Observations from an X-Ray Diffraction Study of Poly(ethylene Terephthalate) Film and Fiber

INTRODUCTION

With an increasing interest in semicrystalline polymers as tough composite matrix materials, poly(ethylene terephthalate) (PET), a thoroughly studied semicrystalline polymer, was selected as a model system for the development of a characterization methodology for future polymers with controlled crystallinity. Structural information such as unit cell dimensions and the position of polymer chains within cell geometry is important to thinking about crystallinity and the physical changes involved in the modification of this parameter.

A currently accepted unit cell for PET, derived from an X-ray diffraction study of drawn fibers, is that of Daubeny, Bunn, and Brown[1] and has yielded the following lattice parameters (DBB cell):

$$a = 4.56 \text{ Å}, \quad b = 5.94 \text{ Å}, \quad c = 10.75 \text{ Å}, \quad \alpha = 98.5°, \quad \beta = 118°, \quad \gamma = 112°$$

Another structural study of this polymer, based upon electron diffraction of uniaxially stretched film, is that of Tomashpol'skii and Markova[2] and has yielded the following lattice parameters (TM cell):

$$a = 4.52 \text{ Å}, \quad b = 5.98 \text{ Å}, \quad c = 10.77 \text{ Å}, \quad \alpha = 101°, \quad \beta = 118°, \quad \gamma = 111°$$

Both cells are assumed to be in space group $P\bar{1}$ and to have the aromatic nucleus essentially parallel to the (100) plane. The densities corresponding to the above lattice parameters are, respectively, 1.457 and 1.477 g/cc. In addition to the earliest cell, of a different orientation,[3] there are at least two other published unit cells for PET,[4,5] both having densities above 1.5 g/cc, which, because of the specimens upon which they are based, are not thought to be pertinent to the present work.

The 100 spacing is the most intense reflection of an X-ray diffractogram of PET as would be supposed from the positioning of the contents of the unit cell. The intensity of this spacing has been used as the basis of a method for crystallinity determination.[6] In wide angle X-ray scattering measurements of film and bulk resin this spacing has been observed[6–9] to occur at higher angles ($2\theta \geq 26.0°$) than one would expect from calculations using the generally accepted unit cell.[1] Similar measurements for the fiber[8,10,11] have not shown this trend, the spacing generally occurring at $2\theta \leq 25.7°$. (CuK$_\alpha$ radiation used in all cases.) On the basis of these published discrepancies, it was decided to measure the d spacings for commercial film and fiber and compare them with those calculated from the two unit cells.

ANALYTICAL

The methods of determining the angular position of a crystalline reflection vary from drawing sloping lines on a recorder chart to curve fitting of intensity data such as the three-point fit to a parabola used in residual stress measurements[12] and the multipoint fit to a linear combination of Gaussian and Cauchy functions as used to resolve multipeak data in the X-ray analysis of polymers.[13] The mathematical formulation for describing each crystalline reflection in terms of three parameters (intensity, 2θ position of peak maximum, and width at $\frac{1}{2}$ maximum) and the representation of paracrystalline scatter in terms of a third-degree polynominal as presented in the past reference[13] was incorporated into a computer program which solves a system of nonlinear equations in the least-squares sense, utilizing Levenberg–Marquardt and Gauss algorithms.[14] This program was used to resolve X-ray diffraction data into seven crystalline reflections for PET film and three reflections for PET fibers. The paracrystalline contribution was also computed for each case.

X-ray diffraction data was taken for thermally annealed commercial film and commercial PET fiber in the form of 100-s counts every 0.1 deg in the range $2\theta = 12$–$32°$. Copper radiation was used with an X-ray diffractometer with a flat sample holder and a graphite monochromator. The data is presented as the envelope over the resolved peaks in Figures 1 and 2 for film and fiber, respectively.
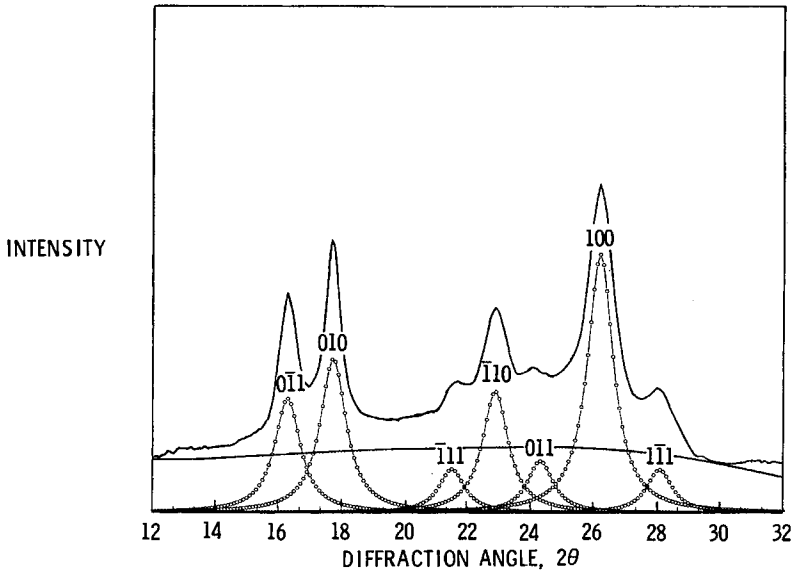
Fig. 1. Resolved crystalline reflections for PET film.

The paracrystalline contribution is represented by the solid curve under the envelope, cutting across the labeled crystalline peaks, which are plotted in circles. The assignments of indices are from the earlier DBB cell,[1] but are equally valid for both. The peak resolution then amounted to solving 201 nonlinear equations in 25 unknowns for the film and 13 unknowns for the fiber. The resolution of the various peaks is relatively insensitive to the initial estimates, either converging to the same solution from various estimates, or, if the initial estimate is too far removed, not converging to a solution.

The measured spacings for both fiber and film, as derived from the computer resolution of the X-ray data, and the calculated spacings from the two published unit cells are presented in Table I. The geometry of the diffraction experiment and the orientation of the fiber limited the measured
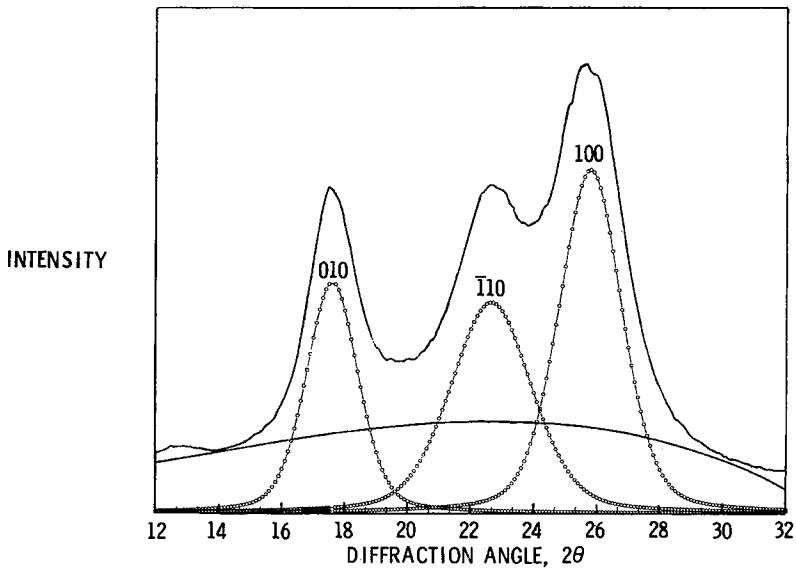

Fig. 2. Resolved crystalline reflections for PET fiber.

TABLE I
Measured and Calculated Interplanar Spacings

hkl	d_{hkl}[a]	d_{hkl}[b]	d_{hkl}[c]	d_{hkl}[d]
0$\bar{1}$1	5.43	5.51	—	5.40
010	5.01	5.03	5.04	5.06
$\bar{1}$11	4.11	4.12	—	4.17
$\bar{1}$10	3.89	3.92	3.93	3.94
011	3.66	3.69	—	3.78
100	3.40	3.42	3.45	3.47
1$\bar{1}$1	3.18	3.18	—	3.20

[a] Measured, film (Å).
[b] Calculated, unit cell of Tomashpol'skii and Markova.[2]
[c] Measured, fiber.
[d] Calculated, unit cell of Daubeny, Bunn, and Brown.[1]

fiber spacings to those characterized as hk0. It is immediately obvious that the measured film spacings (with the exception of the 0$\bar{1}$1 spacing) are closer to those of the TM cell, while those of the fiber are intermediate between the spacings calculated from the two cells. The 100 spacing of the fiber, however, is closer to the spacing calculated from the unit cell of Ref. 1. On the basis of a statistical analysis the measured film spacings are more highly correlated (e. g., have a correlation coefficient closer to 1.0) to the spacings calculated from the TM cell than to those calculated from the DBB cell. The reverse trend is shown by the fiber spacings, their being more highly correlated to the spacings calculated from the DBB cell.

Any generalized correction to the data set, e. g., for a bias leading to higher angles being measured than appropriate, would, while making the film spacings closer to the spacings from the TM cell, also make the measured fiber spacings closer to those of the DBB cell. The three systematic factors causing profile displacement in the diffractometer (flat sample surface, absorption, and vertical divergence), as well as displacement from the rotation axis, lead to a shift toward smaller Bragg angles[15] and would thus tend to result, in the present case, in better agreement between the film data and the TM cell and the fiber data and the DBB cell. The differences in d spacings between film, fiber, and the respective cells are, however, in the proper direction to be produced by residual compressive stresses.

CONCLUDING REMARKS

The results presented in Table I (as well as the implication of the referenced observations on the position of the 100 spacing) suggest that the TM cell is applicable to PET film and the DBB cell (which was, as noted, obtained from a fiber specimen) is applicable to PET fibers for the purpose of crystallinity studies. It is also suggested that the uniaxial stretching of the electron diffraction specimen of Ref. 2 did not achieve a fibrous condition (if that were the purpose) but did provide a specimen suitable for studies concerned with PET film. Perhaps, a unit cell obtained from a perfect PET crystal would not be suitable as a model for studies of semicrystalline films and fibers, each with their own characteristic strains.

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