4.1 INTRODUCTION

Characterization of the structure of semi-crystalline polymers, such as polyester, requires a knowledge of the amount, size and orientation of the ordered or crystalline regions. X-ray diffraction is considered to be the most reliable technique to provide such information regarding crystallinity.

In this part of the study, structural changes that occur due to the drawing and heatsetting processes were examined, and quantitative estimations of crystallinity, size and orientation of crystallites, were obtained using the well known X-ray diffraction methods of analysis.

4.2 EXPERIMENTAL

X-ray Diagrams:

WAXS diffraction patterns for different drawn and heat-set polyester fibres and films were obtained with the beam incident perpendicular, and in a few cases parallel, to the fibre or draw axis using a semi-cylindrical Camera and Nickel filtered CuKα radiation.
4.21 Diffractometry

For crystallinity and crystallite size determinations, a vertical Philips Powder Diffractometer (PW 1050) equipped with a curved crystal focalizer (PW 1075) and aligned with a transmission set-up was employed.

For crystallinity determinations, powder diffractograms were obtained from pellets prepared from a finely cut powder. This pellet could be mounted in the specimen holder of the diffractometer in the usual manner and rotated in its own plane by means of a motor.

For crystallite size determinations, X-ray radial scans of equatorial, as well as meridional, reflections were recorded using a parallel bundle of filaments mounted on a specimen holder designed especially for this purpose.

For determining crystallite orientations, parallel bundles of filaments mounted on a specimen holder were used and azimuthal profiles of equatorial as well as meridional reflections were obtained employing a Philips Texture Goniometer (PW 1048/10).

In all cases, the diffracted beam was monitored by a scintillation detector used in conjunction with a Philips Pulse Height Discriminator (PW 1355) to mono-chromatize the diffracted intensity.
4.3 RESULTS AND DISCUSSION

Improvement in mechanical properties and dimensional stability in synthetic fibres is achieved by inducing in them a high degree of orientation and crystallinity through drawing and heatsetting processes respectively. Molecular orientation in fibres or films is usually obtained by stretching the fibre at a temperature either below, or above, the glass transition temperature of the undrawn fibre, whereas the dimensional stability is achieved by heatsetting them. Considerable changes in structure, and consequently in mechanical properties, can occur by varying the parameters and conditions during these drawing and heatsetting processes.

4.3.1 Effect of Drawing and Heatsetting on Fibre Structure

The effect of drawing on the structure of polyester has been thoroughly investigated in the past by several workers\textsuperscript{1-13}, and different structural models were proposed to describe the structure of polyester materials in their highly oriented state\textsuperscript{13,14-26}. In spite of this plethora of information, the nature of deformation during these drawing processes and the structure of the material in its unoriented, amorphous state are still not fully understood. It is said that the actual structure, rather than the amount of the non-crystalline phase present, is more important in determining the mechanical
and other technological properties for semi-crystalline polymers like polyester.

The effect of room temperature drawing on X-ray diffraction patterns for an initially unoriented amorphous tow (as-spun polyester filament) is shown in Figure 1.

The undrawn amorphous fibres (Figure 1(a)) showed an isotropic halo in their X-ray diffraction pattern. Apparently, the samples drawn up to 200% (Figure 1(c)) indicated no differences in crystallinity or orientation, while above 300% extension, some indication of molecular orientation could be noticed. However, again, the samples drawn above 300% (Figure 1(d)) and upto 400% (Figure 1(f)) extensions did not show any discernible differences in their X-ray diffraction patterns.

In contrast to the X-ray diffraction patterns, remarkable changes in molecular order by drawing were indicated by birefringence, sonic modulus, density and free enthalpy (DSC) values.

The samples which were drawn upto 200% (Figure 1(c)) showed a birefringence of 0.180 and sonic modulus 57.9 g/den. DSC traces showed that the "crystallization" peak disappeared by drawing the fibres upto 200% extension. These results suggested that a considerable amount of molecular order is already achieved at low extensions (200%), but the corresponding X-ray diffraction patterns showed only a non-crystalline
Fig. 1 (a) to (f) : X-ray Diagrams of Amorphous Tow Polyester Filaments Drawn by Various Extension Ratios
halo of intensity. This appeared to be in confirmation with Bonart's\textsuperscript{27} observation that the non-crystalline halo in the X-ray diffraction pattern is often associated with a relatively high degree of order in the mutual arrangement or one-dimensional register of the molecular chains along the draw direction.

Bonart\textsuperscript{27} reasoned that during the initial stages of drawing, a nematic type paracrystalline ordering of the molecule results, and on further drawing to higher draw ratios, the nematic type ordering is transformed into a smectic type paracrystalline ordering of the molecules (Figure 2).

The structure at low draw ratios may be viewed as numerous small nematic-type ordered regions, embedded in an unoriented amorphous matrix. Within the nematic crystals the molecules are nearly aligned along the stretching direction, but due to the statistical fluctuations of the inter-chain distances and also due to the small dimensions of these ordered regions, the X-ray diffraction pattern still showed only an isotropic (non-crystalline halo even for draw extensions up to 200\% (Figure 1(c)).

As this nematic-type paracrystalline ordering could be associated with a large change in free enthalpy, the characteristic exothermic crystallization peak in the DSC trace disappeared on drawing the fibres above 200\% extensions.
Fig. 2: BONART's Representation of Paracrystalline Structures
(a) Nematic (b) Smectic
Sudden increase in birefringence, tensile modulus and the occurrence of strain hardening on drawing to 200% extension must therefore be due to the nematic-type ordering of the molecules.

On further extension, only the geometrical ordering of the molecules is improved, whereby the nematic-type structure is converted into a smectic-type structure. An improvement in the statistical disorder in the inter-chain distances and an increase in the size of the ordered regions are indicated by smectic-type ordering of the molecules. As a result, for higher extensions there were only small variations in the birefringence, density, and sonic modulus values, while the X-ray diffraction patterns showed a gradual concentration of intensity distribution of the halo on the equator. Further higher extensions involved only the orientation of crystalline and non-crystalline regions in the direction of drawing and thus no further changes in X-ray diffraction patterns for fibres drawn above 300% extension, were observed, whereas birefringence, sonic modulus and density continued to increase.

Thus different degrees of molecular orientation and molecular order resulted from cold drawing the undrawn fibres to various drawing extensions. The effect of this premolecular orientation and premolecular ordering on the subsequent crystallization process was further examined by X-ray diffraction methods and
the corresponding X-ray diffraction patterns after heat-
setting under tension at 200°C for 5 minutes are shown in
Figure 3.

For undrawn amorphous fibres after heatsetting (Figure 3(a))
the X-ray diffraction patterns indicated an unusual orienta-
tion. The intensity maxima for 100 reflection, which usually
appears on the equator for oriented fibres, was seen in this
case on the meridian, whereas the intensity maximum for the
010 reflections appeared on the equator as usual. The
diffraction intensities for the \( \overline{1}10 \) and \( \overline{1}11 \) reflections
showed a random distribution or powder ring.

This type of diffraction pattern is indicative of a-axis
orientation of crystallites parallel to the fibre axis and
the molecular chains (c-axis) in this case tend to orient
perpendicular to the fibre axis. Birefringence of these
samples showed negative values, confirming the perpendicular
orientation in these fibres.

With increasing pre-extension, intensity maxima for 100
reflection gradually shifted from the meridian to the equator,
the \( \overline{1}10 \) showed its intensity maxima on the equator; also the
resolution of 0\( \overline{1}1 \) and 010, as well as 1\( \overline{1}1 \) and \( \overline{1}10 \) reflections
gradually improved while the azimuthal spread of their
intensity distribution gradually decreased. The sharpness
and resolution of the diffraction spots also increased with
Fig. 3(a) to (f): X-ray Diagrams of Amorphous Tow Drawn to Various Drawing Extensions and Heat-set at 200°C Under Tension (Tension Quenched)
increasing pre-extension. Above 300% extension (Figure 3(d)), well resolved, more or less sharp, diffraction patterns were observed after heatsetting. In all cases, birefringence and sonic modulus increased with increased pre-extension after heatsetting which indicated that molecular orientation occurred during thermal crystallization processes.

Different workers proposed different structural models to explain the occurrence of a-axis orientation or tilting away of the molecular chain axis (c-axis) from the fibre axis direction.

Bonart\textsuperscript{28} assumed that one-dimensional ordering of chain molecules in a crystallographic plane (100) already exists in the molten state of the polymer. This ordering may be due to the interaction between ester dipoles of adjacent parallel segments of molecular chains. On subsequent heatsetting in the free state, these ribbon-like molecular bundles fold in such a way that the (100) plane is perpendicular to the stretching direction (Figure 4). This resulted in a-axis oriented crystallite growth.

Liska et al.\textsuperscript{29} explained the a-axis orientation on the basis of "Meander" or a tightly folded molecular bundle. According to them, in melt quenched amorphous PET, near-range order existed in the form of chain "Meander" or tightly folded molecular bundles. These structured elements are
Fig. 4: BOKART's Folded Ribbon Model to Explain a-axis Orientation in PZT
anisotropic within themselves and they tend to orient along the stretching direction. On subsequent thermal treatment orientation disappeared, while the adjacent a-axis oriented molecular layers favoured the growth of a-axis oriented crystallites.

For very high extensions the meanders are fully unfolded and a fibrillar structure is formed, where almost all the molecules are nearly arranged in the stretching direction and hence only c-axis orientation is possible.

Biangardi and Zachmann\textsuperscript{30}, on the other hand, preferred to explain this change using a twisted lamellar crystalline structure originally proposed for polyethylene by Keller and Machin\textsuperscript{31}. In the initially undrawn amorphous fibres spherullitic crystallite growth occurred, where the radially growing twisted lamellar crystals are the building blocks of the spherullites. Stress induced crystallization in the undrawn amorphous material leads to row nucleation of crystals. For weakly oriented fibres, lamellae growth in the direction of stretching is hindered while lamellae readily grow in the direction perpendicular to the stretching direction, which resulted in flattened spherullites with the lamellae twisted mainly perpendicular to the stretching direction. Due to the rotational symmetry of the crystals about the twisting axis of the lamellae, a-axis orientation occurred.
For higher extensions, density of nuclei along the rows perpendicular to the stretching direction increased considerably, thereby inhibiting the lamellar growth in that direction also. Due to this reason, lamellar growth is stopped before any torsion in the lamellae could occur and therefore only almost straightened lamellae, oriented perpendicular to the stretching direction, resulted. This may be the reason for the observed c-axis preferred orientation of crystallites in highly drawn materials.

The following studies on the effect of tension and setting temperature on the crystallization behaviour of polyester films of various draw ratios, as well as amorphous filaments (tow), revealed that none of the above models can explain the preferred orientation of crystallites in these materials satisfactorily.

4.32 Effect of Tension and Temperature on the Structure of Heat-Set Unoriented Amorphous Polyester Filaments

Figures 5(a) and (b) show the X-ray diffraction patterns for the undrawn polyester (tow) filaments heat-set for 5 minutes while slack as well as under tension (not allowed to shrink) at 3 different temperatures, namely, 165, 200 and 230°C.
Fig. 5: X-ray Diagrams for Undrawn Polyester Tow Filaments Heat-set at Various Temperatures
For slack heat-set fibres (Figure 5 (a)), at low temperatures of heatsetting (165°C) although almost isotropic Debye ring patterns were observed, a little concentration of intensity at the equator can be noticed for all the three reflections (010, 110, 100). At a heatsetting temperature of 200°C the maxima of the intensity distribution for 100 reflection was found on the Meridian indicating a-axis orientation, or a 90° tilt of a few crystallites from the fibre axis direction. At very high setting temperatures (230°C) an almost isotropic intensity distribution for all the reflecting planes was again observed.

Tension heat-set unoriented filaments, on the other hand, showed initially a 45° crystallite tilt at low heatsetting temperatures as can be seen from the intensity distribution of the 100 reflection in the X-ray diffraction pattern. At higher setting temperatures the intensity maximum for 100 reflection shifts to the meridian indicating a-axis orientation.

In general, it can be seen that a more pronounced a-axis orientation, or crystallite tilt, was always observed in tension heat-set fibres, while slack heat-set fibres showed almost random distribution of crystallite orientations, particularly for very high heatsetting temperatures.
At low temperatures under tension-heatsetting very little or no tilting of crystallites at all occurred and for higher setting temperatures tilting of crystallites was more pronounced.

Birefringence measurements for all these materials showed that almost all of them had negative birefringence. While slack heat-set fibres showed no improvement in sonic longitudinal modulus, tension set fibres showed a considerable increase in modulus which suggested that tension set fibres were better (perpendicularly) oriented.

From Bonart's hypothesis, for poorly oriented fibres, it is expected that slack heatsetting should lead to folding of ribbon-like molecular bundles with the 100 planes oriented normal to the stretching direction, while heatsetting under tension prevents or hinders such folding. On this basis, slack heat-set fibres should exhibit a more pronounced a-axis orientation in comparison with tension heat-set fibres, which was opposite to the trends observed here.

On the basis of twisted lamellar theories as well, the slack heat-set fibres should show a greater tendency for a-axis orientation as larger torsion of the lamellae are expected during free annealing than during taut annealing. Secondly, it can not be explained by this model why high torsion of lamellae (no a-axis orientation) was noticed at low temperatures of heatsetting.
A different explanation was offered by Dulmage and Geddes\textsuperscript{14} who suggested that during the crystallization process, the crystallite nuclei were tipped about axis which are approximately perpendicular to the fibre axis of the crystal and parallel to the (100) planes, and as a result the preferred fibre axis direction tended to become perpendicular to the stretching direction.

Earlier it was proposed that, during the initial stages of drawing of an amorphous polyester fibre, a nematic-type paracrystalline ordering of the molecules occurred, and for low extensions the structure can be viewed as numerous nematic-type paracrystallites embedded in an unoriented amorphous matrix. During the stretching operation these nematic-type ordered regions tend to orient along the stretching direction and the net work of chains in the amorphous regions is also simultaneously stretched. On subsequent thermal treatments the molecular chains in the amorphous net work tend to relax and the contractile forces generated might cause the tipping of the nematic-type ordered regions into a perpendicular direction, which later may act as crystallite nuclei.

During crystallization, the chains in the amorphous regions tend to rotate and align along the direction of these pre-existent tilted crystallite nuclei inorder to facilitate the
crystallization of the material and thereby perpendicular orientation of the molecular chains perhaps occurred.

During tension-heatsetting, length contraction is prevented and therefore the chain molecules in the amorphous net work are not allowed to relax. Consequently, due to the large contractile forces generated in the process, large tipping of crystallite nuclei might have resulted. On slack heat-setting the undrawn fibres, large length contraction (50%) was noticed, which may be due to the complete relaxation of the molecular chains in the amorphous net work. The effect of contractile forces on the tipping of crystallite nuclei is comparatively less in the slack heat-set fibres which might be the reason for the reduced tendency towards perpendicular molecular orientation in those materials.

When the heatsetting temperature is low, the effective contractile force is much less and the rate of crystallization is also much slower. Due to this reason any small tipping of crystallite nuclei might have subsequently disappeared because of the re-orientation of the nuclei along the fibre axis direction before the crystallization process set in. This may be the reason why the low temperature heat-set filaments did not show any detectable tilt in the crystallite orientation or perpendicular molecular chain orientation.
The fact that tipping of crystallite nuclei might have been caused by the contractile forces generated in the amorphous network is partially supported by the experimental observation that the negative birefringence noticed in the unoriented samples after heat treatments was always found to be proportional to the positive birefringence shown by the material prior to heatsetting.

For moderately oriented filaments (e.g., polyester tow drawn above 100% extension) the crystallite nuclei are tipped through lower tilting angles, with increasing preorientation (Figure 3).

Since in this case many of the crystallite nuclei are nearly aligned parallel to the stretching direction, large tilting angles become less probable during the subsequent crystallization process and therefore with increasing pre-orientation the tilting angles decreased.

On further drawing (above 200%) stress induced crystallization might have occurred because of the high alignment of molecular chains in the amorphous network and decrease in the inter-chain distances (which is clearly manifest in DSC traces where the characteristic crystallization (exothermic) peak was not observed for the filaments drawn above 200% extension). Since nearly all the crystallite nuclei are arranged in a direction parallel to the fibre...
axis and the orientation being locked in by possible stress induced crystallization, no tilting of crystallite nuclei occurred for highly drawn (above 200%) fibres after heat-setting.

In these cases the orientation distribution of c-axis around the fibre axis varied with increasing pre-orientation. The diffuse background observed in the X-ray diffraction patterns for filaments extended above 200% and below 400% might be due to the scattering from the unrelaxed oriented non-crystalline matrix as the materials were not allowed to shrink during the heat treatments.

For very high extensions (nearly 400% extension) the nematic-type paracrystalline ordering is converted into a more stable smectic-type ordering and the crystallization occurred perhaps at the expense of the oriented non-crystalline phase leading to a highly oriented (c-axis orientation) fibrillar structure.

4.33 The Effect of Uniaxial Drawing and Heatsetting on the Structure of PET Films

Commercial films hot drawn (above the glass transition temperature) at 80°C to three different draw ratios 1:2, 1:3 and 1:4, and their corresponding tension and slack heat-set samples at 230°C for 5 minutes, were chosen for this study. The respective X-ray diffraction patterns are shown in Figure 6.
Fig. 6(a) to (c): X-ray Diagrams of Commercial Drawn Films of Different Draw Ratios
(a) 1:2    (b) 1:3    (c) 1:4
The 1:2 draw ratio film before heatsetting showed only a non-crystalline halo, while 1:3 draw ratio film showed a little concentration of the intensity of the halo along the equator. Both of these samples showed poor three dimensional order. The high draw ratio film (1:4), on the other hand, showed a slightly discrete but still diffuse X-ray pattern.

On heatsetting, large differences in X-ray diffraction patterns were observed depending upon the pre-orientation (draw ratio) and tension during setting.

For low and intermediate draw ratios, 1:2 and 1:3 respectively crystallinity and crystallite orientation both were seen to be significantly affected by tension during heatsetting.

For 1:2 draw ratio film, after heatsetting under tension, the diffraction patterns showed that the intensity maxima for 100 reflection did not lie on the equator and the intensity maxima for 01T, 010, 111, and 110 reflections were all found on the equator. This pattern was nearly similar to that obtained for amorphous filaments drawn to 100% extension and heat-set under tension (Figure 3) shown earlier.

In addition, the 105 peak was not observed on the Meridian. This pattern is indicative of a tilt in the crystallographic c-axis with respect to the fibre axis. The reflections 01T and 010, as well as 111 and 110 were not resolved which may be due to the large azimuthal spread of the intensity.
distribution as a result of poor crystallite orientation. In contrast to this, the slack heat-set films of the same draw ratio showed a different type of diffraction pattern. In this case, the intensity maxima for the principal reflections 100, 110, 100 were all found to be on the equator and the resolution was much better. However, the azimuthal spread of the intensity distribution is still large. The 105 intensity maxima was found on the Meridian in the X-ray diffraction patterns for these slack set films. This pattern indicated that the c-axis was preferentially aligned along the deformation direction, but the orientation of crystallites is still poor though better than that in the case of tension heat-set films.

The corresponding unheat-set film (1:2) showed no indication of molecular order as can be seen from its diffraction pattern. Unpolarized infrared spectra of these films (see Chapter V), showed the existence of a high "gauche" content and very poor "trans" content. Polarized infrared spectrum showed very little or no dichroism of absorption bands for this draw ratio. All these results suggested that no large scale orientation of molecular chains occurred at this draw ratio (1:2). However, the corresponding slack and tension heat-set films indicated considerable orientation of the chain molecules along the draw axis. Since the initial samples were almost without any orientation, it must be due
to the thermally induced crystallization that the orientation of chain molecules occurred after the heatsetting process. This is possible only when there are already a few, but small, ordered regions aligned along the stretching direction which act as crystallite nuclei during the subsequent crystallization process. It must be assumed that, the structure at low draw ratios consist of a few short range ordered regions aligned along the stretching direction and embedded in a pre-dominantly isotropic amorphous matrix. Crystallization is facilitated by the thermally induced rotation and alignment along the draw direction of the chain segments in the amorphous regions.

While on tension heatsetting, due to the contractile forces induced by thermal energy, the prealigned crystallite nuclei are tilted in a direction perpendicular to the stretching direction and during subsequent crystallization process, the chain molecules in the non-crystalline phase rotate and align along the direction of these tilted nuclei and then crystallize which might be the reason for the observed crystallographic tilt in these films. Additionally, due to the crystallization induced molecular orientation, the chains in the amorphous regions are highly stressed leading to a diffuse non-crystalline background in the X-ray diffraction pattern.
During the slack treatments, the chains in the amorphous regions are allowed to relax and orientation of the crystallite nuclei along the stretching direction occurred rather than tilting. The subsequent crystallization process led to a preferred c-axis oriented crystalline structure.

The polarized infrared spectra for these heat-set low draw ratio films exhibited considerable dichroism for all the absorption bands and the unpolarized infrared spectra showed a pronounced reduction in the "gauche" band intensities and considerable enhancement in the "trans" band intensities. These results confirm the observation that thermal treatments on low draw ratio films resulted in a rotation and orientation of the molecular chain segments along the draw direction.

Crystallite orientation (as obtained from infrared studies) is comparatively poorer in tension heat-set films which is also in agreement with the X-ray diffraction results.

In the case of intermediate draw ratio films (1:3), no tilt of crystallites is indicated in their X-ray diffraction patterns both for slack and tension heat-set films. While for tension heat-set films the X-ray diffraction pattern consisted of discrete crystalline reflection with a diffuse amorphous scattering superposed on them, a better resolved discrete crystalline pattern was obtained for slack heat-set films for this draw ratio (1:3).
The X-ray diffraction patterns for this 1:3 draw ratio film before heatsetting showed a concentration of the intensity of the halo at the equator. The corresponding unpolarized infrared spectrum indicated a high "trans" content and the polarized spectrum showed high dichroism for both "trans" as well as "gauche" sensitive absorption bands. It appeared from these results that the fairly high extension and alignment of chain segments existing at this draw ratio may mean that almost all the crystallite nuclei are aligned along the stretching direction. In addition to this, some stress induced crystallization in these films is not ruled out. The rate of crystallization is reported to increase significantly with increasing draw ratio. All these results combined together would explain why no crystallite tilting was observed in these intermediate draw ratio films after heatsetting. The diffuse background observed in the X-ray diffraction patterns for the tension heat-set film may be due to the scattering from the unrelaxed oriented non-crystalline phase.

For high draw ratios, both slack and tension heat-set films showed well resolved discrete X-ray diffraction patterns with the difference that for slack heat-set films a slight crystallite disorientation was indicated.

The unheat-set high draw ratio (1:4) film showed some indication of stress induced crystallization. As it was
assumed earlier, on drawing the less stable nematic para-
crystalline ordering is converted into the more stable
smectic-type of paracrystalline ordering for high draw ratios.
Since all the molecular chains are already aligned along the
draw direction, heatsetting leads only to the relaxation of
the chain molecules in the non-crystalline regions and
perfection of crystallites already formed at high draw ratios.
As relaxation was much better during slack heatsetting,
slight disorientation of crystallites occurred in slack
heatsetting.

4.331 Uniplanar Orientation

Unlike fibres, in films in addition to the uniaxial orienta-
tion where the molecular axis orients preferentially in the
stretching direction a crystallographic plane (100) for PET
film was also often found to align preferentially parallel
to the plane of the film on uniaxial drawing. This type of
orientation is identified as uniaxial-uniplanar orientation.
Supporting evidence for the existence of such type of
orientation in drawn PET films was provided by X-ray, as well
as infrared spectroscopy, studies by various workers\textsuperscript{8,14,15,19}
in the past.

In fibres, due to the cylindrical symmetry, only uniaxial
orientation is observed and in the corresponding diffraction
patterns, the diffracted intensity from the (100) planes was
always stronger than the diffracted intensities from the other two planes (010, 110) on the equator. In contrast to this, in uniaxially drawn films either no diffraction, or only a weak diffraction, from (100) planes was noticed on the equator. This is because, in commercial uniaxial hot drawing of the film the (100) plane tends to align parallel to the plane of the film, and since the X-ray beam is incident perpendicular to the plane of the film (parallel to the normal to the 100 plane), no diffracted intensity from this (100) plane can be recorded on the photographic film if high uniplanar orientation is achieved in these films by drawing.

On visual examination of the diffraction patterns in Figure 6 of the uniaxially hot drawn and subsequently heat-set films of different draw ratios, it was noticed that the diffracted intensity from the (100) plane gradually diminished with increasing draw ratio for both tension as well as slack heat-set films. The diffracted intensity from this plane is much weaker for the tension heat-set films for all the three different draw ratios. In particular, high draw ratio (1:4) tension heat-set film showed almost no diffracted intensity from this plane in the corresponding X-ray diffraction patterns, due to very high preferential uniplanar orientation.
Since the diminishing diffracted intensity from the (100) plane is indicative of increasing orientation of that plane parallel to the plane of the film (uniplanar orientation) it can be deduced from the above results that the uniplanar orientation steadily increased with increasing pre-orientation or draw ratio, and also that uniplanar orientation is better retained by heatsetting the films under tension than while slack in the free state.

Similar conclusions have been obtained from infrared spectroscopic studies carried out on the same films (see Chapter V).

**4.34 Effect of Cold Drawing and Heatsetting on the Structure of Undrawn Amorphous PET Films**

In Figure 7 the effects of cold drawing and heatsetting on the X-ray diffraction patterns for an undrawn amorphous PET film can be seen.

The undrawn film showed an isotropic halo, while the film cold drawn to the maximum (520% extension) showed a concentration of intensity on the equator, indicating an improvement in the molecular order by cold drawing. On heatsetting the undrawn films, both while under tension as well as slack, the X-ray diffraction patterns showed concentric Debye rings indicating a random distribution of crystallite orientations in these materials.
Untreated

Tension Heat-set 200°C

(a) Undrawn

(b) Cold Drawn to 520%

Fig. 7(a) & (b): X-ray Diagram of Undrawn and Cold Drawn Polyester Films
A highly oriented crystalline structure was indicated by the X-ray diffraction patterns of the cold drawn to 520% and subsequently heat-set films. It can also be observed that better orientation of crystalline regions was achieved by heatsetting the films under tension. For both slack and tension heat-set cold drawn films, the X-ray diffraction patterns showed strong diffracted intensity from the (100) plane on the equator which suggested that uniplanar orientation is less predominant in cold drawn films. Earlier it was shown that the commercial, uniaxially drawn (draw temperature 80°C) films showed a clear indication of uniplanar orientation in them as noticed from their X-ray diffraction patterns.

Infrared spectroscopic studies (to be reported in Chapter V) also confirmed these observations suggesting that in cold drawn films relatively poor uniplanar orientation occurred as compared to the hot stretched.

A possible explanation for pronounced uniplanar orientation in hot drawn films with high draw ratios could be that in hot drawing both crystallization and orientation are simultaneously taking place. The small crystallites or nuclei that are developed at the drawing temperature above Tg are subsequently oriented in the later drawing stages.

It is known from the crystal structure of PET that the plane
of the benzene ring in the PET molecule tends to lie in the (100) crystallographic plane and this plane therefore tends to orient itself in the plane of the film on subsequent drawing. This simultaneous crystallization and stretching leads to preferred uniplanar orientation. On the other hand, in cold drawing below Tg, no crystallization occurs and only orientation, or one-dimensional register, takes place. Subsequently, the crystallites are formed with good orientation in the direction of drawing but with cylindrical symmetry about this direction. There is thus no uniplanar orientation introduced because drawing and crystallization are sequential (first drawing or orientation and then crystallization) and not simultaneous. In the sequential treatments the crystallites when formed have no chance to orient themselves with the (100) planes in the plane of the film because the orientation process was over earlier when the material was amorphous. Thus hot drawing leads both to uniaxial and uniplanar orientation because of simultaneous crystallization and orientation while sequential cold drawing followed by hot crystallization produces good uniaxial orientation in the direction of stretch it does not result in any uniplanar orientation in films.

The type of orientation in polyester films may therefore differ depending on the conditions and temperature of drawing.
4.35 **Effect of Setting Temperature on the Structure of Oriented Crystalline (Commercially Drawn) Polyester Fibres**

Figure 8 shows the effect of different heatsetting temperatures on the diffraction patterns for commercially drawn polyester filaments heat-set under two different conditions (a) slack, and (b) under tension without being allowed to shrink.

For slack set fibres (series a), the crystallinity increased and crystallite orientation decreased with increasing heat-setting temperature from 165° to 240°C. Large disorientation of crystallites was noticed for high setting temperatures (240°C). For tension heat-set filaments (series b) orientation of crystallites appeared to improve up to the setting temperature of 200°C, but for higher setting temperatures (240°C), crystallite disorientation occurred, indicating that larger structural relaxation occurred in these materials even when the shrinkage was prevented.

For both slack and tension heat-set films at high setting temperatures, the equatorial broadening of the diffraction spots reduced considerably which may be indicative of either larger size of crystallites or greater perfection of crystallites. It can also be noticed that greater perfection (or larger crystallite sizes) resulted by setting the fibre in the free state at very high temperatures.
Fig. 8(a) & (b): X-ray Diagrams of the Commercial Drawn Polyester Filaments Heat-set at Different Temperatures
4.36 **Radial Structure Perpendicular to the Fibre Axis**

Due to cylindrical symmetry in polyester fibres, they are expected to be radially isotropic transverse to the fibre axis. Information on the radial structure of fibres perpendicular to the fibre axis can be had by recording the X-ray diffraction patterns, keeping the incident X-ray beam parallel to the fibre axis.

Figure 9 shows such patterns obtained for a completely unoriented, amorphous (Tow) fibre Figure 9(a), a cold drawn oriented amorphous (Tow) Figure 9(b) and a commercially drawn fibre Figure 9(c) as well as the corresponding slack and tension quenched heat-set fibres at 200°C for 5 minutes. All the patterns gave isotropic Debye rings indicating more or less a transversely isotropic texture. Both the undrawn (a) and cold drawn (b) amorphous fibres showed a diffuse halo with no resolution of the pattern indicating no crystallinity or lateral order. The drawn fibres (b) show increased intensity and a sharper halo. This suggested that on cold drawing only one dimensional ordering of the molecular chains takes place, while lateral order perpendicular to the fibre axis is poorly developed. On the other hand commercially hot drawn fibres showed some resolution of the pattern suggesting improved lateral order.
Fig. 9(a) to (c): X-ray Diagrams Taken Keeping the Fibre Axis Parallel to the Beam
(a) Undrawn Tow
(b) Tow Cold Drawn to 400%
(c) Commercial Drawn Polyester Filament
In all the three cases, i.e., undrawn, cold drawn and commercially hot drawn fibres well resolved Debye rings were obtained after heatsetting. Always the slack set fibres (in the middle row in Figure 9) showed intense and sharper diffraction rings than the tension heat-set fibres which suggested that the lateral order is better developed in slack heat-set fibres than in tension heat-set fibres. The lateral order developed due to heatsetting is considerably less in the unoriented fibres (series a) in comparison to the oriented fibres (series c). This again indicated different morphologies for unoriented and oriented crystalline fibres.

4.37 Determination of Crystallinity

There are a number of methods suggested in literature to determine the degree of crystallinity in semi-crystalline polymers.

Gupta reviewed the various methods for determining the degree of crystallinity in polymers and from his own experimental observations he concluded that Statton's method seems to be better for obtaining relative crystallinity, as all the other methods overestimated the degree of crystallinity.
The degree of crystallinity in the present work was determined by the Correlation Method proposed by Wakelin et al.\textsuperscript{34} which was applied to poly(ethylene terephthalate) by Statton\textsuperscript{35}. The details of the method were described earlier in Chapter II. For comparison purposes, X-ray crystallinities and density crystallinities (taken from Chapter VI) have been listed in Table I.

A plot of X-ray crystallinity against density crystallinity (Figure 10) showed a linear relationship with some scatter. It was observed that for all unoriented crystalline materials a least squares fitting of the linear relationship resulted in a line (broken in Figure 10) with unit slope, while for the oriented crystalline materials a similar least squares fitting resulted in a straight line with a slope less than unity, which suggested that for oriented crystalline materials the density method seems to overestimate crystallinity when compared to the X-ray method. While obtaining the crystallinity values from density, it is assumed that the densities of totally amorphous and totally crystalline regions are invariant. It was, however, reported\textsuperscript{36} that the unit cell dimensions, as well as density of non-crystalline regions, may vary depending on the sample treatments and orientation. The results obtained here therefore seem to confirm these views.
Fig. 10: X-ray Crystallinity Vs Density
Crystallinity
## TABLE I

**COMPARISON OF X-RAY AND DENSITY CRYSTALLINITIES**

<table>
<thead>
<tr>
<th>Sample Particulars</th>
<th>X-ray Crystallinity (%)</th>
<th>Density Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. As-spun (Tow Unoriented Amorphous)</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>2. As-spun Heat-set SQ 165°C</td>
<td>48</td>
<td>55</td>
</tr>
<tr>
<td>3. As-spun Heat-set SQ 200°C</td>
<td>54</td>
<td>56</td>
</tr>
<tr>
<td>4. As-spun Heat-set SQ 230°C</td>
<td>63</td>
<td>61</td>
</tr>
<tr>
<td>5. As-spun Heat-set TQ 165°C</td>
<td>46</td>
<td>54</td>
</tr>
<tr>
<td>6. As-spun Heat-set TQ 200°C</td>
<td>56</td>
<td>54</td>
</tr>
<tr>
<td>7. As-spun Heat-set TQ 230°C</td>
<td>59</td>
<td>58</td>
</tr>
<tr>
<td>8. As-spun Drawn by 200% Untreated</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>9. As-spun Drawn 300% and TQ 200°C</td>
<td>40</td>
<td>51</td>
</tr>
<tr>
<td>10. As-spun Drawn by 300% Untreated</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>11. As-spun Drawn by 300% and TQ 200°C</td>
<td>42</td>
<td>54</td>
</tr>
<tr>
<td>12. As-spun Drawn by 400% Untreated</td>
<td>19</td>
<td>28</td>
</tr>
<tr>
<td>13. Drawn by 400% and SQ 165°C</td>
<td>50</td>
<td>52</td>
</tr>
<tr>
<td>14. Drawn by 400% and SQ 200°C</td>
<td>53</td>
<td>56</td>
</tr>
<tr>
<td>15. Drawn by 400% and SQ 230°C</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>16. Drawn by 400% and TQ 165°C</td>
<td>35</td>
<td>52</td>
</tr>
<tr>
<td>17. Drawn by 400% and TQ 200°C</td>
<td>49</td>
<td>55</td>
</tr>
<tr>
<td>18. Drawn by 400% and TQ 230°C</td>
<td>45</td>
<td>59</td>
</tr>
<tr>
<td>19. Control (commercial) Untreated</td>
<td>32</td>
<td>38</td>
</tr>
<tr>
<td>20. Control SQ 165°C</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>21. Control SQ 200°C</td>
<td>48</td>
<td>55</td>
</tr>
<tr>
<td>22. Control SQ 230°C</td>
<td>49</td>
<td>60</td>
</tr>
<tr>
<td>23. Control TQ 165°C</td>
<td>43</td>
<td>47</td>
</tr>
<tr>
<td>24. Control TQ 200°C</td>
<td>45</td>
<td>54</td>
</tr>
<tr>
<td>25. Control TQ 230°C</td>
<td>40</td>
<td>58</td>
</tr>
<tr>
<td>26. Control SA 200°C</td>
<td>51</td>
<td>65</td>
</tr>
<tr>
<td>27. Control TA 200°C</td>
<td>52</td>
<td>63</td>
</tr>
</tbody>
</table>
Effect of Drawing and Heatsetting on X-ray Crystallinity

The dependence of X-ray crystallinity on the heatsetting temperature for unoriented and oriented crystalline polyester fibres is shown in Figure 11. For undrawn (unoriented) fibres, crystallinity increased very linearly with increasing setting temperature, both in the case of slack as well as tension heat-set materials. For cold drawn (oriented) fibres, dependence on setting temperature differed for different setting conditions (slack or tension). For cold drawn slack heat-set fibres, X-ray crystallinity increased curvilinearly, with temperature first rapidly then slowly. It showed only a small but continuous increase in crystallinity with increasing setting temperature above 165°C. Cold drawn, tension heat-set fibres, on the other hand showed an increase in crystallinity with increasing setting temperature up to 200°C, but at higher setting temperatures crystallinity was found to decrease. Similar results were also shown in the case of commercially drawn heat-set fibres (Figure 12). A small but steady increase in crystallinity occurred with increasing setting temperature for slack set commercially drawn fibres, whereas for tension heat-set fibres crystallinity increased with increasing setting temperature up to about 200°C, but at higher temperatures it appeared to decrease.
Fig. 11: X-ray Crystallinity Vs. Setting Temperature for Undrawn as well as Cold Drawn Polyester Tow Filaments

Fig. 12: X-ray Crystallinity Vs. Setting Temperature for Commercial Polyester Filaments
For all oriented fibres, the slack set ones always showed higher crystallinities than the tension heat-set ones. It is also interesting to note that at any given setting temperature the undrawn heat-set fibres always showed higher crystallinities than their drawn or oriented counterparts. Differences in crystallinity due to variation in heatsetting temperature are comparatively much more pronounced in undrawn crystallized fibres.

These results appeared to suggest that both high molecular orientation, as well as tension during heatsetting, will limit the attainable crystallinities at any given setting temperature. It was earlier postulated by Roe, Smith and Krigbaum\(^{37}\) that the build up of strain in the amorphous regions limits the degree of crystallinity which can be achieved at any given temperature. They\(^{37}\) reasoned that the free energy change associated with the crystallization of bulk polymers consisted of two parts, namely, the "single crystal" term corresponding to the transfer of units from a disordered amorphous region to the ordered crystalline and secondly that arising from the deformations produced in the intervening amorphous regions as crystallization proceeds further crystallization ceases when the latter term offsets the former.

Following this line of reasoning the experimental results obtained here can easily be explained. In unoriented fibres
molecular chains are almost in a stress-free state. Since the rate of crystallization is very slow in these undrawn materials internal stresses built up during crystallization are also small and hence high crystallinities are easily attainable. Both slack and tension heat-set unoriented fibres therefore developed almost the same amount of crystallinity at any given setting temperature.

In oriented drawn fibres, the molecular chains are in a highly stressed state in the crystalline regions due to frozen-in drawing stresses. Although heatsetting the drawn fibres in free or slack state relieves some of these internal stresses, due to the faster rates of crystallization, the attainable crystallinities are limited by the building up of further residual stresses in the non-crystalline regions. Hence, even by heatsetting in the free state, only lower crystallinities are attained in oriented drawn fibres than in the case of undrawn fibres for all setting temperatures.

In tension heat-set fibres, the frozen-in drawing stresses are not relieved due to the prevention of length contraction during setting and crystallization process. This constraint will definitely lead to additional building up of stresses in the non-crystalline regions, the net result of which would be to further lower the attainable crystallinities at any given setting temperature.
However, the lower crystallinities attained at high setting temperatures for tension heat-set fibres cannot be due to high internal stresses in the amorphous regions, since considerable structural relaxation is permitted at high setting temperatures. The lower limit of attainable crystallinity in this case may be due to the impingement of crystallities on one another and to the lack of nuclei for growth at high setting temperatures.

Effect of drawing on crystallinity is shown in Figure 13. Only a slight increase in crystallinity seems to have occurred on cold drawing alone. On subsequent heatsetting under tension the attainable crystallinities decreased initially with increasing extension up to 200%, and for extensions above this the attainable crystallinities increased with increasing extension.

It was recently reported\(^{38}\) that cold or hot drawing of polyester fibres leads to lowering of the molecular weight. Since lower molecular weight of the polymer results in better attainable crystallinities, the increase in crystallinities for higher extensions may be due to the decreased molecular weight of the material.
Fig. 13: X-ray Crystallinity Vs Drawing Extension

Fig. 14: X-ray Diffractograms for Different Molecular Weight Polyester Chips
4.372 Effect of Molecular Weight on Crystallinity

Polyester chips of four known molecular weights were used in this study. These chips were heat-set at 200°C for one hour in order to examine the effect of molecular weight on thermal crystallization.

X-ray diffractograms recorded for these different molecular weight polyester samples, both before and after heatsetting, are shown in Figure 14.

It is clearly seen from these diffractograms that for the unheat-set samples (broken line in Figure 14) the molecular order decreased with increasing molecular weight and the highest molecular weight polyester gave a diffractogram almost similar to that of a completely amorphous polyester, while the lowest molecular weight material gave a diffractogram that is typical of a moderately crystalline material.

These differences in crystallinity for different molecular weight polyester persisted even after slak heatsetting them at 200°C (full lines in Figure 14). Peak resolution improved as the molecular weight of the samples decreased. This suggested that the overall attainable crystallinity for polyester samples by thermal crystallization is largely dependent upon their initial molecular weights.
Using these diffractograms, quantitative measurements of crystallinity were also carried out using the same correlation crystallinity method described earlier. The crystallinity values before and after heatsetting for these different molecular weight materials are listed in Table II.

### TABLE II

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molecular Weight</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$</td>
<td>$M_w$</td>
</tr>
<tr>
<td>4300</td>
<td>15,500</td>
<td>29,000</td>
</tr>
<tr>
<td>5300</td>
<td>17,000</td>
<td>34,000</td>
</tr>
<tr>
<td>6502</td>
<td>21,500</td>
<td>46,800</td>
</tr>
<tr>
<td>8502</td>
<td>27,700</td>
<td>63,000</td>
</tr>
</tbody>
</table>

In Figures 15 and 16 crystallinity is plotted against both number ($M_n$), as well as weight average ($M_w$) molecular weights respectively. Both before and after heatsetting, the crystallinity decreased with increasing molecular weight. Although the increase in crystallinity on heatsetting is greater for the highest molecular weight, the overall crystallinity of the highest molecular weight heat-set materials still remained lower than those of the lower molecular weight heat-set materials.

It was suggested that higher crystallinities achieved for lower molecular weight materials may be due to the complete crystallization of the free chain ends.
Fig. 15 : Crystallinity Vs. Number Average Molecular Weight

Fig. 16 : Crystallinity Vs Weight Average Molecular Weight
In addition to this, a large number of molecular chain entanglements in the polymer net work due to higher molecular weights may hinder the crystallization process considerably and thereby leading to lower attainable crystallinities in higher molecular weight materials.

4.310 Effect of Dyeing on Crystallinity

The effect of dyeing on crystallinity for a few selected polyester samples of different prehistories was also examined in this work. Since the dyeing was effected without any carrier at a temperature of 90°C, some crystallization took place during dyeing.

A plot of crystallinity before dyeing, against the change in crystallinity as a result of dyeing showed (Figure 17), a non-linear relationship. It was noticed from this plot, that the amorphous or unheat-set fibres showed a large increase in crystallinity considerably after dyeing, while the heat stabilized fibre crystallinites slightly decreased after slack dyeing.

Since for unheat-set materials, the glass transition temperature is lower than the dyeing temperature, some crystallization occurred due to dyeing. The lower the glass transition temperature below the dyeing temperature the
Fig. 17: Crystallinity Before Dyeing vs Change in Crystallinity After Dyeing
higher seems to be the increase in crystallinity after dyeing. For heat stabilized materials, the glass transition temperature is reported to be much higher than the dyeing temperature (90°C) and no additional crystallization could be observed after dyeing. The decrease in crystallinity after dyeing, for some of the more crystalline samples may be due to the introduction of some defects in the structure during dyeing.

4.38 Crystallite Orientation

The crystallite orientation functions were determined using the two different methods described in Chapter II.

The normalized azimuthal X-ray diffraction curves for the off-meridional 705 reflection for four different sets of samples are shown in Figure 18, 19, 20 and 21. Resolutions of the overlapping peaks were carried out assuming symmetric Gaussian distributions as shown in the Figures. From these resolved curves $<\cos^2 \theta_{105}>$ were graphically evaluated (Chapter II) and the crystallite orientation functions ($f_0$) were determined.

The crystallite orientation functions so determined were compared with the orientation functions determined by making use of three equatorial reflections 010, 710 and 100. The data are presented in Table III. It can be seen from this
Fig. 18 & 19: 705 Off-Meridional Azimuthal Diffraction Curves
Fig. 20 & 21: 705 Off-Meridional Azimuthal Diffraction Curves
<table>
<thead>
<tr>
<th>Sample Particulars</th>
<th>Crystallite Orientation Function</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{C,m}$</td>
</tr>
<tr>
<td>1. Control (commercial)</td>
<td>0.92</td>
</tr>
<tr>
<td>2. Control TQ 200°C</td>
<td>0.94</td>
</tr>
<tr>
<td>3. Control SQ 200°C</td>
<td>0.93</td>
</tr>
<tr>
<td>4. Control TA 200°C</td>
<td>0.95</td>
</tr>
<tr>
<td>5. Control SA 200°C</td>
<td>0.93</td>
</tr>
<tr>
<td>6. Amorphous Tow Drawn by 400%</td>
<td>0.84</td>
</tr>
<tr>
<td>7. Amorphous Tow Drawn by 400% and TQ 200°C</td>
<td>0.95</td>
</tr>
<tr>
<td>8. Amorphous Tow Drawn by 400% and TQ 200°C</td>
<td>0.88</td>
</tr>
<tr>
<td>9. Amorphous Tow Drawn by 200% and SQ 200°C</td>
<td>0.92</td>
</tr>
<tr>
<td>10. Amorphous Tow Drawn by 300% and TQ 200°C</td>
<td>0.93</td>
</tr>
<tr>
<td>11. Amorphous Tow TQ 200°C</td>
<td>-</td>
</tr>
</tbody>
</table>

$f_{C,m}$ = $f_C$ obtained using off-Moridional 105 peak

$f_{C,eq}$ = $f_C$ obtained using three equatorial peaks (100, 110 and 010)

data that both the methods gave comparable values of crystalline orientation functions ($f_C$) for all the samples examined and therefore anyone of the methods can be used to determine the orientation functions for the crystalline regions for polyester fibres.

The cold drawn series, showed that, crystallite orientation increased with increasing drawing extension after thermal crystallization. However, high crystallite orientation was
attained even at low draw ratios (200%) by heatsetting. It implied that almost all the crystallite nuclei are aligned along the direction of the fibre axis by cold drawing the fibre to 200% extension, and that subsequent heatsetting leads to crystallization by rotation and alignment of chain segments in the non-crystalline regions along the direction of fibre axis thus producing highly oriented crystalline structures.

Higher crystallite orientation after thermal crystallization occurred both in the cold drawn, as well as the commercially drawn filaments. Heatsetting in free state (slack) led to lower crystallite orientations than by heatsetting under constraint (tension). Crystallite orientation therefore appears to depend upon the orientation and disorientation processes occurring in the non-crystalline regions during thermal crystallization.

Lower crystallite orientation attained by heatsetting in the free state (slack) can be due to disorientation of molecular chains in the non-crystalline regions because of shrinkage. However, the differences in crystallite orientations in both slack (SQ) and tension (TQ) heat-set fibres are only marginal and cannot account for the large differences in the mechanical properties and dye diffusion behaviour between these two different sets of samples. It must be the non-crystalline regions, which have a greater influence on the mechanical
and dye diffusion properties of polyester.

4.381 Amorphous, or Non-Crystalline Orientation

Non-crystalline orientation function \( (f_{am}) \) for semi-crystalline polymers is generally determined by combining the X-ray diffraction data either with birefringence data or with sonic modulus data.

The two-phase equations relating birefringence and sonic modulus with crystallinity and orientation are given in equations (1) and (2) below:

\[
\Delta n = \beta f_C \Delta C + (1 - \beta) f_{am} \Delta_{am} \quad (1)
\]

\[
3/2 (\Delta E^{-1}) = \frac{\beta f_C}{E^c_{t,C}} + \frac{(1 - \beta) f_{am}}{E^c_{t,am}} \quad (2)
\]

The values of \( \Delta C, \Delta_{am}, E^c_{t,C} \) and \( E^c_{t,am} \) were independently obtained experimentally and given in Chapter VI. Those values have been assumed here.

Using the values for crystallinity \( (\beta) \) as determined from density data, crystallite orientation function \( (f_C) \) obtained from X-ray diffraction data, orientation function for the non-crystalline fractions \( (f_{am}) \) were determined independently using both the equations (1) and (2). These values are compared in the Table IV.
### TABLE IV

**AMORPHOUS ORIENTATION (CALCULATED BY TWO DIFFERENT METHODS)**

<table>
<thead>
<tr>
<th>Sample Particulars</th>
<th>Crystallite Orientation Function ($f_c$)</th>
<th>Amorphous Orientation Function ($f_{am}$)</th>
<th>$f_{a,b}$</th>
<th>$f_{a,s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (commercial)</td>
<td>0.92</td>
<td>0.87</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Control TQ 200°C</td>
<td>0.94</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>Control SQ 200°C</td>
<td>0.93</td>
<td>0.66</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>Control SA 200°C</td>
<td>0.93</td>
<td>0.47</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>Control TA 200°C</td>
<td>0.95</td>
<td>0.78</td>
<td>&gt;1.0</td>
<td></td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 400% and TQ 200°C</td>
<td>0.84</td>
<td>0.99</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 400% and SQ 200°C</td>
<td>0.95</td>
<td>0.99</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 200% and TQ 200°C</td>
<td>0.88</td>
<td>0.77</td>
<td>&gt;1.0</td>
<td></td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 300% and TQ 200°C</td>
<td>0.93</td>
<td>0.89</td>
<td>&gt;1.0</td>
<td></td>
</tr>
</tbody>
</table>

- $f_{a,b}$ = Amorphous orientation obtained using Birefringence data.
- $f_{a,s}$ = Amorphous orientation obtained using sonic modulus data.

It is noticed from these results that with the exception of the amorphous Tow cold drawn to 400%, for all the other samples the non-crystalline orientations determined from sonic modulus data are always much higher than those determined from birefringence data. For the cold drawn fibres, amorphous orientation determined from birefringence data is incredibly high (0.99), while the same determined from sonic modulus data is substantially lower.
For highly oriented crystalline materials also both the methods gave incredibly high amorphous orientations (nearly equal to unity) values. This suggests that almost all the molecular chains are nearly aligned parallel while the material still remains non-crystalline (e.g., cold drawn to 400% polyester tow).

It was shown by Berg in his report on structure-property relationships for polyester fibres, that a good correlation existed between measured birefringence and half integral breadth of 010 reflections from X-ray diffraction measurements. He concluded there that birefringence is largely influenced by the orientation of the crystalline regions and its dependence on non-crystalline orientation is substantially less.

On the other hand, Devries et al. showed that only the amorphous phase gives a substantial contribution to the short-time compliance (sonic compliance) and that the crystalline phase contribution was always very small and varied very little in absolute value.

It is perhaps due to these different structure dependence of both the measurements that the observed discrepancies in the non-crystalline orientation values might have resulted.
In the light of these facts, there arises a question as to which of the methods used earlier is to be employed to obtain the non-crystalline orientation. It is particularly important to bear in mind that for very highly oriented crystalline materials both methods failed to obtain reasonable values for non-crystalline orientation.

In the present work, it was earlier shown that reliable values for non-crystalline orientation can be obtained by combining the birefringence and sonic modulus data with the crystallinity data determined from density measurements. Non-crystalline orientation was determined by solving the two simultaneous equations (1) and (2).

The amorphous or non-crystalline orientation determined by this later method gave reasonably good correlation with the mechanical and dyeing properties of polyester (see Chapters VIII and IX).

4.39 Determination of Lateral Order and Crystallite Dimensions

To determine the lateral order and the lateral dimensions of the crystallites, X-ray equatorial fibre diffractograms were obtained for few selected samples. Similarly for determining the longitudinal dimensions of the crystallites (lengths) X-ray meridional fibre diffractograms were obtained. Lateral order and size were thus obtained from radial intensity distributions.
4.391 a-Axis Orientation in Undrawn Crystallized Fibres

The equatorial and Meridional diffraction curves for the unoriented crystalline fibres are shown in Figures 22(a) and (b).

Figure 22(a) shows the equatorial diffractograms and Figure 22(b) shows the Meridional diffractograms for the unoriented, amorphous Tow and corresponding slack and Tension heat-set fibres. On comparison of both the Figures, one would notice that the 100 reflection shows maximum intensity distribution along the Meridian (Figure 22(b), a-axis orientation along fibre axis) and the 010 reflection shows maximum intensity distribution along the equator. Similarly, the 005 peak which usually appears along the Meridian for highly oriented crystalline polyester showed its maxima of intensity distribution along the equator (Figure 22(a)), particularly for the tension heat-set fibres (c-axis along equator).

This confirmed the view that for unoriented crystalline material, the crystallographic a-axis tended to align along the fibre axis and the molecular chains (c-axis) tended to orient perpendicular to it.
Fig. 22: Radial Diffractograms for Undrawn Polyester Tow Filaments

Fig. 23: Determination of Lateral Order from Equatorial Radial Diffractograms after H-Berg

Degree of Lateral Order \( d^* = 1 - \sqrt{(a+c)/2b} \)

when, \( a = b = c \) \( d^* = 0 \); \( a = c = 0 \) \( d^* = 1 \)
4.392 **Lateral Order**

Degree of lateral order was arbitrarily determined by the method suggested by Berg$^{42}$ from the equatorial diffractograms as defined and shown in Figure 23. The data on Lateral Order (d*) is presented in Table V.

**TABLE V**

DEGREE OF LATERAL ORDER

<table>
<thead>
<tr>
<th>Sample Particulars</th>
<th>Degree of Lateral Order d*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Commercial)</td>
<td>0.39</td>
</tr>
<tr>
<td>Control SQ 200°C</td>
<td>0.55</td>
</tr>
<tr>
<td>Control TQ 200°C</td>
<td>0.49</td>
</tr>
<tr>
<td>Control SA 200°C</td>
<td>0.58</td>
</tr>
<tr>
<td>Control TA 200°C</td>
<td>0.48</td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 400%</td>
<td>0.07</td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 400% SQ 200°C</td>
<td>0.63</td>
</tr>
<tr>
<td>Amorphous Tow Drawn by 400% TQ 200°C</td>
<td>0.45</td>
</tr>
<tr>
<td>Amorphous Tow SQ 200°C</td>
<td>0.21</td>
</tr>
<tr>
<td>Amorphous Tow TQ 200°C</td>
<td>0.36</td>
</tr>
</tbody>
</table>

It can be seen from this data that considerable improvement in lateral order occurred on heatsetting, and that the degree of lateral order is always higher in the slack heat-set fibres. This may mean that good lateral cohesion between crystalline regions exist in slack set materials as compared to tension set materials.
Lateral order developed in unoriented crystalline materials is much lower than that in oriented crystalline materials. This again indicated the differences in morphologies between the unoriented and the oriented crystalline fibres.

These differences in degree of Lateral order can perhaps explain the differences in dimensional stability and torsional rigidity properties of fibres.

4.393 Resolution of Overlapping Equatorial Diffraction Peaks for Polyester Filaments

For determining the lateral size of crystallites in polyester, it is a general practice to obtain equatorial diffractometer scans. These scans consist of three overlapping strong reflections 010, 110 and 100. In order to determine the lateral sizes of crystallites, which requires the true value of half width of each profile, it is obvious that the three individual diffraction profiles should be resolved.

The problem of resolution of overlapping peaks lies in ascertaining by what kind of line or profile shape would best fit the experimental traces. The two most commonly employed line shapes are the Gaussian and the Cauchy. These are presented in equation (3) and (4) below:

\[ f(x) = I_0 \frac{1}{1 + 4Z^2} \quad \text{(Cauchy)} \]  
\[ f(x) = I_0 2^{-4Z^2} \quad \text{(Gauss)} \]
where, \( f(x) \) is the function representing the bell shaped curve, and \( Z = \frac{X - X_0}{H} \).

Both of these functions contain three parameters each: \( I_0 \), the intensity at the centre, \( X_0 \), the position of the centre, and \( H \), the half width of the peak (width at half intensity).

Heuvel et al.\(^{44,45}\) found that a better fitting of the experimental traces could be obtained by using the Pearson VII function which contains four parameters and is given by:

\[
f(x) = \frac{I_0}{\left[1 + 4Z^2(2Z^m - 1)\right]^m} \quad \text{(Pearson VII)}
\]

where, \( Z = \frac{X - X_0}{H} \) \(^{(5)}\)

In this function, in addition to the peak intensity (\( I_0 \)), peak position (\( X_0 \)), and peak half width (\( H \)), one more parameter, \( m \) - the shape parameter, is introduced. This extra shape parameter (\( m \)) increases the flexibility of the function and thus a wide variety of line shapes can be described with the help of this function. The pure Cauchy profile is represented by the case where \( m=1 \), whereas the Gaussian shape can be obtained by using an infinite value in the Pearson curve (\( m=\infty \)). Thus both the Cauchy and the Gaussian curves are particular cases of the more general Pearson VII profile which is extremely flexible and can be made to fit almost any diffraction profile shape. The shape
of the profile particularly the tail changes most markedly for values of \( m \) between 0.5 and 2.0 (i.e., on either side of the Cauchy value of \( m=1 \)). Hence a small change in \( m \) on either side of unity can cause a large change in the shape of the reflection tail. Hence small changes in \( m \) in the range 0.8 to 1.5 are significant. For \( m \), the restriction \( m > 0.5 \) should be taken into account because the area under the curve does not converge for values below this limit.

The flexibility of the Pearson VII curve is about the same as that of the product functions, and the sum functions, of the Gaussian and Cauchy distributions used by some authors\(^ {46-48} \), which also contain four parameters.

The resolution of the three overlapping equatorial diffraction peaks was carried out in the present work using a computer programme, in FORTRAN IV developed by Heuvel et al.\(^ {44} \) and a Pearson VII profile shape. With the help of this program the experimental diffractometer traces were fitted to the sum of a base line and a number of bell shaped curves.

The general formula used for the composite intensity \( (I) \) is given by:

\[
I = P + QX + \sum f_i(X)
\]  

(6)

where, \( f_i(X) \) are the Pearson VII functions, \( X \) is twice the diffraction angle \( (2\theta) \) and \( P + QX \) is the equation assumed for the linear base line or background intensity. The
values of P and Q of this linear base line are calculated from least squares analysis and have been included in the fitting procedure of the computer program. The possibility of fixing parameters arbitrarily, or of keeping their values between certain lower and upper limits, during iterations is an essential feature of this program.

Using this computer program, attempts were made here to fit the experimental equatorial diffractometer scans, of eight different structurally modified polyester filament samples. The values of the peak positions \( X_0 \) were fixed in each case as obtained from the experimental data, and the values of the peak intensities \( I_0 \), the half widths \( H \), and shape parameters \( m \) were varied by the computer to obtain the best fittings in each case. The final values of all these parameters were then used to obtain the individual profiles of each of the equatorial reflections, namely, the 010, T10 and 100.

Figures 24 to 26 show the curve fittings, as well as the three individual resolved profiles, for the eight different polyester samples. The full line indicates the original experimental diffractometer curve, the dotted curve shows the best fit obtained by fitting Pearson VII functions with suitable selected values of half width \( H \), and shape parameters \( m \). The dashed lines show the individual resolved profiles for each of the three equatorial reflections.
Fig. 24: Equatorial Radial Diffractograms Showing Observed Composite Intensity and the Experimental Curve Fittings Obtained by Computer Programme

CONTROL UNTREATED

CONTROL SQ 200°C

CONTROL TQ 200°C

EQUATORIAL RADIAL ANGLE (2θ) →

ARBITRARY INTENSITY

Experimental

Calculated Composite

Individual Resolved Profiles
Fig. 25: Equatorial Radial Diffractograms Showing Observed Composite Intensity and the Experimental Curve Fittings Obtained by Computer Programme
Fig. 26: Equatorial Radial Diffractograms Showing Observed Composite Intensity and the Experimental Curve Fittings Obtained by Computer Programme
Crystallite Dimensions

The lateral dimensions of the crystallites were obtained from the resolved equatorial diffractograms using the half maximum intensity breadths (H) of the intensity distributions for the reflections 010, β10 and 100 obtained from the computer output. The longitudinal dimensions of the crystallites were determined from the half maximum intensity breadths of the near Meridional 705 peaks. These values are given in Table VI.

TABLE VI

<table>
<thead>
<tr>
<th>Sample Particulars</th>
<th>Lateral Crystallite Sizes (Å)</th>
<th>Longitudinal Crystallite Sizes (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>010</td>
<td>ß10</td>
</tr>
<tr>
<td>Control (Partially Crystalline)</td>
<td>35</td>
<td>29</td>
</tr>
<tr>
<td>Control SQ 200°C</td>
<td>49</td>
<td>41</td>
</tr>
<tr>
<td>Control TQ 200°C</td>
<td>43</td>
<td>37</td>
</tr>
<tr>
<td>Control SA 200°C</td>
<td>51</td>
<td>43</td>
</tr>
<tr>
<td>Control TA 200°C</td>
<td>47</td>
<td>34</td>
</tr>
<tr>
<td>Tow Cold Drawn by 400% (Amorphous)</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>Tow Cold Drawn by 400% SQ 200°C</td>
<td>51</td>
<td>45</td>
</tr>
<tr>
<td>Tow Cold Drawn by 400% TG 200°C</td>
<td>45</td>
<td>38</td>
</tr>
</tbody>
</table>
Heatsetting generally increased both length as well as lateral dimensions of crystallites. While the lateral dimensions of the crystals were larger in the slack set fibres, better longitudinal (length parallel to fibre axis) growth of crystallites were indicated in the tension-set fibres. This is rather expected, because on heatsetting in the free state, shrinkage and extensive chainfolding occur which would favour greater lateral growth of crystalline regions than longitudinal growth. On the other hand, shrinkage and chainfolding are prevented during tension setting and therefore the crystallites preferentially grow in the direction parallel to the fibre axis and increase in length when tension set.

These results appeared to support the morphological models proposed by Statton\textsuperscript{49} for slack and tension heat-set fibres respectively (See Figure 11, Chapter I). These models predict relaxed amorphous regions and somewhat distinct boundaries between crystalline and non-crystalline regions for slack set fibres, and taut or oriented non-crystalline regions with less distinct boundaries between crystalline and amorphous regions for tension heat-set fibres.

Table VII lists the Pearson Parameters, $m$, for the various slack (SQ) and tension (TQ) heat-set oriented fibres. This parameter '$m$' can be assumed to provide some information
on the distribution of crystallite sizes about the arithmatic mean (i.e., the spread, or standard deviation), as well as represent some measure of crystallite imperfections with in crystallites. Lower values of \( m (<1) \), which indicate longer intensity tails for the reflections on either side of the peak central positions than in a Cauchy distribution, suggest a greater degree of imperfection in crystallites as well as a wider distribution in particle sizes, particularly on the lower side of the mean size indicated by the half-width (i.e., a larger number of smaller crystallites). Higher \( m \) values, greater than unity (Cauchy), indicate better crystallite perfection and a narrower spread in crystallite sizes about the average.

**TABLE VII**

PEARSON PARAMETER (\( m \))-A MEASURE OF SIZE DISTRIBUTION AND PERFECTION

<table>
<thead>
<tr>
<th>Sample Particulars</th>
<th>Pearson Parameter (( m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0(10)</td>
</tr>
<tr>
<td>Control (Commercial)**</td>
<td>0.92</td>
</tr>
<tr>
<td>Control SQ 200°C</td>
<td>0.98</td>
</tr>
<tr>
<td>Control TQ 200°C</td>
<td>1.00</td>
</tr>
<tr>
<td>Control SA 200°C</td>
<td>1.02</td>
</tr>
<tr>
<td>Control TA 200°C</td>
<td>1.08</td>
</tr>
<tr>
<td>Tow Cold Drawn by 400%**</td>
<td>0.94</td>
</tr>
<tr>
<td>Tow Cold Drawn to 400% TQ 200°C</td>
<td>0.96</td>
</tr>
<tr>
<td>Tow Cold Drawn to 400% SQ 200°C</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* Partially crystalline.
** Amorphous (only one dimensional order).
From Table VII, it can be seen that heatsetting in general increases the values of m (improves crystal perfection and reduces the spread of the crystallite size distribution). It can also be seen from these values that slack set fibres have larger m values than the tension set fibres, which implied that slack setting improves lateral crystal perfection better than tension setting. In the cold drawn fibres, the effect of condition of treatment (slack or tension) on 'm' values is more clearly brought out than in the hot drawn (control, commercially drawn) samples. In the later cases the m values hardly change from the untreated control to the heat-set fibres. The 'm' values obtained for the annealed fibres (slowly cooled to room temperature after heatsetting) are larger than in the case of quenched fibres (rapidly cooled to room temperature after heatsetting). Annealing treatments therefore appear to bring about a greater perfection in crystallites than quenching treatments.

4.4 GENERAL CONCLUSIONS

It has been shown that the initial molecular orientation influences the structural or morphological modifications that occur due to the thermal crystallization process.

Depending on the initial molecular orientation, perpendicular, random or highly parallel orientation of structural elements may result after heatsetting. The poorly oriented
amorphous materials always showed high crystallinities and perpendicular orientation of structural elements, while the initially highly oriented fibres showed lower crystallinities and high parallel alignment of the structural elements after thermal crystallization.

The structural changes due to heatsetting have been shown here to be very sensitive to setting temperature and tension. It was also shown that tension during heatsetting hinders the crystallization process to a certain extent and lower crystallinities resulted when fibres were heat-set at high setting temperatures under tension.

The lateral and longitudinal dimensions of crystallites differed for slack and tension heat-set fibres. Better lateral order, with larger lateral crystallite sizes were achieved by heat setting the fibres in the free state than under tension. The results appeared to support the morphological models proposed by Statton for slack and tension heat-set PET fibres.

These results will help in understanding the differences in dimensional stability, tensile and torsional properties and dye diffusion behaviour of polyester materials.
CHAPTER IV

REFERENCES


49. Statton, W.O., (To be Published)

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