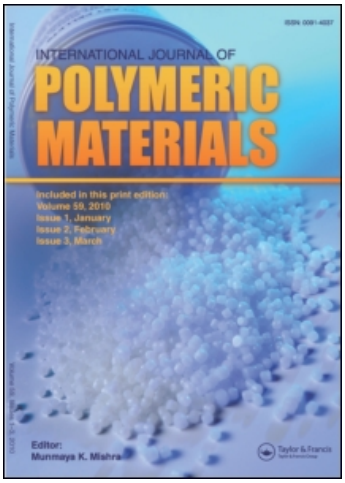

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Determination of the Orientation of Crystallites in PET Fibres

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A method for the determination of the average angle of orientation of crystallites φ from the azimuthal record of the meridional reflection of the $\bar{1}05$ diatropic plane for PET fibres is widely used. The $\bar{1}05$ reflection is the closest to the meridian and the normal to this plane making an angle of approximately 10° with the c axis. The intensity distribution measured by this method reflects the distribution of the $\bar{1}05$ plane normals and therefore it comprises: the distribution of the $\bar{1}05$ plane normals relative to the c crystallographic axis, the distribution of the crystallites relative to the reference fibre axis and the tilted orientation; that is the molecular chain axis inclined by some degrees with respect to the fibre axis. By the studying of the diffraction intensity distribution from the $\bar{1}05$ diatropic plane this particularly should be taken into account. The sub-meridional ($\bar{1}05$) reflection was scanned in two different geometries: omega and chi scan.

Supercritical CO_2 fluid as an alternative dyeing medium changes the fibre structure to a certain extent in dependence on the treatment temperature and pressure used. Therefore the changes of crystalline orientation in poly(ethylene terephthalate) (PET) fibres as brought about under the influence of supercritical CO_2 fluid were investigated.

Keywords: PET fibres; x-ray analysis; WAXS; wide angle x-ray scattering; orientation of crystallites; meridional (– 105) reflection; geometry of measurement; supercritical CO_2 fluid dyeing

INTRODUCTION

The determination of the crystalline orientation in PET is complicated by the absence of a truly meridional reflection (001). For the determination of the Hermans' orientation factor f_c for PET two

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methods are available [1].

- Method of Wilchinsky. Wilchinsky [2] showed that it is possible to evaluate the value of $\overline{\cos^2 \varphi}$ (φ is the average angle of orientation of crystallites) and hence the value of the orientation coefficient f_c from the measure of the azimuthal x-ray intensity distribution of five independent (h01) reflections or of three independent (hk0) reflections.

$$\overline{\cos^2 \varphi_{(hkl)}} = \frac{\int_0^{\frac{\pi}{2}} I_{hkl}(\varphi) \cdot \cos^2 \varphi \cdot \sin \varphi \cdot d\varphi}{\int_0^{\frac{\pi}{2}} I_{hkl}(\varphi) \cdot \sin \varphi \cdot d\varphi} \tag{1}$$

$\overline{\cos^2 \varphi_{(hkl)}}$ is calculated from the azimuthal intensity distributions $I(\varphi)$ of the three reflections: (100), (1 $\bar{1}$ 0) and (010) [1]. From these an average value, $\overline{\cos^2 \varphi}$, of the direction of molecular chains in the crystals is obtained

$$\overline{\cos^2 \varphi} = 1 - A \cdot \overline{\cos^2 \varphi_{100}} - B \cdot \overline{\cos^2 \varphi_{010}} - C \cdot \overline{\cos^2 \varphi_{1\bar{1}0}} \tag{2}$$

where A, B and C are coefficients dependent of the structure of the unit cell ($A = 0.3481$, $B = 0.8786$, $C = 0.7733$ [3]).

- Method of Azimuthal Breadth (Method of Dumbleton and Bowles). Dumbleton and Bowles [4] developed a method for the determination of the average angle of φ from the azimuthal record of the meridional reflection of the $\bar{1}$ 05 diatropic plane for PET fibres. The $\bar{1}$ 05 reflection is the closest to the meridian, the normal to this plane making an angle χ of approximately 10° with the c axis [4]. Therefore azimuthal scans with 2θ fixed at 43° [4] are composed of two overlapping components situated at 10° on either side of the meridian. The method is widely used for orientation determination of PET. The maximal mistake of the method could be estimated [1].

The intensity distribution measured by this method reflects the distribution of the $\bar{1}$ 05 plane normals and therefore it comprises [5]:

- the distribution of the $\bar{1}$ 05 plane normals relative to the crystallographic axis c
- the distribution of the crystallites relative to the reference fibre axis and
- the tilted orientation; that is the molecular chain axis inclined by some degrees with respect to the fibre axis [6].

By the studying of the diffraction intensity distribution from the $\bar{1}05$ diatropic plane this particularity should be taken into account.

- Evaluating the total $\bar{1}05$ reflection leads to an orientation parameter containing the information about the tilt of the crystallites, the tilt of the $\bar{1}05$ plane normals according to the c-axis and the tilted orientation of PET fibres.
- By resolving the diffraction intensity profile into individual, nearly symmetrical $\bar{1}05$ peaks and determining the orientation parameter from the intensity distribution of a single maximum, the angle between the $\bar{1}05$ plane normal and the crystallographic axis c is eliminated. The distribution of a single peak comprises only the angle between the fibre axis and the c direction of the crystallites and the tilt angle ϕ.
- An additional correction for the tilt angle ϕ in calculating the orientation parameter has been established by Auriemma *et al.* [6]. This method implies as the first step the determination of the tilt angle ϕ, and then the decomposition of the azimuthal profile of the $(\bar{1}05)$ reflection, calculation of $\overline{\cos^2\varphi}$ with the functions describing the $(\bar{1}05)$ reflection, but centered according to the tilt angle ϕ.

An expression to take into account the off-meridional nature of the $(\bar{1}05)$ reflection has been proposed [7] but was later on criticized [1, 6].

$$\overline{\cos^2\varphi} = \frac{\overline{\cos^2\varphi_{(\bar{1}05)}}}{\cos^2\chi} \tag{3}$$

$\varphi_{(\bar{1}05)}$ is the angle which the $(\bar{1}05)$ plane normal makes with the fibre axis,
χ the angle between the normal to plane $(\bar{1}05)$ and the c direction,
φ the angle between the fibre axis and the c direction.

EXPERIMENTAL

Preparation of the Samples

PET samples were blind dyed in SCF, water medium and hot air treated, respectively (*cf.* Tab. I). The SCF blind dyeing was performed in an apparatus consisting of an autoclave with a volume of 500 ml

TABLE I The treatment conditions of the PET fibres

Sample	Temperature (°C)	Pressure (MPa)	Time (min)	Method
UT	–	–	–	–
T1	130	40	60	SCF
T2	130	–	60	water-treated
T3	130	–	60	air-treated

and a high pressure pump. The blind-dyeing in the water medium was performed in the laboratory dyeing apparatus Ahiba. Dyeing was started at 70°C, afterwards the temperature was raised to 130°C at a heating rate of 2°C/min. Dyeing was carried out at this temperature for 60 min. The cooling rate of the dyeing bath was the same, 2°C/min. The fibres were hot air treated in a forced draft oven at the same temperature conditions as the blind water dyeing of the fibres. All thermal treatments were performed with the yarn wound up on perforated cylinders.

Experimental Methods

Wide-angle x-ray scattering (WAXS) curves were obtained on a diffractometer Siemens D 500 equipped with a Huber texture attachment. For measuring the x-ray scattering samples of very carefully paralleled fibres were prepared. Filaments were wound tightly and parallel to one another in about 10 layers.

The crystalline orientation was determined from scans of the $(\bar{1}\,05)$ reflection at $2\theta = 42.9°$, which is a diatropic slightly off-meridional reflection [4]. The scanning was carried out with two different geometries of measurement:

- meridional omega scan: asymmetrical transmission
- meridional chi scan: symmetrical transmission

The starting-point positions of the 4 diffractometer circles (*cf.* Tab. II) were adapted according to the measured reflection.

In Table III. The measuring conditions are collected.

On azimuthal scans of oriented fibres, the $(\bar{1}\,05)$ peak consists of two components situated 10° on either side of c direction. The two overlapping peaks of the $(\bar{1}\,05)$ reflection were analysed by fitting

TABLE II The starting-point positions of the diffractometer circles

Measuring geometry	2θ	ω	χ	φ
Meridional omega scan	42.9°	−5	90°	0°
Meridional chi scan	42.9°	21.45	65°	0°

TABLE III The measuring conditions on the diffractometer

Measuring geometry	*Range of measurement*	*Measuring time*	*Step width*
Meridional omega scan	$\omega = -5° - 45°$	20 s	0.4°
Meridional chi scan	$\chi = 65° - 115°$	20 s	0.4°

a model curve of two bell-shaped pseudo-Voigt functions to the experimental curve [8]. The orientation parameter $\langle \cos^2\varphi \rangle$ was determined from the integral azimuthal distribution width of the reflections.

From the resolved peaks the orientation parameter $\langle \cos^2\varphi \rangle$ was determined. For this purpose the equation [1] was used. The mean cosine factor was determined:

- for the total $\bar{1}\,05$ profile, that means for both maxima together.
  From the total intensity distribution the orientation parameter $\langle \cos^2 \varphi_{\bar{1}\,05} \rangle$ containing information about the angle which the $(\bar{1}\,05)$ plane normal makes with the fibre axis was determined.
- for each of the resolved peaks separately; $\langle \cos^2 \varphi_{\text{uncorr}} \rangle$.
- for each of the resolved peaks separately by correcting the position of the maximum for the tilt angle $\pm\phi$; $\langle \cos^2 \varphi_{\text{corr}} \rangle$.

RESULTS

Omega scanning of the $(\bar{1}\,05)$ reflection yielded scattering distributions with two overlapping peaks at angles ω of about 14° and 30°, respectively (Fig. 1). The raw data were subjected to an absorption correction and to subtraction of a constant background. The corrected data were then analysed by fitting two pseudo Voigt functions to the experimental data as shown in Figure 1.

Chi scanning of the $(\bar{1}\,05)$ reflection yielded the diffraction curves presented in Figure 2. An absorption correction was unnecessary for

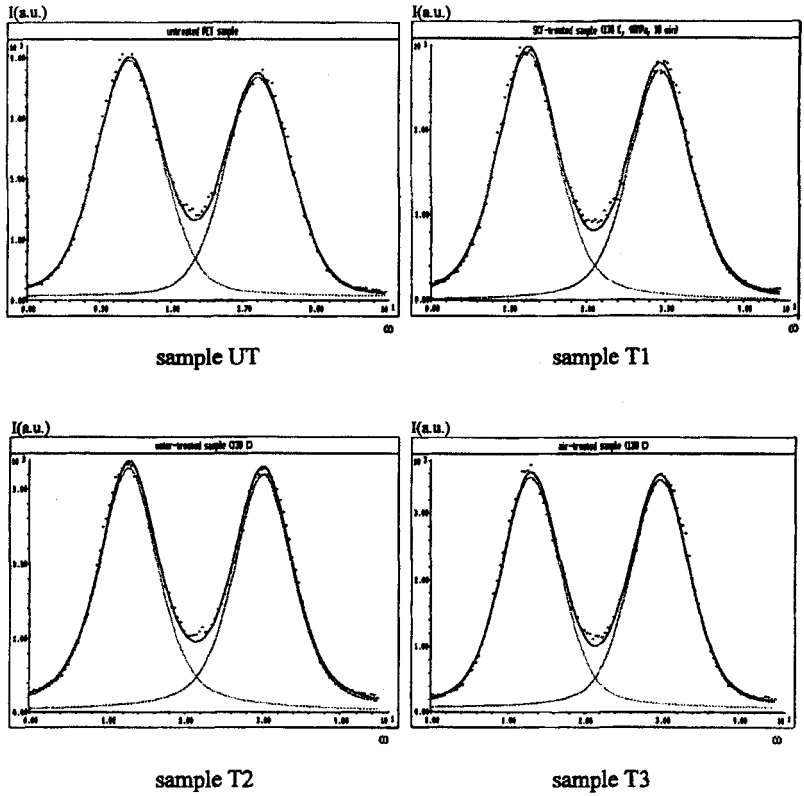

FIGURE 1 Omega scans of the untreated PET sample (sample UT) and of PET samples treated with SCF (sample T1), water (sample T2) and hot air (sample T3), respectively, and modelling (——) of the experimental ($\bar{1}05$) reflection (***) by two pseudo-Voigt functions (· · · ·).

this kind of measurements, but subtraction of a constant background from the measured data was performed. Here, the maxima of the two overlapping peaks are situated at angles χ of about 81° and 99°, respectively. Examples for the decomposition of the corrected experimental curves into two model curves (pseudo Voigt functions) are also shown in Figure 2.

The values of $\langle \cos^2 \varphi_{\bar{1}05} \rangle$ that were deduced by evaluating the total ($\bar{1}05$) reflection of experimental and model curves, respectively, are reported in Tables IV and V. The values are generally high, those derived from the model curves are usually slightly larger.

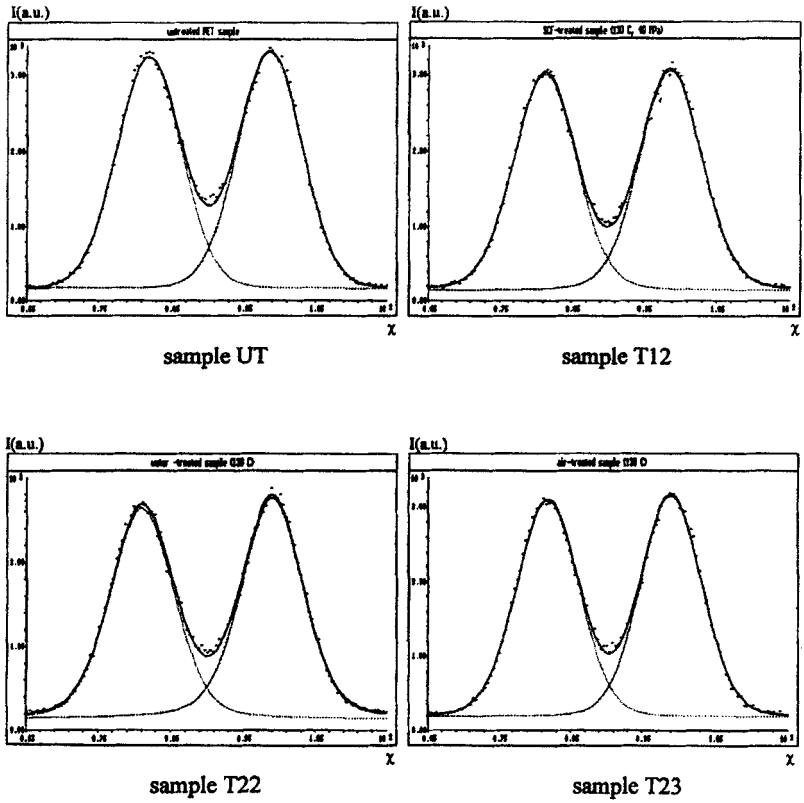

FIGURE 2 Chi scans of the untreated PET sample (sample UT) and of PET samples treated with SCF (sample T1), water (sample T2) and hot air (sample T3), respectively, and modelling (——) of the experimental ($\bar{1}$ 05) reflection (***) by two pseudo-Voigt functions (····).

In order to eliminate the influence of the angular displacement of the peaks from the centre of the curves, each of the two pseudo Voigt functions modelling the ($\bar{1}$ 05) reflection was shifted to 0° and evaluated separately. The mean square cosine values obtained from this "single peak evaluation", $\langle \cos^2 \varphi_{\text{uncorr}} \rangle$, are listed in Tables VI and VII.

According to the WAXS studies of untreated samples the crystallites are almost perfectly aligned along the drawing direction and any treatment at elevated temperature causes only some very slight changes, $\langle \cos^2 \varphi \rangle$ when followed by chi scanning of the ($\bar{1}$ 05) reflection and a single peak evaluation shows a very slight increase of mean

TABLE IV Orientation parameter $\langle \cos^2 \varphi_{\bar{1}05} \rangle$, determined from the total $(\bar{1}05)$ reflection of experimental and modelled scattering distributions as obtained from omega scans

Treatment	$\langle cos^2\varphi_{\bar{1}05} \rangle$ *Experimental curve*	$\langle cos^2\varphi_{\bar{1}05} \rangle$ *Model curve*
UT	0.9608	0.9627
T1	0.9535	0.9580
T2	0.9548	0.9541
T3	0.9535	0.9580

TABLE V Orientation parameter $\langle \cos^2 \varphi_{\bar{1}05} \rangle$, determined from the total $(\bar{1}05)$ reflection of experimental and modelled scattering distributions as obtained from chi scans

Treatment	$\langle cos^2\varphi_{\bar{1}05} \rangle$ *Experimental curve*	$\langle cos^2\varphi_{\bar{1}05} \rangle$ *Model curve*
UT	0.9585	0.9586
T1	0.9571	0.9572
T2	0.9552	0.9555
T3	0.9576	0.9577

TABLE VI Orientation parameter $\langle \cos^2 \varphi_{\text{uncorr}} \rangle$, determined by single peak evaluation of the modelled $(\bar{1}05)$ reflection as derived from omega scans, and the average of the two mean square cosines

Treatment	$\langle cos^2\varphi \rangle$ *1st maximum*	$\langle cos^2\varphi \rangle$ *2nd maximum*	$\langle cos^2\varphi \rangle$ *Mean value of both maxima*
UT	0.9823	0.9878	0.9851
T1	0.9841	0.9833	0.9837
T2	0.9822	0.9828	0.9825
T3	0.9860	0.9843	0.9852

TABLE VII Orientation parameter $\langle \cos^2 \varphi_{\text{uncorr}} \rangle$, determined by single peak evaluation of the modelled $(\bar{1}05)$ reflection as derived from chi scans, and the average of the two mean square cosines

Treatment	$\langle cos^2\varphi \rangle$ *1st maximum*	$\langle cos^2\varphi \rangle$ *2nd maximum*	$\langle cos^2\varphi \rangle$ *Mean value of both maxima*
UT	0.9826	0.9824	0.9825
T1	0.9844	0.9853	0.9849
T2	0.9849	0.9842	0.9846
T3	0.9842	0.9843	0.9843

cosine value, in contrast to the other method where a slight decrease is observed.

Some differences between the results appear by the calculation of cosine factor from the whole curve and from the separated peaks due to the particularity of the methods.

Deviations between the orientation parameters determined from the first and the second maximum are negligible (mean variation coefficient of two maxima for all measured samples is only about 0.04%).

A slightly different trend of changes is observed by means of both measuring techniques of the meridional reflection (*cf.* Tab. VIII). The values obtained by omega scanning of the untreated fibre are slightly higher, nevertheless a slight decrease of orientation is observed by means of omega scanning of the ($\bar{1}$ 05) reflection and an increase is found by means of chi scanning of the same reflection. But as only negligible differences are observed according to the different conditions of treatment they are probably mainly arising from experimental errors and the crystalline orientation remains probably unchanged after the treatment.

Additionally the tilt angle ϕ between the c-axis of crystallites and the fibre axis was estimated by the method of Auriemma *et al.* [6]. Considering the tilt angle ϕ corrected parameters $\langle\cos^2\varphi_{corr}\rangle$ were calculated. For this correction each of the maxima of the modelled ($\bar{1}$ 05) reflection was shifted to the position $\pm\phi$ (instead of 0°) and analysed by single peak evaluation. From the averaged $\langle\cos^2\varphi_{corr}\rangle$ values finally Hermans' orientation function f_c was calculated. The results are given in Table IX.

The differences between the results obtained from the single peak evaluation with the correction for the tilt angle ϕ or without this correction are negligible (*cf.* Tabs. VII, VIII and IX).

TABLE VIII Hermans' orientation functions f_c for untreated and various treated samples, calculated from the averaged mean square cosines $\langle\cos^2\varphi_{uncorr}\rangle$ as determined by single peak evaluation of the modelled omega and chi scans, respectively

Treatment	f_c *Omega scan*	f_c *Chi scan*
UT	0.9777	0.9738
T1	0.9756	0.9774
T2	0.9738	0.9769
T3	0.9778	0.9765

TABLE IX Hermans' orientation functions f_c for untreated and various treated samples, calculated from the averaged mean square cosines $\langle \cos^2 \varphi_{corr} \rangle$ as determined by single peak evaluation of the modelled omega and chi scans, respectively, taking into account the tilt angle ϕ

Treatment	$\langle cos^2 \varphi \rangle$ *omega* 1*st max*	$\langle cos^2 \varphi \rangle$ *omega* 2*nd max*	f_c *omega*	$\langle cos^2 \varphi \rangle$ *chi* 1*st max*	$\langle cos^2 \varphi \rangle$ *chi* 2*nd max*	f_c *chi*
UT	0.9798	0.9853	0.9738	0.9810	0.9809	0.9714
T1	0.9832	0.9825	0.9743	0.9838	0.9846	0.9763
T2	0.9816	0.9822	0.9729	0.9842	0.9835	0.9758
T3	0.9851	0.9834	0.9764	0.9836	0.9837	0.9755

It has been reported [7] that there is in general a decrease in crystalline orientation with increase in heat-setting temperature in free-annealed samples and an increase in the case of taut-annealed fibres. The fact that the structural relaxation of the oriented domain is greatly reduced or entirely suppressed when the macroscopic shrinkage is prevented, indicates that various domains in the fibre are interconnected [9, 10]. As all the treatments were performed with the samples wound up on a cylinder, the free shrinkage of the fibres was prevented. The taut position of the fibres during the treatment is the reason that changes of orientation of the crystallites did not occur to a greater extent.

CONCLUSIONS

The differences between the results obtained by the different measurement techniques are not significant. Because of the geometrical conditions, the results obtained from chi scanning appear to be more objective than those from omega scanning. Omega scans present a more asymmetrical diffraction curve, possibly due to some insufficiencies in the absorption correction applied.

The observed differences between the $\langle \cos^2 \varphi_{\bar{1}05} \rangle$ values on one side and the values of $\langle \cos^2 \varphi_{uncorr} \rangle$ and $\langle \cos^2 \varphi_{corr} \rangle$ on the other side are expected and due to the geometrical position of the $(\bar{1}05)$ plane. However, the differences between the uncorrected cosines $\langle \cos^2 \varphi_{uncorr} \rangle$ and the values corrected for the tilt angle ϕ, $\langle \cos^2 \varphi_{corr} \rangle$, are rather small. The same conclusions hold for the values of the orientation functions f_c.

In general the orientation parameter is very slightly increased after the treatment, with no influence of the medium used.

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