} These procedures are operationally fixed, that is, they involve measurement of x-ray intensity at specified angles (2θ). One of these fixed point methods (crystalline two-point) is based upon the maximum of the fairly sharp 100 diffraction peak of PET,³ which has been shown to shift to higher angles with increasing annealing temperature. It would seem that the fixed-point estimation of the maximum is actually measuring portions of the peak's shoulder for certain specimens. There is another index type method in which an estimate of the per cent amorphous character is based upon the intensity of a point at some low angle portion of the gently varying glass curve.¹² This amorphous two-point method is of interest because it requires only one standard and because it appears to be more insensitive to minor misalignment of the powder sample to the diffractometric axis than a measurement based upon a peak maximum.

In order to compare the amorphous two-point index and the crystalline two-point index (corrected for peak shifting) with previously determined indices,³ these two indices were calculated from intensity data taken at every 0.3° interval in the angular range, $2\theta = 10.0$ – 34.0 (average of the three closest of five 10-sec. counts), for the series of melt quenched PET specimens. In the present use of the amorphous two-point index, the intensity at 13.9° is taken as the estimate of the amorphous contribution and the samples are normalized for mass^{3,12} by division by the intensity at 28.6°, both intensities being corrected for background by subtraction of the background intensities at the specific angles as calculated by linear interpolation of the intensities at 10.0° and 34.0°. (The background correction is necessary.) The crystalline two-point method was corrected by

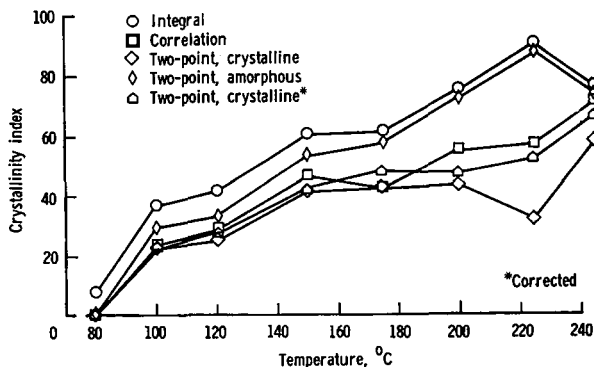


Fig. 2. Comparison of crystallinity index calculations.

using a Fortran IV computer program to: (a) multiply the intensity at each angle by its appropriate Lorentz and polarization correction; (b) search for and determine the maximum of the set of 81 points plus a point on either side of the maximum; (c) calculate by the three-point parabolic method⁴ the angle of the maximum of the curve which contains the three points; and (d) by using the previous information, calculate the intensity at this angle. The equation of the least-squares fit of the data in the range, $2\theta = 28.0 - 34.0^\circ$, to the general cubic polynomial is then used by the program to calculate the intensity of the mass related peak at $2\theta_{\max} + 2.6^\circ$ (following Bosley³). Background related corrections, like the one used for the amorphous two-point data, were found to be effective for the higher temperature specimens but produced erratic results for the lower temperature data.

The newly calculated amorphous two-point and corrected crystalline two-point indices are compared with the previously determined² correlation, integral, and crystalline two-point indices on Figure 2. The data appear to split into the groups: (a) integral and amorphous two-point, (b) correlation and crystalline two-point, corrected and uncorrected. The integral and correlation indices, which are based upon all 81 points in the angular range, seem to be measuring different aspects of the polymer's constitution and thus yield different crystallinities.¹⁰ The corrected crystalline two-point index matches the correlation in a more precise manner than the uncorrected, but at the cost of its utility. The amorphous two-point index is particularly appealing (at least for melt quenched specimens) in view of its simplicity, operational ease, and the fact that it and the integral display the maximum which one would expect on kinetic grounds.^{13,14} Kilian et al.⁹ report that PET reaches its maximum crystallinity when annealed at 230°C .

It had been hoped that the *d*-spacing measurements would lead to an estimate of crystallinity with an absolute bound. Such does not appear to be the case, although the 100-spacing angles vary somewhat like the indices. The method of determining crystallinity is still a matter of personal choice.

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