# AN X-RAY DIFFRACTION STUDY FOR ISOTACTIC POLYPROPYLENE FIBRES PRODUCED WITH TAKE-UP SPEEDS OF 2500-4250 M/MIN

## 2500-4250 M/DAK. SARMA HIZLARINDA ÜRETİLEN İZOTAKTİK POLİPROPİLEN LİFLERİ İÇİN BIR X-IŞINI DİFRAKSİYONU ÇALIŞMASI

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**ABSTRACT**

X-ray diffraction and differential scanning calorimetry (DSC) studies of isotactic polypropylene fibres, produced by melt spinning with take-up speeds of 2500-4250 m/min, showed the presence of polymorphism where the α-monoclinic and the smectic phases coexist together with an amorphous phase. X-ray diffraction was used for the determination of the unit cell dimensions, crystalline density, crystallinity and the crystallite size using an analysis of the equatorial traces whereas DSC was used for the evaluation of the melting enthalpies, melting temperatures and the crystallinity as a function of take-up speed. Crystallinity evaluated with the X-ray diffraction and the DSC techniques are compared and found that the X-ray crystallinity values are on average 8-14% higher than the DSC crystallinity values. Crystallite sizes are evaluated after curve fitting of X-ray diffraction traces for the (110), (040) and (130) reflections due to the α-monoclinic phase. The results show the crystallite size distribution of 116-136 Å, 108-118 Å and 89-97Å for the α-monoclinic phase reflections, whereas smectic phase reflection showed smaller crystallite size of 11-13 Å due to large intensity distribution of this peak.

**Key Words:** Isotactic polypropylene fibre, Differential scanning calorimetry, X-ray diffraction, Crystallinity, Crystallite size.

**ÖZET**

Eriyikten çekme yöntemi ile 2500-4250 m/dak. arası sarma hızlarında üretimi yapılan izotaktik polipropilen liflerinin X-ışını difraksiyonu ve diferansiyel taramalı kalorimetre çalışmalarında α-monoklinik ve smektik fazlarının aynı zamanda amorf faz ile beraber eş zamanlı olarak mevcut oluğu gösterilmiştir. X-ışını difraksiyonu birim hücre parametreleri, kristal yoğunluğu, kristalinite ve kristalit boyutlarının hesaplanmasında, öbür taraftan DSC ise erime entalpileri, erime sıcaklıkları ve kristalinite değerlerinin sarma hızlarına bağlı olarak elde edilmesinde kullanılmışır. X-ışını difraksiyonu ve DSC ile elde edilen kristanilite değerleri karşılaştırılmış ve X-ışını ile elde edilen kristalinite değerlerinin DSC ile elde edilen değerlerden ortalama %8-14 daha fazla olduğu bulunmuştur. α-monoklinik faza ait (110), (040) ve (130) yansımalarının kristlit boyutları X-ışını difraksiyonu grafiğinin eğri analizinden sonra hesaplanmıştır. α-monoklinik yansımalan kristalit boyut dağılımı değerleri 116-136 Å (110), 108-118 Å (040) and 89-97Å (130) olarak bulunmuştur, öbür taraftan smektik faza ait yansımanın kristalit boyutu daha küçük olup bu pikin daha geniş şiddet dağılımından dolayı 11-13Å arasında gerçekleşmiştir.

**Anahtar Kelimeler:** İzotaktik polipropilen lifi, Diferansiyel taramalı kalorimetre, X-ışını difraksiyonu, Kristalinite, Krital boyutu.

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## INTRODUCTION

Due to a range of desirable properties (i.e. low density, resistance to a wide range of chemicals, good mechanical properties), polypropylene has been produced in a wide range of forms including filaments, staple fibers, injection molded articles as automotive parts, packaging, toys and various house hold goods. During the last two or so decades, the use of polypropylene in the production of nonwovens, especially in the hygienic sector and in the area of technical applications in road and bridge construction projects has been phenomenally sucesssful. The recyclability of polypropylene has been another advantage for its use in the authomotive sector (1). Polypropylene staple fibres are increasingly used in the construction industry as a concrete reinforcing material (2).

In terms of the total fibre consumption and production, PP fibre occupies the 4th place after polyester, polyamide and acrylic fibres. Polypropylene is the 4th organic polymer based fibre developed commercially. Its production reached 2.6 million tons per annum for filaments and staple fibres (3). Polypropylene resin can be produced in the form of multifilaments by well-established melt-extrusion technique, though the operating conditions need

to be refined and or adjusted depending on the intended final product type. Spun-bonding and melt-blowning techniques are well known for the production and processing of non-wovens from isotactic polypropylene resins (4).

Polypropylene polymer chain consists of carbon-chain backbone with methyl groups (-CH$_3$) forming attachments which project from the sides of the chain. This results in the three dimensional structure of the molecule existing in a variety of forms which differ in their spatial arrangement. Isotactic, syndiotactic and atactic forms are the three corresponding structures for polypropylene (5). In isotactic polypropylene all the propylene methyl groups are arranged along the same side of the main chain polymer backbone. Due to this regular, repeating arrangement, isotactic polypropylene tends to have a high degree of crystallinity. Whereas in syndiotactic polypropylene, alternate pendant methyl groups are on opposite sides of the polymer backbone, with exactly the opposite configurations relative to the polymer chain (6).

Finally, random placement of the methyl groups along the main chain leads to atactic polypropylene. Isotactic and syndiotactic polypropylene show regular ordered structures and subsequently these regular structures enable the molecules to pack together in an efficient manner, and consequently these polymers show characteristic crystalline structures, whereas atactic polypropylene, due to its poor molecular symmetry, shows little or no order. As far as the commercial aspects are concerned, 90% of the polypropylene resin is produced in isotactic form due to its desirable fibre forming characteristics, low density and satisfactory mechanical properties.

Isotactic polypropylene is known to have three crystalline modifications as α-monoclinic,

β-hexagonal and γ-orthorhombic forms. The α-monoclinic form first proposed by Natta and Corradini (7) is the most well known and well established crystalline structure for isotactic polypropylene. The conditions for the occurence of β-hexagonal and γ-orthorhombic forms seem to be dependent on molecular weight, the

degree of isotacticity, and thermal treatment of the sample (8). α-phase is usually obtained from slowly crystallized unstrained melt or solution (7). The β-hexagonal phase was first reported in 1959 by Keith and coworkers (9]. According to the published reports, the conditions for the formation of β-hexagonal phase are: (i) crystallization from the melt with operation temperatures ranging from 100°C to 130°C (10), (ii) crystallization from an oriented melt, (iii) crystallization from the melt in the presence of nucleating agent, such as pimelic acid and calcium stearate (11). Li et al. (12) produced 100% pure β-hexagonal phase polymer for thermal studies.

The possible hexagonal unit cell or the β-form was suggested by Keith et al. (9) and Addink and Beintema (8). The hexagonal crystals are present in the strongly birefringent spherulites (8). The helical chains in alternate rows are of opposite hand. The axial repeat distance is slightly less than that found in the β-monoclinic unit cell. Addink and Beintema (8) suggested that there was no reason for doubling the a-axis as was proposed by Keith et al. (9).

The aim of the present study is to characterize and establish the structure-processing relationships of isotactic polypropylene fibres produced by melt-spinning with an extrusion temperature of 235°C and in the extrusion speed range of 2500-4250 m/min using the measurements of differential scanning calorimetry and X-ray diffraction with the ultimate aim of establishing structure-processing-property relationships.

## EXPERIMENTAL DETAILS

### Fibre Production

The melt spinning of isotactic polypropylene fibres were carried out using Barmag® CF spinning machine operating at an extrusion temperature of 235°C with a constant throughput of 9.12 g/min. In the present investigation, extrusion speeds ranging from 2500 to 4250 m/min with increments of 250 m/min were employed. Basell Polyolefins isotactic granules with a melt flow index of 35 g/10 mins, with weight average molecular weight of 179000 and polydispersity (M$_w$/M$_n$) of 4.6 were utilized to produce fibres. The melt-extruded filaments were immediately solidified with the assistance of cooling air speed of 40-

70 m/s and a cooling air blow temperature of 18-19°C. During the melt-extrusion stage, a spinnerette pressure of 60-70 bar and spinnerette hole diameter of 200-400 μm was utilized. Filaments had a trilobal cross-sectional shape. Melt-extrusion was performed with environmental conditions having the typical characteristics of 70% relative humidity and 15°C temperature.

## EXPERIMENTAL DATA COLLECTION

### X-ray diffraction

Wide-angle X-ray diffraction traces were obtained using a Bruker® AXS D8 Advance X-ray diffractometer system utilizing nickel filtered CuK$_\alpha$ radiation (wavelength of 1.54056 Å) and voltage and current settings of 40 kV and 40 mA, respectively. Counting was carried out at 10 steps per degree. The observed equatorial X-ray scattering data in the 5-35º 2θ range was corrected for Lorentz, polarization and incoherent scatter effects and finally normalized to a convenient standard area.

### Thermal Analysis

The differential scanning calorimetry (DSC) experiments were carried out using a Perkin Elmer Diamond DSC system. Typical sample weights used were approximately 5 mg. The heating rate of 10°C/min and an upper temperature range of 250$^o$C were selected. Indium (m.p. 156.5°C and ΔH = 28.45 J/g, Figure 1) was used for heat flow calibration standard. Indium and zinc (m.p. 419.51°C) standards were used for the temperature calibration. Specimens were always tested under a nitrogen flow rate of 50 ml/min.

## EXPERIMENTAL DATA ANALYSIS

### (i) X-ray data-curve fitting

All the X-ray diffraction traces obtained from the extruded isotactic polypropylene samples were fitted with a curve fitting procedure developed by Hindeleh et al. (13) to separate overlapping peaks. Each profile is considered to have the combination of Gaussian and Cauchy functions. When the observed and the calculated intensity traces converge to the best acceptable parameters, the computer program provides the list of accurate peak parameters in terms of
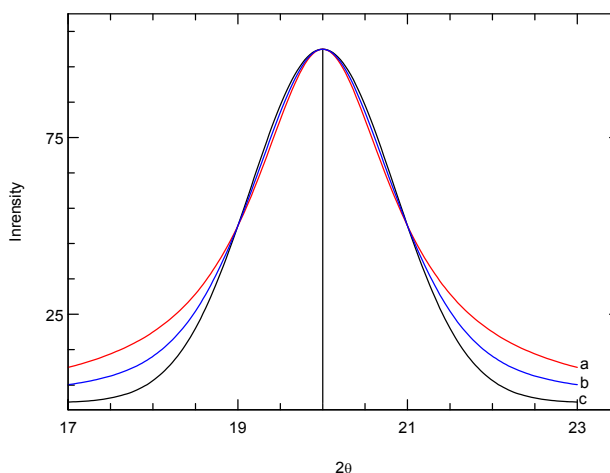
profile function parameter (f), peak height, peak breadth and peak position. In the curve fitting program, profile function parameter also known as peak shape factor is allowed to vary between 0 and 1 and effectively describes the tail region of the profiles. When profile function parameter (f) is equal to unity gives a Gaussian intensity distribution (Figure 2.c) and when equal to zero gives a Cauchy distribution (Figure 2.a). Initially, a value of f equal to 0.5 (Figure 2.b) is given to start the fitting process and then the minimization procedure finds the best peak parameters.
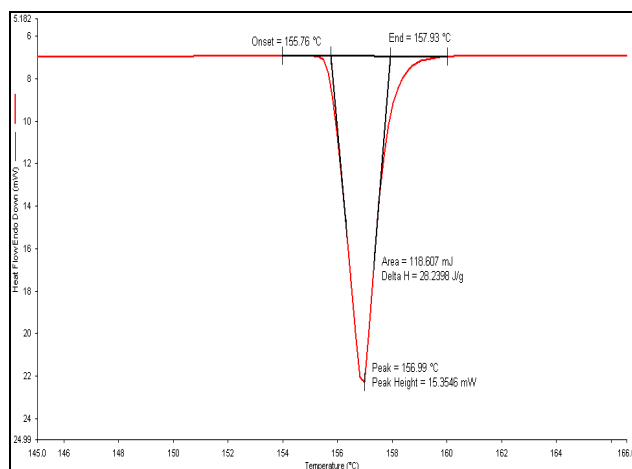


**Figure 1.** Typical indium DSC thermogram used for the heat flow and temperature calibrations.



**Figure 2.** Definition of profile function parameter. (a) f = 0 (100% Cauchy profile); (b) f = 0.5 (50% Gaussian + 50% Cauchy); ( c) f = 1 (100% Gaussian profile).

### (ii) Evaluation of the apparent crystallite Size

The peak widths at half-height have been corrected using the Stoke's deconvolution procedure (14). Finally, the apparent crystallite size of a given reflection was calculated using the Scherrer equation:

$$L(hkl) = \frac{K.\lambda}{\beta.\cos(\theta)} \qquad 1$$

Where $\theta$ is the Bragg angle for the reflection concerned, $\lambda$ is the wavelength of radiation (wavelength of 1.54056 Å), L(hkl) is the mean length of the crystallite perpendicular to the planes (hkl), $\beta$ is either the integral breadth or the breadth at half maximum intensity in radians and K is a Scherrer parameter usually taken as 1 for integral breadths and 0.89 for half-height widths. Hexamethylenetetramine compacted at 85°C was used for the instrumental broadening correction.

### (iii) Evaluation of the DSC crystallinity from the melting enthalpy values

Assuming a two-phase model consisting of crystalline and non-crystalline (i.e. amorphous) phase, the degree of DSC crystallinity can be evaluated from the melting enthalpies using the equation (2)

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \qquad 2$$

where $\chi_c$ is the degree of crystallinity evaluated by d.s.c. method, $\Delta H_m$ is the melting enthalpy of the sample and $\Delta H_m^o$ is the melting enthalpy of 100% crystalline sample and is taken as 165 J/g as published in the literature (15).

### (iv) Evaluation of the crystalline density (16)

Evaluation of the crystalline density ($\rho_c$) of $\alpha$-monoclinic structure is performed using the equation (3).

$$\rho_c = \frac{Z \cdot M}{V \cdot A} \qquad 3$$

where, $\rho_c$ (crystalline density, g/cm$^3$), Z (total number of monomers per unit cell is 12, i.e. 4 chains of three monomer unit per unit cell), M (molecular weight of monomer, 42 g/mol), V (unit cell volume in cm$^3$ ) and A (Avagadro number, $6.02257 \times 10^{23}$ mol$^{-1}$) .

### (vi) Evaluation of the X-ray crystallinity

X-ray crystallinity (17) is based on the ratio of the integrated intensity under the resolved peaks to the integrated intensity of the total scatter under the experimental trace. This definition can be expressed as in the equation (4).

$$\chi_c = \frac{\int_0^\infty \mathbf{I}_{cr}(2\theta) d(2\theta)}{\int_0^\infty \mathbf{I}_{tot}(2\theta) d(2\theta)} \qquad 4$$

The area under the background is considered to correspond to the non-crystalline scatter. It should be emphasized that the X-ray crystallinity is defined between two arbitrarily chosen angles and should be considered as an optimum mathematical solution. In this work, X-ray crystallinity was estimated in the 2θ range between 5 and 35°.

### RESULTS AND DISCUSSION

The degree of crystallinity can be determined by a variety of experimental techniques. These include measurements of density, enthalpy of fusion (DSC), X-ray diffraction, infrared spectroscopy and NMR methods. In the present investigation, only X-ray diffraction and differantial scanning calorimetry techniques are used and the results are evaluated accordingly. Crystallite size calculations are obtained from the peak parameters obtained from the curve fitting of the equatorial X-ray diffraction profiles.

## Assessment of the Differential Scanning Calorimetry data

The two separate melting peaks in the DSC endotherms indicate the presence of two structures of differing thermal stabilities. Many investigations have been made to clarify the origin of these double peaks. Samuels (18) has reported multiple melting peaks in the DSC curves of restrained samples, and he suggested that the formation and the location of the peaks are determined by the orientation of the noncrystalline regions. It was concluded that even though the source of the multiple peaks was unresolved, two crystalline species were involved, either with different levels of crystal disorder or different crystal sizes. It is suggested that the melting of different sized crystals or disordered crystals may explain the presence of multiple peaks.

Tanaka et al. (19) have reported the melting behavior of the stretched polypropylene. It was concluded that two different morphologies within the microfibrils were responsible for the double melting peaks. One melting peak was attributed to the chain-folded crystals and the second to the crystals in which a more extended chain conformation is adopted. The latter type structure was referred to as an intermolecular crystal. In a seperate study, Maeda et al. (20) have studied the melting behavior of the extruded polypropylene and observed double melting peaks at extrusion ratios of 5.2-6.5. These workers suggest that the melting peak on the higher temperature side may be attributed to the fusion of crystals reorganized during the heating and provided supporting evidence from the melting of samples etched with concentrated nitric acid.

## Analysis of Differential Scanning Calorimetry Data

DSC traces of isotactic propylene fibres are presented in Figure 3. Figure 4 shows the detailed analysis of the as-spun fibre extruded at 2500 m/min. The as-spun fibres do not show crystallization exotherm during DSC scanning due to the presence of well established $\alpha$-monoclinic crystalline structure. The onset temperatures, melting endotherm peak temperatures, melting enthalpies and crystallinities evaluated from the DSC thermograms are listed in Table 1.

DSC thermograms of all the as-spun fibres showed an onset temperature of 153-156°C. The melting endotherm on the lower temperature side is shown to have a peak temperature range of 160-162°C. This peak is referred to as the first melting peak. Whereas the melting endotherm on the higher temperature side comes with a peak temperature range of 167-170°C. The DSC thermogram of the original polypropylene granule presented in Figure 3.a shows an asymmetrical melting endotherm with a melting point of 167°C. Whereas the DSC thermograms of oriented polypropylene fibres show double melting peaks (Figure 3.b-h). The lower temperature peak will be referred to as the first peak and the higher temperature peak will be referred to as the second peak.

The second melting peak seems to be at least 2-3°C higher than the melting temperature of the pristine granule, possibly due to the orientational effects during the extrusion stage. The appearance of the low temperature peak on the DSC termograms of the samples is possibly due to the oriented paracrystalline chains. Taraiya et.al (36) showed a similar observation with the highly oriented polypropylene rods. These investigators showed the superheating effect on the low temperature peak which they attributed to the behaviour of extended chain crystals. It seems that the second melting peak seen located at about 167-170°C in the DSC thermograms of pristine granules and the polypropylene fibre samples may be due to the melting of folded chain crystals (36).

**Table 1.** Thermal characteristics of isopropylene fibres

| Take-up Speed (m/min) | Melting Endotherm Onset (°C) | Melting Endotherm Peak-1 (°C) | Melting Endotherm Peak-2 (°C) | Melting Enthalpy (J/g) | DSC $X_c$ |
|---|---|---|---|---|---|
| Granules | 156 | - | 167.0 | - | - |
| 2500 | 153.0 | 162 | 169.0 | 102 | 62.5 |
| 2750 | 153.0 | 160 | 169.0 | 103 | 62.0 |
| 3000 | 154.6 | 161 | 169.7 | 104 | 63.0 |
| 3250 | 155.8 | 161 | 169.6 | 104 | 63.0 |
| 3500 | 154.7 | 160 | 169.2 | 103 | 62.5 |
| 3750 | 154.6 | 161 | 169.1 | 103 | 62.5 |
| 4000 | 155.5 | 162 | 169.6 | 103 | 62.5 |
| 4250 | 155.5 | 162 | 169.5 | 104 | 63.0 |
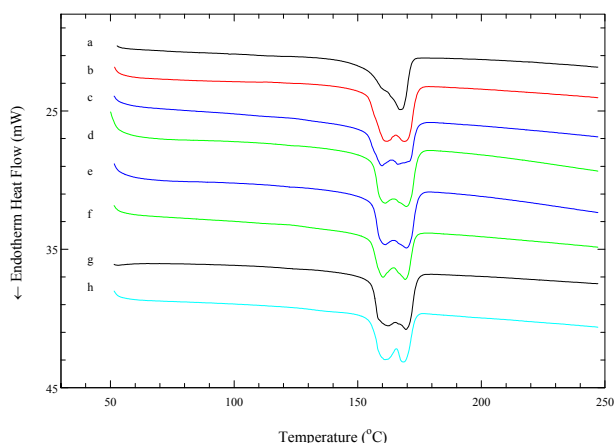
**Figure 3.** DSC termograms of isotactic polypropylene fibres extruded with different extrusion speeds. (a) granular form; (b) 2500 m/mins; (c) 2750 m/mins; (d) 3000 m/mins; (e) 3250 m/mins; (f) 3500 m/mins; (g) 4000 m/mins; (h) 4250 m/mins.
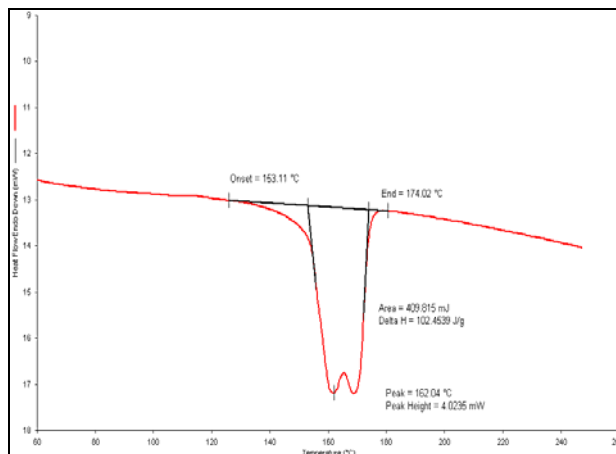


**Figure 4.** DSC thermogram of as-spun isotactic polypropylene fibre extruded at 2500 m/min.

DSC crystallinities evaluated using the equation (2) remain almost unchanged with a fractional crystallinity range of 62-63%.

## ANALYSIS OF WIDE-ANGLE X-RAY DIFFRACTION DATA

### Structure of as-spun fibres extruded with different take-up speeds

Qualitative inspection of equatorial X-ray diffraction traces of as-spun fibres shown in Figure 5 shows 3 well defined and highly intense peaks together with two weak reflections. Equatorial X-ray diffraction trace shown in Figure 6 can be resolved into at least six peaks indexed as 110, 040, 130, 060, 200 and 220, respectively. The indexed peaks are assigned to the $\alpha$-monoclinic phase. There was a need to add an additional peak located at approximately 15.71° (d-spacing of 5.64 Å) to improve the fit in the tail regions of the overlapping peaks. This peak is relatively broad in peak width and exhibits a typical paracrystalline character. Paracrystalline phase was also known as smectic phase (7-9, 21-23). It is known that the smectic phase is metastable, but transforms to the more stable $\alpha$-monoclinic phase on heating to temperatures above 60°C (24-25).

In the present study, the paracrystalline peak in the analysis of the equatorial X-ray diffraction profiles will be referred to as the 'smectic' peak is identified as S1 in Figure 6. X-ray diffraction patterns of isotactic polypropylene fibres produced from rapidly quenched melt containing smectic phase reveals two broad reflections with d-spacings of 5.64 Å

at 2θ = 15.71° and 4.0 Å at 2θ = 22°, respectively. The 1st smectic peak with a d-spacing of 0.564 nm is reported to disappear from the equatorial layer line and apparently moves to the first layer line when a highly oriented and drawn sample is produced (26). This is the main reason why only one peak at 2θ = 15.7° was used in the curve fitting of the equatorial X-ray diffraction traces of the as-spun fibers.

Curve fitting of the X-ray diffraction traces provides accurate peak parameters. Especially, the d-spacings are important in the determination of the unit cell parameters and also in the determination of the values of the crystalline densities.

Table 1 shows the comparison of the observed and the calculated d-spacings for the sample extruded at a take-up speed of 2500 m/min, whereas Table 2 shows the observed d-spacings of the $\alpha$(110), S1, $\alpha$(040) and $\alpha$(130) reflections. The d-spacing for the (110) peak assigned to $\alpha$-monoclinic structure shows variation between 6.23 and 6.26 Å. Similarly, d-spacings assigned to $\alpha$-(040) and $\alpha$-(130) peaks show variations between 5.22 and 5.23 Å and 4.76 and 4.78 Å, respectively.

The average unit cell parameters derived from the peak parameters obtained after the curve fitting of all the samples are as follows: a= 6.66 Å, b=20.88 Å, c=6.50 Å, $\alpha$=90°, $\beta$=99.5°,

$\gamma$=90° (monoclinic unit cell). The unit cell contains 12 monomeric units and the average volume of the unit cell is 891.5 Å$^3$.

As can be seen from the data obtained from the published literature, there are some variations and differences between the unit cell dimensions (see Table 3). This is particularly true for the crystalline densities calculated using the equation 3. In this study, the average calculated crystalline density for all the as-spun fibre samples is found to be 0.9387 g/cm$^3$. The published crystalline density values vary between 0.936 and 0.943 g/cm$^3$ (Table 3). The crystalline density evaluated in the present study is found to be between the published results and it seems to be in good agreement with the reported values. It is clear that the variations of the unit cell dimensions will inevitably lead to differences in the crystallographic volume of the unit cell and the crystalline density.

### Evaluation and the assessment of the crystallite sizes

Crystallite size calculations usually take into account the broadening imposed by the finite width of the X-ray diffractometer beam. This behaviour is reflected as a broadening of the peak width and must be corrected using an appropriate procedure. Two most common methods available for the correction of the peak widths are due to Jones (27) and Stokes (14).
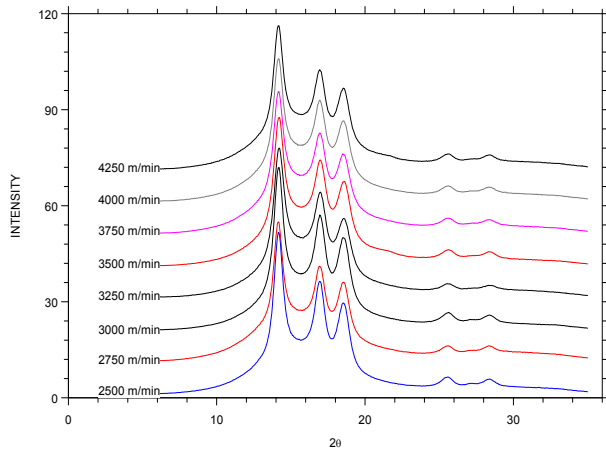
**Figure 5.** Equatorial X-ray diffraction traces of isotactic polypropylene as-spun fibres. Extrusion speeds are shown on the left hand side of the X-ray diffraction traces.
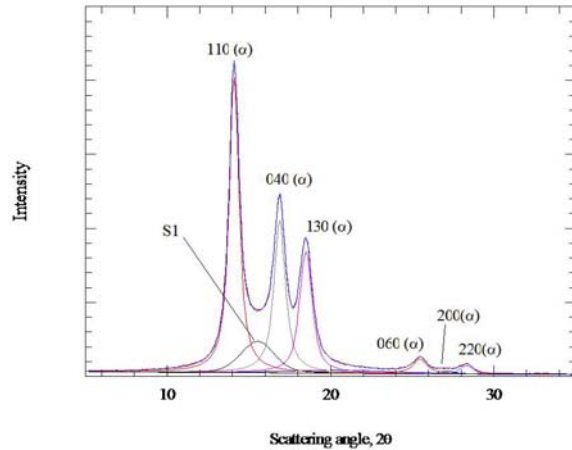


**Figure 6.** Curve fitting of equatorial X-ray diffraction trace of isotactic polypropylene fibre extruded at 2500 m/min.

**Table 1.** Resolved peak parameters of curve fitted equatorial X-ray diffraction trace of isotactic polypropylene fibre extruded at a take-up speed of 2500 m/min

| Peak ref. | f | A (Height) | W (Width) | Position (2θ) | d-obs spacing (Å) | d-calc spacing (Å) |
|---|---|---|---|---|---|---|
| 1 (α110) | 0.17 | 38.9 | 0.76 | 14.16 | 6.25 | 6.26 |
| 2. (S1) | 0.64 | 13.2 | 7.83 | 15.71 | 5.64 | 5.53 |
| 3. (α040) | 0.29 | 21.7 | 0.82 | 16.95 | 5.23 | 5.22 |
| 4. (α130) | 0.59 | 18.5 | 1.00 | 18.57 | 4.78 | 4.78 |
| 5. (α060) | 0.00 | 3.3 | 1.11 | 25.54 | 3.48 | 3.48 |
| 6. (α200) | 1.00 | 0.7 | 0.81 | 27.11 | 3.28 | 3.28 |
| 7. (α220) | 0.00 | 2.7 | 1.25 | 28.36 | 3.14 | 3.13 |

**Table 2.** d-spacings in (Å) of as-spun isotactic polypropylene fibres

| Take-up speed (m/mins) | d-spacings (Å) | | | |
|---|---|---|---|---|
| | α-$d_{110}$ | S1 | α-$d_{040}$ | α-$d_{130}$ |
| 2500 | 6.25 | 5.64 | 5.23 | 4.78 |
| 2750 | 6.26 | 5.64 | 5.23 | 4.78 |
| 3000 | 6.25 | 5.64 | 5.22 | 4.77 |
| 3250 | 6.23 | 5.64 | 5.22 | 4.76 |
| 3500 | 6.24 | 5.64 | 5.22 | 4.76 |
| 3750 | 6.25 | 5.64 | 5.23 | 4.77 |
| 4000 | 6.25 | 5.64 | 5.23 | 4.77 |
| 4250 | 6.25 | 5.64 | 5.23 | 4.78 |

**Table 3.** Unit cell dimensions of α-monoclinic crystal form for the as-spun isopropylene fibres

| a | b | c | α | β | γ | $\rho_c$ g/cm$^3$ | Ref. |
|---|---|---|---|---|---|---|---|
| 6.66 | 20.88 | 6.50 | 90 | 99.50 | 90 | 0.9387 | This work |
| 6.65 | 20.96 | 6.500 | 90 | 99.30 | 90 | 0.9360 | 7 |
| 6.66 | 20.78 | 6.495 | 90 | 99.62 | 90 | 0.9430 | 10 |
| 6.64 | 20.88 | 6.51 | 90 | 98.70 | 90 | 0.9380 | 31 |
| 6.56 | - | 6.50 | - | - | - | 0.9400 | 32 |
| 6.50 | 21.40 | - | - | - | - | - | 33 |
| 6.66 | 20.87 | 6.488 | 90 | 98.20 | 90 | 0.9370 | 34 |
| 6.65 | 20.96 | 6.50 | 90 | 99.30 | 90 | 0.9360 | 34 |
| 6.67 | 20.80 | 6.50 | 90 | 98.67 | 90 | | 35 |
| 6.65 | 20.73 | 6.50 | 90 | 98.67 | 90 | | 35 |

In the case of Jones method, specific functions are derived for the uncorrected and instrumental broadening profiles. According to this method, if the shape of the uncorrected peak profile happens to be Gaussian, then the width correction is $\beta^2 = B^2 - b^2$ and if the uncorrected peak profile is Cauchy, then the width correction is $\beta = B - b$ where $\beta$ is the corrected peak width, B is the observed peak width, and b is the instrumental peak width. Jones method usually uses integral peak widths but some investigators in the past used half-height widths instead. In the case of Stokes method, the deconvolution procedure takes into account the full peak profile thus making the whole correction more reliable. Stokes procedure is essentially a Fourier transform method where limitations must be exercised in transform space to obtain reliable results.

Once the observed half-height widths are corrected for the instrumental effects, then the corrected half-height widths can be used in the crystallite size calculations. For this reason, Scherrer's equation (1) is used for the determination of the crystallite sizes arising from the $\alpha$-monoclinic and smectic structures.

### Assessment of the α (110) peak parameters

Uncorrected peak widths of the (110) peak due to the $\alpha$-monoclinic phase shows variation between 0.72 and 0.85° whereas the corrected half-height widths of the same peak is reduced to 0.68-0.77° range. This is the narrowest peak in the equatorial X-ray diffraction trace which gives the highest crystallite size in comparison with the other peaks. Crystallite sizes obtained following the half-height width correction shows a variation between 116 Å and 136 Å (Figure 7) corresponding up to 21 chains in the direction of the planes responsible for the formation of this reflection.

### Assessment of the α (040) peak parameters

Uncorrected peak widths of this peak shows variation between 0.83-0.89° whereas corrected peak widths are reduced to 0.76-0.83° following the correction procedure. Corresponding

crystallite size variation is 108 Å -118 Å corresponding up to 23 chains in the direction of the planes responsible for the formation of this reflection (Figure 7). The crystallite size for this peak shows slight decrease with increasing take-up speeds. This may be due to the restructuring effect in response to the orientational improvement along the chain axis direction.

### Assessment of the α (130) peak parameters

Uncorrected peak widths of this peak shows variation between 0.93-1.06° whereas corrected peak widths are reduced to 0.92-1.01° following the correction procedure. Crystallite size variaton after the correction is between 89 and 97Å corresponding up to 21 chains in the direction of the planes responsible for the formation of this reflection (Figure 7). The crystallize size of this peak is the lowest among the $\alpha$-monoclinic phase peaks.

### Assessment of the smectic peak parameters

Uncorrected half-height widths show variation between 7-8° with corresponding crystallite sizes between 11-13 Å. Due to the spread of this peak, only an average 2 chains are responsible for the formation of the peak profile. This half-height width is the lowest in the equatorial region due to the paracrystalline nature of the structure consisting of chains with good alignment along the fibre axis direction but with poor lateral packing.
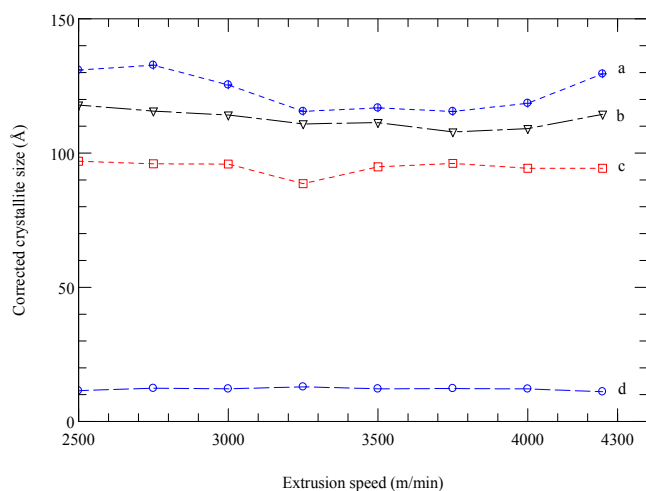
### Assessment of the X-ray Crystallinity Measurements

Crystallinity can be defined as the relative fraction of ordered materials existing in a material and is usually the most directly measured by the X-ray diffraction technique. Due to the high sensitivity of the X-ray diffraction to highly ordered regions, it is usually more reliable than the other methods of measuring crystallinity. Despite the reliability of X-ray diffraction method, X-ray crystallinity may still contain small amounts of non-crystalline material, but this amount is not expected to be significant. This kind of uncertainty is usually made ineffective with the efficient use of curve fitting procedures. The classical methods of the

measurement of crystallinity (28) ignores the possibility of peak overlap where the peaks and the background are separated by an arbitrary procedure.

Farrow and Preston (29) used the diffraction trace of an amorphous polyethylene terephthalate fibre as a base template and reduced the diffraction trace proportionally until the observed trace of a partially crystalline sample is met at one or several contact points where the amorphous trace goes through the arbitrarily selected minimum points. These procedures are bound to contain serious errors. In many cases the crystallinty values can be underestimated or sometimes seriously overestimated due to a lack of reliable procedure. Peak separation using the curve fitting procedure solved all the above problems and over the number of years it proved to be a reliable and robust technique with many successful applications in polymer and textile science research programs.

X-ray crystallinity values evaluated from the equatorial X-ray diffraction traces using peak separation procedure can be viewed as a measure of lateral order. The use of the equatorial X-ray diffraction traces is advantageous from the viewpoint of easy sample preparation, too. X-ray crystallinity values evaluated using the equation (4) are shown in Figure 8. Total X-ray crystallinity values range from 71 to 77% whereas the X-ray crystallinity of $\alpha$-monoclinic phase varies between 28 and 35%. Smectic phase fraction found to be higher than the $\alpha$-monoclinic phase fraction and is found to vary between 40 and 46%. It is clear that the structure is composed of a polymorphic structure with the main constituents being the $\alpha$-monoclinic and the smectic forms together with the totally disordered and unoriented amorphous phase. Amorphous phase fraction is found to vary between 23 and 29%. It is interesting to note that the total X-ray crystallinity (Figure 8.a) and $\alpha$-phase crystallinity (Figure 8.d) both show the tendency of a decrease after a take-up speed of 3000 m/min which seems to be at the expense of the increasing smectic fraction (Figure 8.c)

**Figure 7.** Comparision of crystallite sizes due to (a) α-(110); (b) α-(040); (c) α-(130) and (d) β-(300)
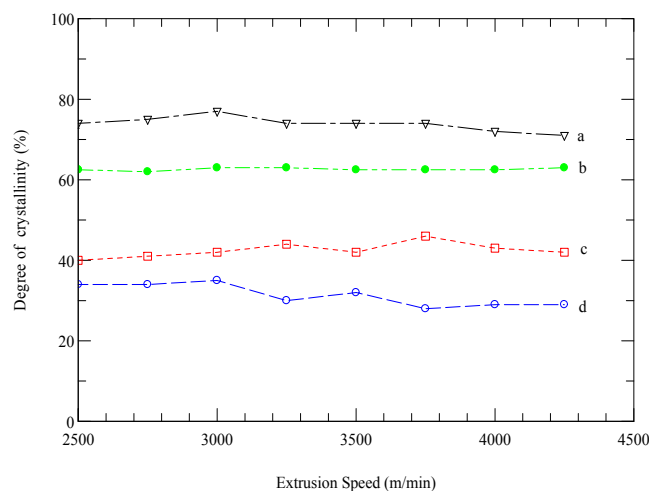
**Figure 8.** Comparison of the crystallinity fractions as a function of take-up speed. (a) Total X-Ray Crystallinity (α+smectic); (b) DSC crystallinity; (c) X-ray smectic fraction; (d) X-ray α-phase crystallinity

## Comparision of crystallinities obtained X-ray diffraction and Differential Scanning Calorimetry

Figure 8 shows that comparison of crystallinity values obtained from the X-ray diffraction and the differential scanning calorimetry. X-ray crystallinity values are consistently, on average, 8-14% higher than the DSC crystallinity values. The same conclusion was also observed in annealed polyethylene terephthalate fibres (30).

The differences between the crystallinity measuring methods may be explained as follows. X-ray diffraction method is basically the method of measurement of the crystallinity fraction of equatorial region, which, in principle, measures the degree of lateral order within a predefined region. In effect, large scattering angle and higher layer line reflections (off-equatorial, meridional and off-meridional) could be taken into account. In research laboratories spreading the angular range too wide may take too much time and may be regarded as impractical. It is possible that the separation of crystalline and non-crystalline region may not be 100% efficient which may, in theory, contain small amount of non-crystalline material but is not expected to be too high.

Differential Scanning Calorimetry data are most often complicated by the presence of the crystallization exotherms which may take place before the melting process in the samples with low crystallinity values as well as the possible errors introduced during the formation of the baselines necessary for the calculation of the melting enthalpies. Since there is no clear and well defined crystallization exotherm seen in the DSC thermograms of the samples investigated but the possibility of error still remains in the positioning of the baselines for the evaluation of the melting enthalpies. Despite this possibility, the introduction of small errors is expected to be very small indeed. DSC crystallinity values are also dependent on the choice of the melting enthalpy for 100% crystalline material. In the published literature, there appears to be different values but not all are 100% proof from uncertainties.

## CONCLUSIONS

Isotactic polypropylene fibres produced by melt spinning with take up speed range of 2500 –4250 m/min show the existence of polymorphism where α-monoclinic and smectic phases coexist together with an amorphous phase. The unit cell dimensions, crystalline density, crystallinity and crystallite size evaluations were carried out using the peak parameters obtained following the curve fitting of the equatorial X-ray diffraction profiles. Melting temperature, melting enthalpy and the crystallinity were obtained using differential scanning calorimetry technique as a function of take-up speed.

Crystallinity values evaluated using the X-ray diffraction and the DSC techniques are compared and the results show that the X-ray crystallinity values are, on average, 8-14% higher than the DSC based crystallinity values. Peak parameters obtained from the X-ray diffraction traces, after curve fitting procedure, are used for the determination of the crystallite sizes of (110), (040) and (130) reflections due to the α-monoclinic phase. The results show that the crystallite size of the (110) reflection is the largest followed by the descending order of (040) and (130) reflections. Due to the large intensity distribution of the S1 peak due to the smectic phase, the crystallite size is found to vary between 11 and 13 Å. The results show that the fractional crystallinity values of α-monoclinic phase is slightly lower than that of the smectic-phase. It is possible to perform extended annealing treatment to improve the crystallinity and the mechanical properties of the present polypropylene fibres. With annealing below the melting temperature significant proportion of metastable smectic structure should be converted to more stable α-monoclinic structure. Work is in progress with the annealing treatment and will be the subject of another report.

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