Crystalline Structures of Poly(ethylene Terephthalate) Fibers

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Synopsis

A graphic multiple peak resolution method by wide angle X-ray scattering (WAXS) pattern was described and used to estimate the interplanar spacings, crystallinities, and crystalline sizes of eight poly(ethylene terephthalate) (PET) fibers. The values for interplanar spacings of Dacron 54 suggested that the unit cell model by Daubeny et al. was appropriate for Dacron fibers. In general, crystallinities of the eight PET fibers ranged from 44.7% for Dacron 54 to 62% for Dacron 56 with the copolymers in between. Crystallinity by density measurements was determined and compared to that by WAXS in both fabric and ground fiber forms. Crystallinity values for each fiber derived by these three methods were different. For each fiber, crystallinity was lowest by WAXS in the ground fiber form, followed by the density measurement and WAXS in the fabric form.

INTRODUCTION

Poly(ethylene terephthalate) (PET) has been the most common polymer for making polyester fibers. The constituent and the manufacturing process of the fibers are often engineered in order to achieve certain performance qualities for different fiber end-use applications. The purpose of this study was to investigate the effects of constituents and processing on the crystalline structures of selected PET fibers.

X-ray diffraction methods have been widely used in studying the unit cell structure[1-4] and crystallinity[5-12] of PET. In some earlier work, the determination of crystallinity of PET by X-ray diffraction was compared with that by density measurement. Johnson[8] concluded that there was a linear relationship between specific volume and X-ray diffraction measurements whereas Farrow and Preston[13] found no relationship between density and X-ray diffraction data. In addition, while the estimation of crystallinity by X-rays were claimed inherently superior to density measurements,[14] the limitation of each method has made it difficult to justify the superiority of one method over the others.[5]

In this study, a graphic multiple peak resolution method in estimating crystalline structures of PET by wide angle X-ray scattering (WAXS) was described. Crystallinity and crystallite size of eight Dacron fibers were determined by WAXS. Due to the convenience and wide use of density measurement for determining the crystallinity of PET, the crystallinity values of

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selected PET fibers were also determined by the density measurement and compared to those by the WAXS method.

EXPERIMENTAL

Material

Eight Dacron fabrics (Testfabric Inc.) made from two classes of DuPont's polyester fibers were used in this study. Dacron types 54 and 56 are spun from a homopolymer of PET and are disperse dyeable. Dacron types 62, 64, and 92 are spun from a copolymer of PET with less than 5% of sulfonated terephthalic acid. The latter types are dyeable with both disperse and cationic dyes. Products spun from the copolymer have lower strength, abrasion resistance, wash-and-wear properties, and are more sensitive to acids and alkalis than those made out of the homopolymer.

Wide Angle X-Ray Scattering (WAXS)

The fabric specimens were prepared by three different methods. The geometric effects of the specimens on WAXS measurements were evaluated in the fabric and powder forms. The fabrics were folded into multilayer of approximately 3 × 4 cm for X-ray scanning. To eliminate the orientation of the fibers in the fabrics, fabrics were ground to pass a 40× mesh. Ground fibers were then packed manually into an aluminum mold approximately 3.8 × 2.5 × 0.3 cm in dimension to be scanned. The amorphous sample of the fibers was prepared by melting the fibers at 275°C and quenched in 0°C water.

The X-ray diffraction patterns of these samples were scanned using a DIAN-XRD 800 diffractometer. The diffractometer which is equipped with a graphite monochromator gives 50 Kv CuKα radiation at 15 mA. Scanning was performed from 10° to 32° at a rate of 1.6 deg/min.

Calculation for Crystalline Structure by WAXS

Crystallite Size

Crystallite size is calculated according to the Sherrer equation[15]:

$$L_{hkl}\,(\text{Å}) = 57.3K\lambda/\beta\cos\theta \tag{1}$$

where L_{hkl} is the mean dimension of crystallites perpendicular to planes hkl, k is the shape factor ($k = 0.9$), λ is the wavelength of X-ray, and 2θ is the Bragg's angle, $\beta = B^2 - b_0^2$, β is the pure broadening profile (rad), B is the measured half-width of the experimental profile (°), and b_0 is the instrumental broadening factor (°).

Crystallinity

The degree of crystallinity (X_c) determined by X-ray diffraction is calculated by a previously established method[16] as follows:

$$X_c = \frac{\Sigma C_{hkl}(\theta) S_{hkl}}{\Sigma C_{hkl} \cdot S_{hkl} + K \cdot S_a} \times 100\% \tag{2}$$

where S_{hkl} = relative area of the crystalline peaks, S_a = relative area of the

amorphous peak, K = the total correction factor = $C(\theta) \cdot k$, $k = 0.9$, $C(\theta)$ = correction factor of amorphous peak, and $C_{hkl}(\theta)$ = correction factor of crystalline peaks. $C(\theta)$ or $C_{hkl}(\theta)$ can be calculated by the following equation:

$$C_{hkl}^{-1}(\theta) = f^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} e^{-2B(\sin\theta/\lambda)^2} = \sum N_i f_i^2 \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} e^{-2B(\sin\theta/\lambda)^2} \right), \tag{3}$$

where f = atomic scattering factor of a repeating unit, f_i = scattering factors of the ith atom, N_i = number of the ith atom in a repeating unit, 2θ = Bragg angle, $(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$ = angle factor (LP), $e^{-2B(\sin\theta/\lambda)^2}$ = temperature factor (T), and $2B = 10$.

The atomic scattering function f_i can be expressed approximately by:

$$f_i\left(\frac{\sin\theta}{\lambda}\right) = \sum_{i=1}^{4} a_i e^{-b_i(\sin\theta/\lambda)^2} + c \tag{4}$$

where values of a_i, b_i, and c are given in Ref. 17.

Crystallinity by Density Measurement

The densities of PET fibers were measured on a Techne Density Gradient Column using a mixture of carbon tetrachloride and xylene at 21°C. The crystallinity (X) of PET fibers was calculated from the density measurement of the fibers (d) by the following equation:

$$\frac{1}{d} = \frac{X}{d_c} + \frac{1 - X}{d_a} \tag{5}$$

The crystalline density (d_c) used was 1.457 g/cm^3 and the amorphous density (d_a) was 1.336 g/cm^3.

RESULTS AND DISCUSSION

Wide Angle X-Ray Scattering Pattern (WAXS) of PET

The WAXS patterns of Dacron 54 polyester were taken in the fabric form [Fig. 1(a)] and in the melted fiber form [Fig 1(b)]. WAXS of the fabric shows three peaks at 2θ of 17.5°, 22.6°, and 25.6°, respectively. These three peaks correspond to the 100, $\bar{1}10$, and 010 spacings. The amorphous peak appears at around 2θ = 23–24°.

Interplanar Spacings

Five unit cell models for PET can be found in the literature[1-4,18] (Table I). The earliest data on the unit cell dimensions reported by Astbury, et al. were quite different than those published later. Only three of the papers (2, 3, 18) included data on the interplanar spacings of the PET materials used. In this study, the interplanar spacings of Dacron 54 were calculated according to Bragg's equation from the X-ray diffraction data. Our calculated data are almost identical to those calculated by Daubeny, et al. Our data also confirm the interplanar spacing data measured by Wakelyn.[19] It suggests that the unit

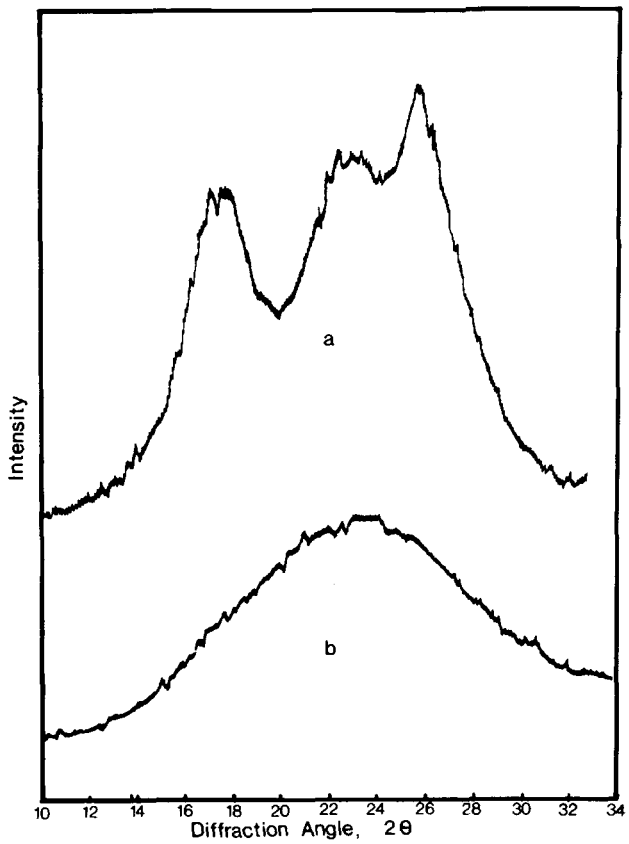

Fig. 1. WAXS of dacron 54 polyester: (a) in the form of fabric; (b) after quenching of the melted fibers.

cell parameters provided by Daubeny and Bunn is more applicable to the crystalline structure of Dacron 54 fiber.

Crystallinity and Crystallite Size of Dacron Fabrics

Due to the ease of measurement in the fabric form, crystallinities and crystallite sizes of eight Dacron fibers were derived by WAXS in the fabric form. Using eqs. (2), (3), and (4), the correction factors of the crystallinity formula for the crystalline and amorphous peaks were calculated and listed in Table II. With the same correction factors, eq. (3) can be further reduced to give

$$X_c = \frac{S_{100} + 2.11S_{1\bar{1}0} + 3.17S_{010}}{S_{100} + 2.11S_{1\bar{1}0} + 3.17S_{010} + 1.58S_A} \quad (6)$$

Equation (6) was used for calculating crystallinity of all PET samples measured by WAXS in this study. Crystallite size of each fiber was calculated using eq. (1).

Table III lists the crystallinity values and crystallite sizes for these fabrics. Crystallinities of these fabrics range from 44.7% for Dacron 54 to 62.0% for

TABLE I
Unit Cell Dimensions and Interplanar Spacing of PET

	Substrate	Method	Density (g/cc)	Unit cell dimensions						Interplanar spacings (Å)		
				a	b	c	α	β	γ			
				(Å)			(°)			010	$\bar{1}10$	100
Dacron 54	Fiber	X-ray diffraction	1.382	—	—	—	—	—	—	5.06	3.93	3.47
Astbury and Brown[1] (1946)	Fiber	X-ray diffraction	1.41	5.5	4.1	10.8	107	112	92	—	—	—
Daubeny et al.[2] (1954)	Fiber	X-ray diffraction	1.457	4.56	5.94	10.75	98.5	118	112	5.06	3.94	3.47
Tomashpol'skii and Markova[18] (1964)	Film	Electron diffraction	1.477	4.52	5.98	10.77	101	118	111	5.03	3.92	3.42
Fakirov et al.[3] (1975)	Fiber	X-ray diffraction	1.515	4.48	5.85	10.75	99.5	118.4	111.2	4.99	3.87	3.41
Kinoshita et al.[4] (1979)	Tube	X-ray diffraction	1.468	4.50	5.90	10.76	100.3	118.6	110.8	—	—	—

TABLE II
Correction Factors of Crystallinity Formulae for Dacron 54 Fiber

	$2\theta(°)$	T	LP	f^2	Correction factors	Total correction factor
Crystalline peaks						
hkl						
100	17.5	0.91	83.4	679.4	1.0	—
$\bar{1}10$	22.6	0.85	49.1	410.7	2.11	—
010	25.6	0.81	37.8	371.3	3.17	—
Amorphous peak						
	23.4	0.86	55.6	428.2	1.76	1.58

TABLE III
Crystalline Structure of PET Fibers[a] by WAXS

Fabrics	Crystallinity (%)	Crystallite size (Å)	
		L_{100}	L_{010}
Homopolymer			
Dacron 54	44.7	37.8	36.0
Dacron 54, heat set	50.5	37.7	34.9
Dacron 54, with optical brightener	43.4	35.4	37.3
Dacron 56	62.0	45.3	55.8
Copolymer			
Dacron 62	49.1	56.6	74.5
Dacron 64	48.1	45.3	31.9
Dacron 64, heat set	58.3	37.7	39.2
Dacron 92	46.1	37.8	37.2

[a]WAXS measured in the fabric form.

Dacron 56 with the copolymers in between. The heat setting process increased crystallinity in both Dacrons 54 and 64 to a large degree. The addition of optical brighteners, on the other hand, only slightly lowered the crystallinity of Dacron 54. The crystallite sizes of the various Dacron fabrics were apparently different. The heat setting treatment on Dacron 64 seems to impose greater changes on crystallite sizes than that on Dacron 54.

Crystallinity of PET Calculated by WAXS and Density Measurement

The crystallinity of four Dacron fabrics was determined by both density and WAXS measurements. The fabrics included Dacrons 54 and 64 and the same fabrics with heat set treatment. WAXS patterns were taken on oriented fabrics as well as randomly oriented ground fibers. The data are listed in Table IV.

Density measurement gave crystallinity values closer to those by WAXS in fabric form than in ground fiber form. The crystallinity values obtained by the density measurements were 2–5% lower than those detected as fabrics by WAXS, but much higher (4–14%) than those detected in ground fiber form. Regardless of the methods used, it was also observed that the crystallinity of

TABLE IV
Crystallinity of PET Fibers

Type	Density (g/cc)	Crystallinity (%) by Density measurement	Crystallinity (%) by WAXS Fabric	Crystallinity (%) by WAXS Ground fiber
Dacron 54	1.3817	39.8	44.7	35.5
Dacron 54, heat set	1.3925	48.8	50.5	40.0
Dacron 64	1.3877	44.8	48.1	35.3
Dacron 64, heat set	1.3999	54.9	58.3	40.8

both Dacrons 54 and 64 was shown to be increased by the heat setting treatment.

With both density and WAXS measurements, the crystallinity of Dacron 64 was somewhat higher than that of Dacron 54. However, the WAXS measurement of the ground fibers showed no apparent differences between these two fibers whether heat-set or not. The grinding process removes preferential orientation of fibers. Theoretically, the random nature of the ground fiber samples should give better estimation of the true crystallinity of the fibers. Realistically, however, the heat generated during grinding could possibly cause partial melting and degradation of the fibers. This may explain the indifference in crystallinity between the two types of fibers after grinding. Crystallinity determination by WAXS measurement in the fabric form, being much easier and quicker than that in the ground fiber form, is thought to be appropriate, especially for comparisons.

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