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The morphology of 50% PET/PEN random copolymer as revealed by high resolution scanning electron microscopy and X-ray diffraction

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Abstract

The microstructure of 50% PET/PEN random copolymer crystallised by uniaxial drawing and subsequent annealing is investigated by two-dimensional wide angle X-ray diffraction and high resolution scanning electron microscopy. Chemical etching was used to reveal the structure after drawing and subsequent annealing. The structure observed was found to be in the order of 100 nm. The results showed fibrillar microstructure parallel to the draw direction that could be associated with the presence of the smectic-A liquid crystalline transient mesophase as a result of the drawing. There was evidence of banding perpendicular to the draw direction when crystallisation started to take place. This banded structure was explained in terms of buckling of the thin polymer film perpendicular to the direction of the draw in an analogy similar to that of liquid crystalline polymers. The wide range of microstructure observed microscopically and reported here are, however, associated with crystallisation.

Keywords: 50% PET/PEN; Crystallisation; Banded structure

1. Introduction

The formation of a smectic-A type intermediate liquid crystalline mesophase prior to crystallisation on annealing of uniaxially drawn PET, PEN and 50% PET/PEN has been confirmed by results reported earlier [1–6]. The effect of the mesophase on the crystallisation process has also been discussed. It was suggested that the degree of crystallisation is dependent on the amount of the oriented mesophase, which is formed as a precursor to the triclinic crystals. SAXS results [4] showed the absence of any microstructure associated with the appearance of the mesophase. In this paper, the morphological changes occurring prior to and during the crystallisation process will be discussed in reference to high resolution scanning electron microscopy (HR-SEM) studies and two-dimensional wide angle X-ray diffraction.

The morphology of PET-like polymers has been of interest for a very long time due to the wide range of applications they are used into. In 1975 Mocherla and Bell [7] studied the morphology of uniaxially oriented PET. They concluded that if samples are drawn at sufficiently fast rates to moderately low draw ratios, 2.0 and 2.5, the deformation process leads to the crystallisation of the chains into folded chain crystals with a large number of irregular folds. As orientation increases, at draw ratios of 3.0–4.0, the irregular folds decrease sharply or even disappear. Chains in the non-crystalline regions become more extended and oriented in the direction of the draw. They also concluded that the *gauche* rotational isomer of the ethylene glycol linkage is converted to the *trans* isomer in the extended chain conformation, and that on annealing the straight chain crystals increase their dimensions. This was also confirmed by a later study [8].

Chang et al. [9] studied the development of microstructure in PET fibres during annealing. They prepared samples for

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TEM using a microtome, but observed that the samples were featureless except for long parallel microtome marks. Fibre streaking in the direction of the draw was also observed in the SAXS images of the same samples. On prolonged annealing, the same samples showed a banded texture perpendicular to the direction of the draw. Other studies, also conducted on PET [10], PET blends [11] and liquid crystalline polymers [12], showed the same banded structure. Similar studies were made on PEN [13] and PET/PEN [14] blends, but most of these studies reported banded structures in non-liquid crystalline polymers without giving an explanation of why they occur.

A detailed review article by Keller and Kolnaar [15] shows images demonstrating the occurrence of *columnar* structures containing lamellae perpendicular to the column, and hence the flow direction, in a sample of polyethylene crystallised under the influence of flow. Another TEM micrograph of polyethylene crystallised from a lightly stretched melt shows *ribbons* transverse to the draw directions. These ribbons are either fully twisted or in varying stages of partial twist. They also showed interlocking shish–kebab structure appearing during flow-induced crystallisation. The important observation here is that the thickness of these columns or ribbons is much greater than that of polyethylene lamellae.

2. Structure characterisation using etching techniques

Revealing the morphology of a polymer sample using TEM or SEM is not always a straightforward technique. TEM samples are commonly heavily stained to reveal lamellar structure. One technique developed by Petermann et al. [16], and published more than two decades ago, involved dissolving the polymer in an organic solvent, dropping it on the surface of an inorganic acid, and then quenching the thin film quickly in water. The film is then picked up on a TEM grid washed, heated to the polymer melting point and quenched in ice to obtain amorphous films. The TEM grid, with the amorphous film on top, is then drawn to the desired draw ratio, quenched and/or annealed at the desired temperature and then examined using TEM. This technique does not involve staining, but still, it is not a commonly used technique because both the organic and inorganic solvent must be chosen very carefully so as not to degrade the polymer and the utmost care must be exerted during the quenching, drawing and annealing of the samples.

Chemical etching came to prominence as a technique used to reveal microstructure in metals, and then was commonly used with polymers. The value of this approach lies in the fact that differential chemical attack based upon physical, chemical or structural inhomogeneities within a material often provides an effective means of investigating its internal structure. Also unlike more conventional mechanical methods, such as sectioning and grinding, specimens prepared in this manner are left strain-free and undistorted. This is an important consideration when investigating polymer samples, as these are often particularly susceptible to damage in this form. The chemical etching, in general, gives a topographic contrast between structurally different regions.

Generally speaking there are two main types of etching techniques known as *mild* or *severe* depending on the proportion of the original material removed during the process [17]. In mild treatments, solvents or solvent vapours are applied to a polymeric substrate to create a surface morphology representative of the underlying microstructure. The etching enables observation in reflected illumination by optical or electron microscopy. In more severe methods, a more substantial fraction of the material is removed and consequently these are not generally suitable for microstructural studies. The work described in the following sections will concentrate on tailoring and using a mild etch to suit the random 50% PET/PEN copolymer which is under consideration here.

2.1. Choice of the etch

In view of the complexity of the chemical process that might be involved in etching methods, great care must be taken in selecting a suitable etching agent for a particular polymer. In particular, the possibilities of microstructural artefacts means that steps must be taken to ensure that the structure produced by etching is indeed due to the underlying inhomogeneities, rather than to a physical or chemical process involved. In an etching process, the reagent is thought to attack the polymer, causing chain scission and producing new molecular species, which are subsequently removed from the site of the reaction. Attack therefore tends to be selective, unlike the dissolution process that occurs randomly and might involve swelling.

In most cases the etching chemical is required to distinguish between inhomogeneities such as crystalline and amorphous components. In this case it is important that the chemical activity of the etch is chosen so as to be sufficient to interact with or cause dissolution of one component or region of the material, mostly the amorphous component, without affecting the other region, the crystalline regions in this case, to the same extent. *Permanganic etch* is an example of an inorganic etchant which is often used in this function. It is often thought to involve an oxidation process, which preferentially attacks disordered regions of the polymer. This etchant is prepared using potassium permanganate with strong acids and was found suitable for polyethylene [18] and poly aryl ether ether ketone (PEEK) [19].

Sodium hydroxide solution was also used with PEN to investigate heavy ion tracks as a result of irradiation [20] but was not considered a selective etchant. Organic hydrocarbons were used to etch nylon and polypropylene [21], while sodium acetate was successfully used to etch polyethylene oxide [22].

Two relatively old publications [23,24] referred to using a 40% aqueous solution of methylamine in selectively degrading PET. These papers showed that methylamine principally attacks amorphous regions. Methylamine is an ideal etchant as it reacts rapidly with PET at room temperature thus minimising side effects due to high temperatures. A more important advantage of choosing such an etchant is that its reactions with esters, *aminolysis*, are very well known [25] and documented in many organic chemistry textbooks.

$$\mathrm{R'COOR} + \mathrm{H_2NR''} \rightarrow \mathrm{R'CONHR''} + \mathrm{ROH} \quad (1)$$

where, $R' = (C_6H_4)$, $R = (CH_2{-}CH_2)$ and $R'' = CH_3$.

Although most of the results presented below are for samples etched in 40% aqueous methylamine solution some samples were investigated without etching to make sure that any structure observed after etching is not a result or a consequence of the chemical reaction.

3. Experimental

3.1. Sample preparation and X-ray diffraction setup

Six different samples have been prepared from the 50% PET/PEN random copolymer. Each sample was chosen to represent a specific stage observed in the WAXS analysis described in Refs. [4–6]. These stages are amorphous, oriented amorphous, mesophase, oriented crystalline and oriented crystalline annealed, in addition to unoriented amorphous annealed sample prepared for comparison reasons.

In order to prepare each microstructural stage, each sample was drawn to a specific draw ratio at a given temperature and then quickly quenched to air or annealed with the ends fixed at a given temperature. Fig. 1 illustrates how each sample was prepared and shows a diffraction 2D diffraction pattern for each sample after preparation.

The X-ray measurements were done on a Philips PW 1729 X-ray generator using a graphite filtered copper Kα X-ray tube producing radiation with a wavelength of 1.54 Å. The measurements were made in transmission mode, using a CCD camera as a detector. The sample-to-film distance was calibrated using silicon powder that gives a sharp (100) ring at a 2θ value of 28.442° (d-value of 3.135 Å).

3.2. Etching procedure and SEM analysis

The 50% PET/PEN random copolymer was etched using 40% aqueous methylamine. The samples were etched by placing them in 10 ml of methylamine for a given amount of time, ranging from a few minutes to a few days. Next they were shaken in an ultrasonic bath for 15 min before washing, first with ethylene glycol and then with acetone to remove all the side products of the etching process and any excess methylamine that might have adhered to the sample surface.

Permanganic etching was also used with some samples. The etching solution was prepared by dissolving 0.7 wt% potassium permanganate ($KMnO_4$) in a 2:1 volume mixture of concentrated sulphuric acid (H_2SO_4) and concentrated orthophosphoric acid (H_3PO_4). The samples were then washed with hydrogen peroxide (H_2O_2) in order to remove the undissolved permanganate crystals that otherwise remain on the sample surface. Acetone was also used as a wide known solvent that might be able to preferentially attack the amorphous component of the 50% PET/PEN. All etching procedure was carried out at room temperature.

After etching, with acetone, methylamine or permanganate, the sample was analysed again using WAXS to make sure that no changes occurred in the crystalline or amorphous state of each sample as a result of etching. Generally, samples did not show any change in their WAXS pattern after etching and accordingly the category under which such sample would be classified is shown in Fig. 1. The sample category will be used to define each sample discussed in this paper.

Before and after chemical etching the samples were analysed using the JEOL 6340F Field Emission Gun Scanning Electron Microscope (FEG-SEM). The microscope is equipped with a cold-field emission cathode that can be operated between 0.5 kV and 30 kV. The secondary electron image resolution is 1.2 nm at 15 kV and 2.5 nm at 1 kV produced by an electromagnetic four-lens system with a semi-in-lens objective lens designed for smallest possible aberrations. Images were displayed as 1280 × 1024 pixels, and the maximum resolution is 2048 × 2048. All sample surfaces were sputtered with gold to prevent charge from building up on the surface of the nonconducting polymer samples. The microscope is equipped with two types of detectors, a *secondary* and a *back-scattered* electron detector. Both of which have been used in the analysis so that we can look at the surface as well as examine deeper inside each sample.

4. Results and discussion

4.1. X-ray diffraction

It is quite clear from the 2D diffraction patterns shown in Fig. 1 of the amorphous and unoriented amorphous annealed sample that there is an obvious diffuse amorphous halo indicating the absence of crystallinity in the sample, as shown in the 2d WAXS patterns in Fig. 1A and B, respectively. After drawing to a draw ratio of two the amorphous halo started to concentrate on the equator, indicating the presence of an oriented, yet amorphous structure as shown in Fig. 1C. Fig. 1E represents the oriented crystalline sample drawn to a draw ratio of 3 where it is obvious that there is a hint of splitting starting to take place in the equatorial reflections indicating the existence of horizontal register between the chains and low, two-dimensional, crystallinity.

Fig. 1F on the other hand obtained by annealing the oriented crystalline sample at 115 °C for 24 h shows distinct splitting of the equatorial reflection into three distinct reflections indicating lateral packing of the chains. The clear first layer lines indicate the development of three-dimensional crystalline structure. The key aspects of Fig. 1D showing the mesophase sample are the high degree of orientation, the almost complete absence of crystallisation. The presence of a sharp meridional peak at a position equivalent to 11.5 Å and the absence of the crystalline order in the interchain packing mean that the sample has order which could well be classified as smectic-A. A more detailed explanation of the development of structure using X-ray diffraction can be found in Refs. [1–4].

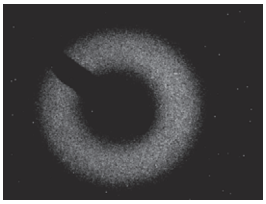
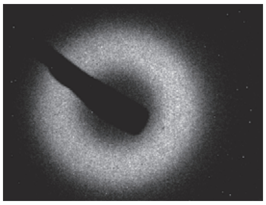
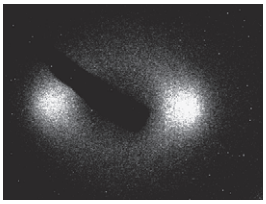
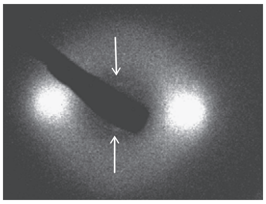
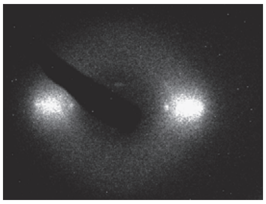
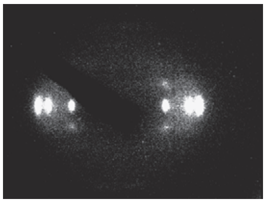
Sample Category	**WAXS Patterns**	**Preparation Mode**
(A) Amorphous		50% PET/PEN, cast film.
(B) Unoriented Amorphous Annealed		50% PET/PEN, cast film annealed at 115 °C for 24 hours.
(C) Oriented Amorphous		50% PET/PEN, cast film drawn at 40 °C using the BIAX machine at 0.1 mm sec^{-1} to a draw ratio of 2.
(D) Mesophase		50% PET/PEN, cast film drawn by hand in a silicon oil bath at 80 °C for a draw ratio of 1.5.
(E) Oriented Crystalline		50% PET/PEN, cast film drawn by hand in a silicon oil bath at 80 °C for a draw ration of 3.
(F) Oriented Crystalline Annealed		50% PET/PEN, cast film drawn by hand in a silicon oil bath at 80 °C for a draw ration of 3 and then annealed with ends fixed at 115 °C for 24 hours.

Fig. 1. 50% PET/PEN samples prepared for etching.

4.2. *SEM of unetched samples*

Various 50% PET/PEN samples were examined under the SEM in order to be able to investigate the morphological changes taking place during uniaxially orienting and/or annealing the sample. Fig. 2 shows the typical surface morphology that was observed for the amorphous (2A) and the unoriented amorphous annealed copolymer (2B). The X-ray diffraction pattern shown in Fig. 1B shows that the amorphous copolymer does not crystallise on annealing and the electron micrographs obtained for both samples are featureless. The micrograph also shows that the annealed sample is rougher, grainier, on the surface. This might be a consequence of uniform shrinkage that can be associated with annealing.

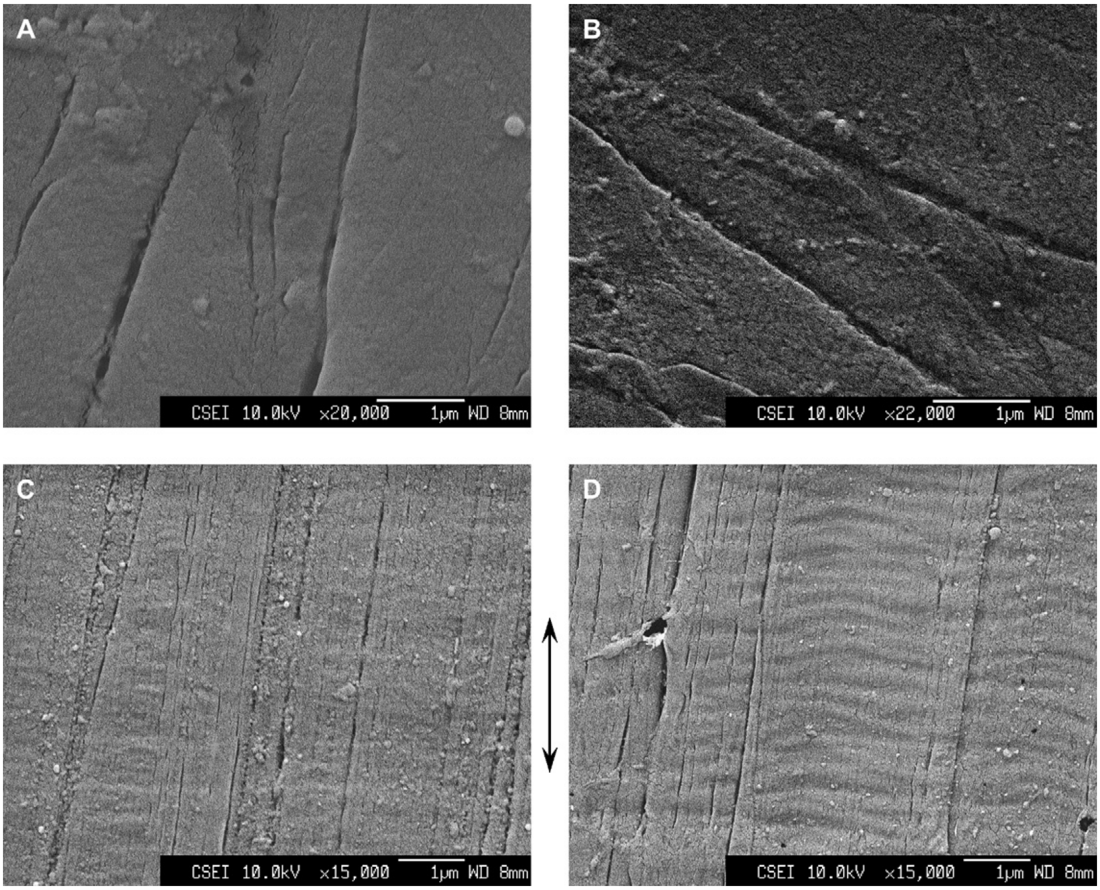


Fig. 2. Electron micrographs of unetched 50% PET/PEN taken at different magnifications. (A) amorphous sample; (B) unoriented amorphous annealed sample; (C) mesophase sample and (D) oriented crystalline sample. The bar represents 1 μm in all micrographs and the double-headed arrow represents the draw direction for samples C and D.

On the other hand the mesophase sample shows fibre streaking in the direction of the draw as illustrated in Fig. 2C. Higher magnification did not reveal any more details on the surface. However, the oriented crystalline sample, Fig. 2D, shows a "*banded*" like texture in a direction perpendicular to that of the draw. Beyond these broad features little else can be resolved in the microstructure.

The use of an etch was found necessary to resolve further structural features. Different etches were used in aiming to selectively and preferentially degrade amorphous regions in order to reveal more of the microstructure of the oriented, mesophase and crystalline regions of different samples.

4.3. The effect of different etches

As discussed above the choice of the correct etch is crucial for revealing the morphological structure of a particular polymeric material and that different etches were developed based on experience in order to suit specific polymers. Attention was focused on the work published on different polymers with similar physico-chemical properties to PET and PEN. In particular polyethylene [18], PEEK [19] and more importantly PET itself [23,24] in this study.

In fact PET, PEN and certainly their random copolymers are considered to have polar molecules due to the presence of the carbonyl and ethylene linkages along the polymer chains. This would imply that these polymers would dissolve in a polar solvent, and since they are composed of non-ionic (all covalent) bonds a *polar aprotic* solvent was thought to be a good etch for such a system. Two organic solvents were used, acetone and methylamine. Also, an inorganic etch that was used successfully with PEEK, permanganate, was used as explained above. This step is meant to determine which etch is the most selective and non-destructive to the sample, i.e. the etch has to selectively dissolve the amorphous regions of the sample without damaging the crystalline regions. Furthermore it should not cause swelling of the polymer, as this will also change its morphology.

4.3.1. Acetone as an etch for 50% PET/PEN

Fig. 3 shows the electron micrographs of amorphous and unoriented amorphous annealed 50% PET/PEN samples etched with acetone for 24 h, Fig. 3A and B, respectively. It is clear, on comparison with the unetched samples shown in Fig. 2, that leaving the sample in acetone for 24 h causes it to swell. Other than the swelling, there is no distinct feature that could be resolved in this case. On the other hand, the

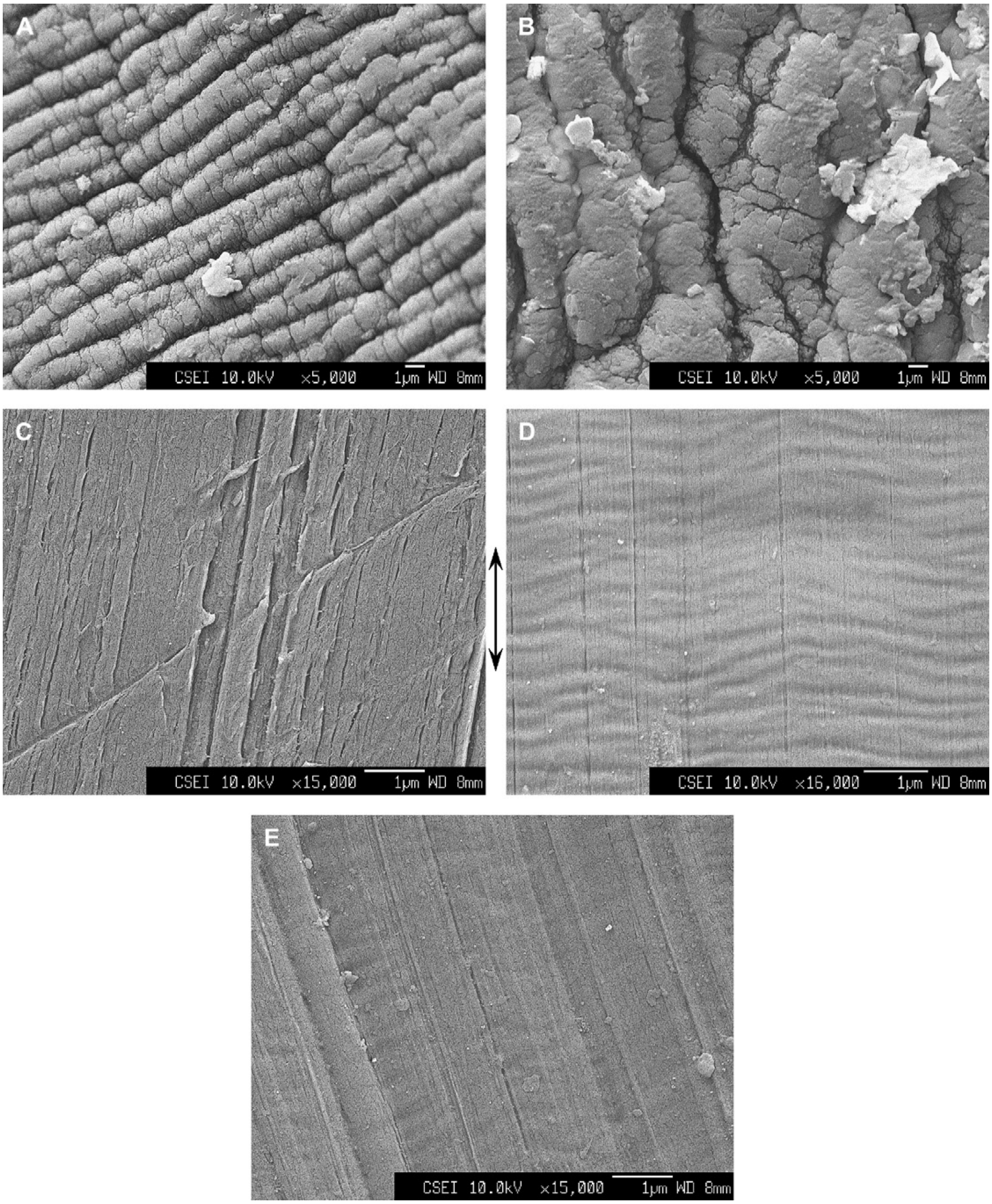


Fig. 3. Electron micrographs of 50% PET/PEN taken at different magnifications etched with acetone for 24 h. (A) amorphous sample; (B) unoriented amorphous annealed samples; (C) mesophase sample; (D) oriented crystalline sample and (E) oriented crystalline annealed sample. The bar represents 1 μm in all micrographs and the double-headed arrow shows the drawing direction of samples C, D and E.

mesophase samples show a distinct fibre-like texture in the draw direction, as seen in Fig. 3C.

Oriented crystalline and oriented annealed samples show a banded structure perpendicular to the direction of the draw, Fig. 3D and E. The thickness of these bands is about 0.1–0.2 μm. This structure is more obvious in the oriented crystalline samples than in the oriented crystalline annealed ones. This might be due to the higher crystallinity of the oriented crystalline annealed samples and consequently, the lower amount of amorphous material that could be removed by acetone, or that the bigger crystals prevented the etch from going through the material to solvate the amorphous regions. This banded structure appears to be a series of ribbon-like columns or strands going through the whole mass of the oriented crystalline and oriented crystalline annealed samples.

4.3.2. *Methylamine as an etch for 50% PET/PEN*

Amorphous and unoriented amorphous annealed samples showed highly random surface features after etching that are similar to each other. This indicates that methylamine is evenly attacking the sample surface without any preferential reactivity between different parts of the sample as shown in

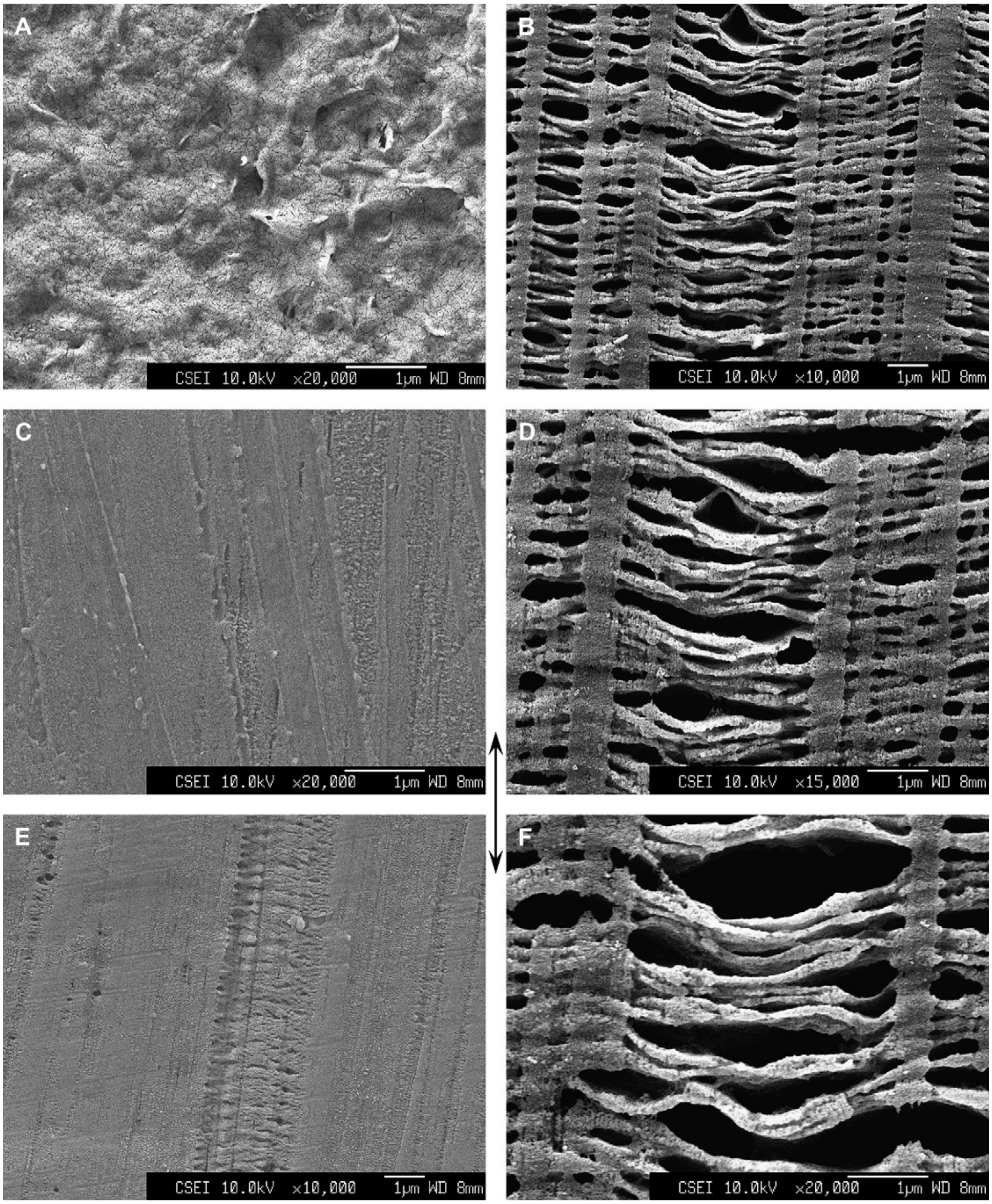


Fig. 4. Electron micrographs of 50% PET/PEN taken at different magnifications etched for 24 h in methylamine. (A) amorphous sample; (B) mesophase sample; (C) oriented crystalline annealed sample; (D–F) samples represent oriented crystalline samples. The scale bar represents 1 μm in all figures and the double-headed arrow represents the draw direction of samples (B–F).

Fig. 4A. Mesophase sample clearly shows fibre streaking in the direction of the draw and they seem to be less affected by the etch than the amorphous samples as shown in Fig. 4B. Oriented crystalline annealed sample also seem to be not affected to a large extent by etching, but the banded structure (or the ribbon-like structure) perpendicular to the draw direction is still clear in Fig. 4C.

It is very difficult to determine the thickness of the bands from Fig. 4C. This kind of structure resembles the columnar structure containing lamellae perpendicular to the columns and hence to the draw direction; similar structures were observed for PE and reported by Keller and Kolnaar [15]. However, the thickness of these lamellae is much larger than the value of the long period observed in the SAXS measurements [4].

Etching the oriented crystalline samples with methylamine as shown in Fig. 4D–F leads to a much better removal of the amorphous content and a very well resolved structure is obtained. This structure can also be described in terms of a banded or ribbon-like structure occurring perpendicular to the draw direction. These bands or ribbons are connected together with fibre-like strands of the polymeric material running parallel to the draw direction. The structure obtained in this case is very well defined, and the fibrous strands range in thickness between 0.5 μm and 1 μm, while the bands or ribbons have thickness ranging between 100 nm and 300 nm.

4.3.3. Permanganate solution as an etch for 50% PET/PEN

Using the permanganic etch directly as explained above proved to be very destructive to the samples and non-selective. In fact, it acted as a solvent and was able to dissolve the whole sample in a few minutes. Accordingly, the concentrated permanganic solution was diluted with distilled water (1:3 by volume) in order to make it less destructive for the sample. Etching the 50% PET/PEN with the diluted permanganic solution for 24 h appeared to be less effective than methylamine as shown in Fig. 5. Similar to those etching results obtained with methylamine or acetone, the amorphous and unoriented annealed samples seem to be evenly etched without any significant features being detected.

Mesophase samples still showed the fibrous streaking in the draw direction and the oriented crystalline samples showed

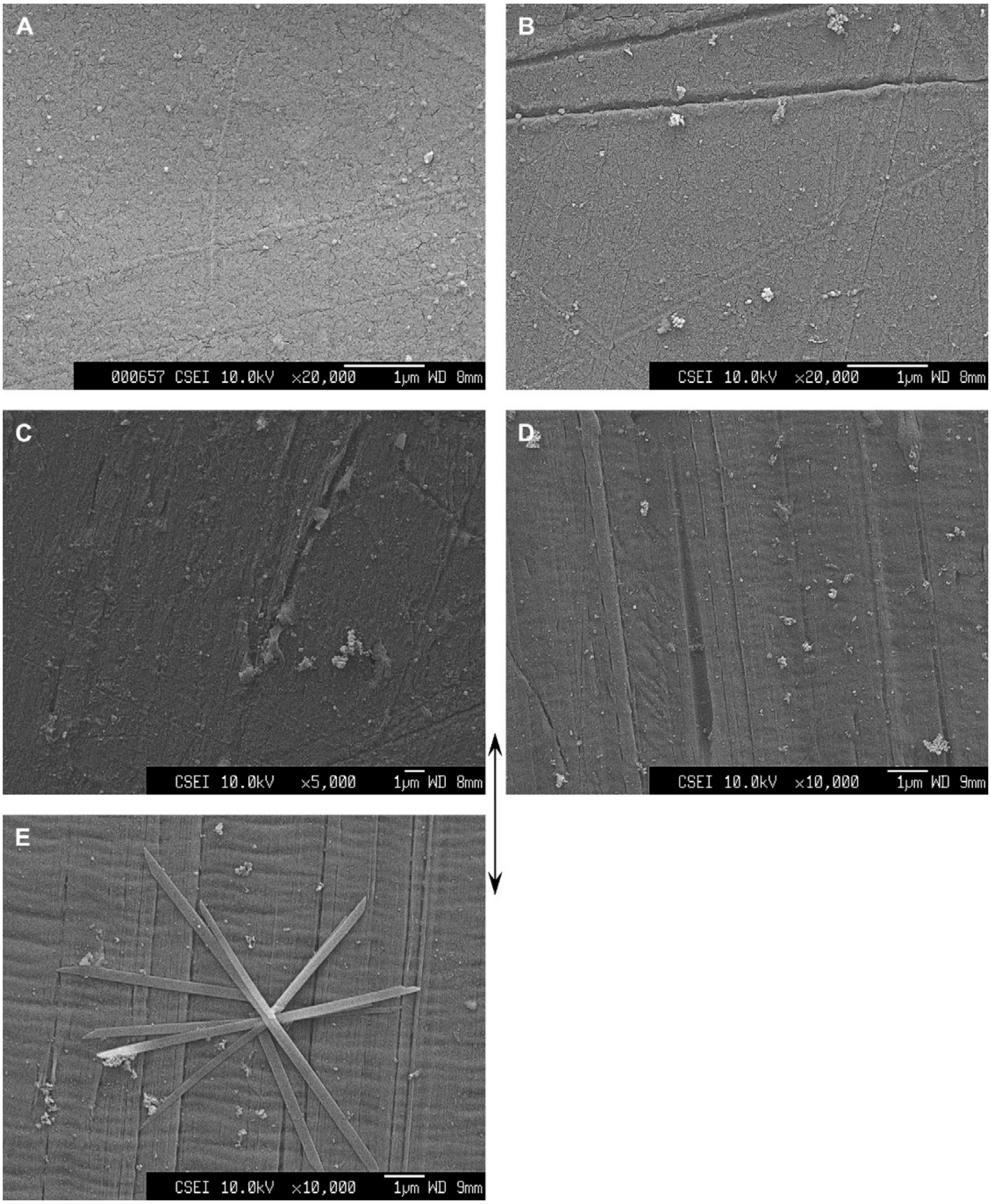


Fig. 5. Electron micrographs of 50% PET/PEN at different magnifications etched for 24 h in permanganic etch. (A) amorphous sample; (B) unoriented amorphous annealed sample; (C) mesophase sample; (D) oriented crystalline annealed sample and (E) oriented crystalline samples. The scale bar represents 1 μm in all figures and the double-headed arrow represents the draw direction of the oriented samples (C–E).

very faint banding perpendicular to the direction of the draw. However, the bands are clearer in the oriented crystalline annealed samples (Fig. 5E), which is also accompanied by some solvent crystallised material that was formed on the sample surface and was not removed during washing the sample with hydrogen peroxide.

Etching results obtained so far strongly suggest that methylamine serves as the best etch for the 50% PET/PEN copolymer and accordingly was chosen to study the structure in more detail as will be discussed below.

4.4. Detailed morphology of 50% PET/PEN after etching with methylamine

Amorphous 50% PET/PEN samples are randomly and heavily affected by methylamine etching as shown in Fig. 6A–C. It is clear that the etch acts to remove successive layers of the amorphous polymer samples continuously and pits and holes are formed on the sample surface after prolonged etching. Similar results are obtained for the unoriented amorphous annealed samples as shown in Fig. 6D–F, owing to

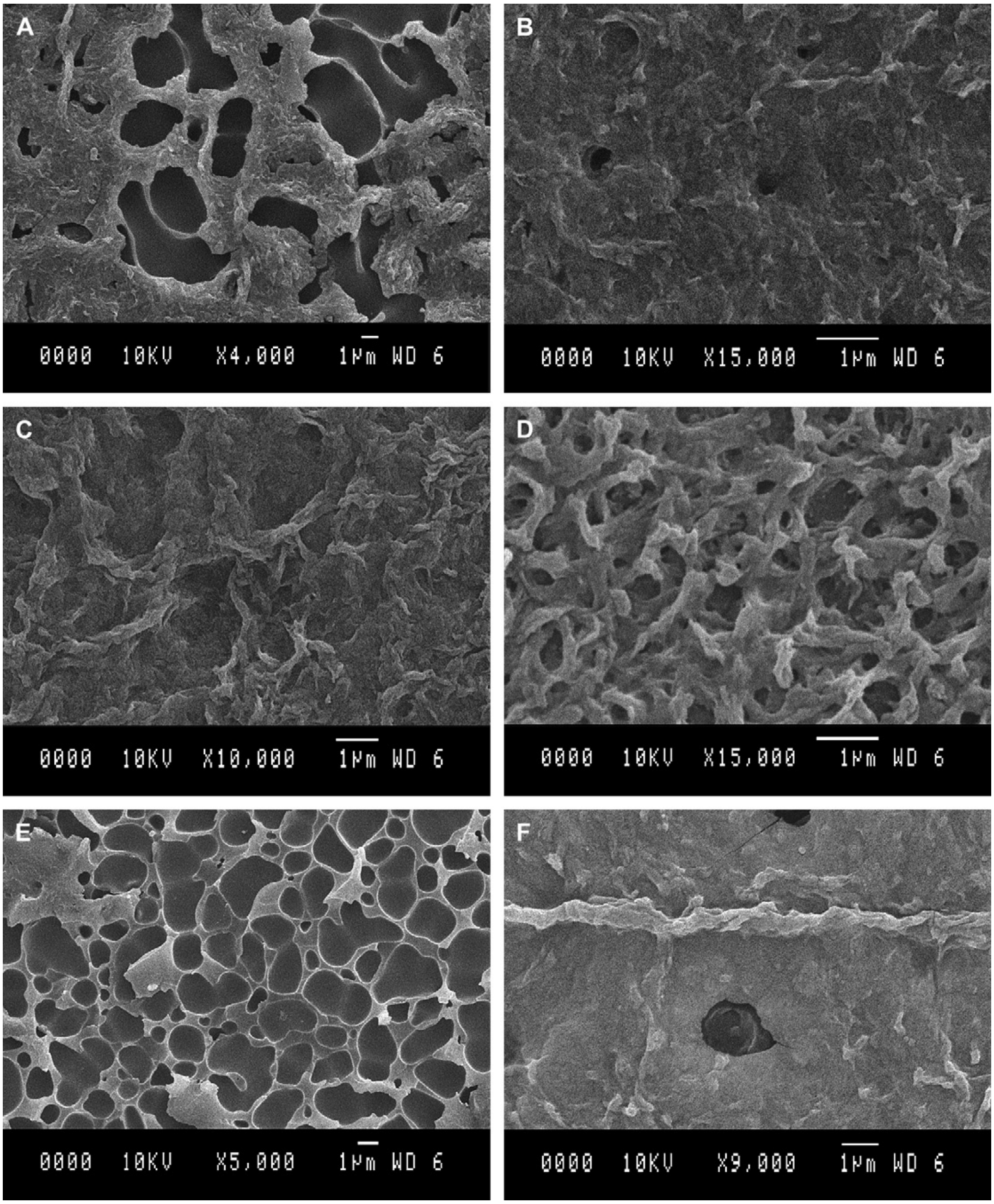


Fig. 6. Electron micrographs of amorphous 50% PET/PEN taken at different magnifications after etching with methylamine for 8 (A), 16 (B), 24 h (C); and electron micrographs of unoriented amorphous annealed 50% PET/PEN taken at different magnifications after etching with methylamine for 8 (D), 16 (E), 24 h (F). The scale bar represents 1 μm in all figures.

the fact that amorphous 50% PET/PEN samples do not crystallise on annealing.

Oriented amorphous samples develop cracks 1–2 μm wide after etching as shown in Fig. 7A. Higher resolution of these cracks shows that the sample is composed of stacks of platelets or sheets on top of each other parallel to the sample surface. The thickness and the spacing of these sheets are about the same, approximately 100 nm. Mesophase samples etched with methylamine for 7 h show fibre-like streaks in the draw direction and highly oriented fibrillar entities parallel to the draw direction. They become more obvious after etching for 12 h. Continuous etching for 24 h reveals the banded structure perpendicular to the draw direction; which is illustrated in Fig. 7B–D.

Once again in this case the WAXS pattern of the sample did not change and this means that the banding is either a sign of high state of orientation rather than the inducing crystallinity or that the crystals formed, if any, are too small in size and too scattered in the oriented mesophase matrix that they could not be detected by X-ray scattering. Further etching causes more damage to the surface and does not reveal any further structure except the gold grains sputtered on the sample surface.

Oriented crystalline 50% PET/PEN samples show banding texture perpendicular to the direction of the draw, the thickness of the bands is approximately 200 nm and could be resolved at high magnifications as shown in Fig. 8A–C. Etching the oriented annealed 50% PET/PEN samples for 16 h shows that the banded structure is inclined with an angle to the direction of the draw as illustrated in Fig. 8D.

Etching the samples for longer time intervals (24 h) as shown in Fig. 9A and B reveals the structure very clearly. The layers of bands in this case are approximately 50–100 nm thick. Further etching for 48 h as shown in Fig. 9C and D causes the breakdown of the platelet bands and their degradation by methylamine. In this case the observed bands are inclined with an angle to the direction of the draw, which can be schematically described as resembling the *herringbone* structure, and they are not perpendicular to the draw direction.

The results discussed above can be summarised as follows:

1. Uniaxial drawing the 50% PET/PEN random copolymer resulted in the formation of a distinct fibre streaking in the direction of the draw characterising the liquid crystalline intermediate mesophase stage that occurs during drawing of the polymer sample to a certain draw ratio at a specific temperature.
2. Further drawing or annealing of the samples leads to the observation of a banded structure that seems to be associated with the crystallisation process in the copolymer. These bands are much thicker than the expected lamellar thickness; they appear to be 0.5 μm thick while the long

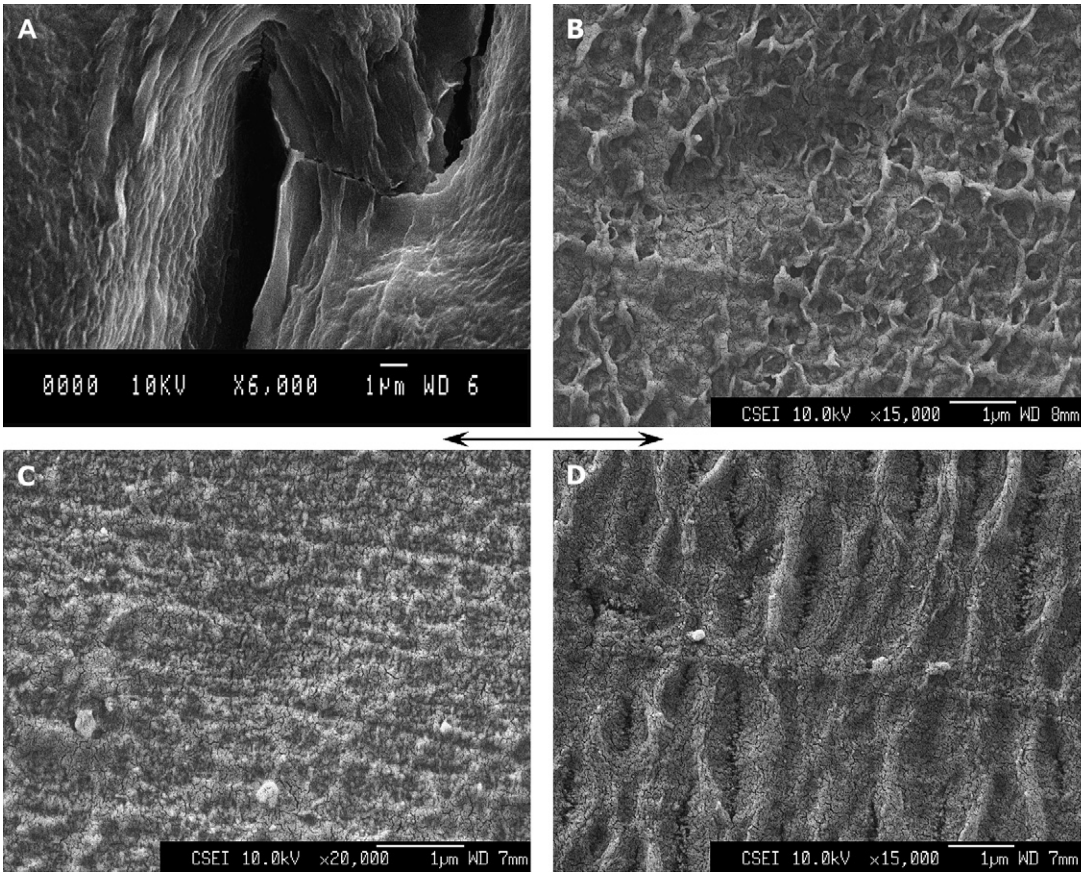


Fig. 7. (A) Electron micrographs of oriented amorphous 50% PET/PEN after etching with methylamine for 8 h; electron micrographs of mesophase 50% PET/PEN samples taken at different magnifications after etching with methylamine for 7 (B), 12 (C) and 25 h (D). The double-headed arrow represents the direction of the draw.

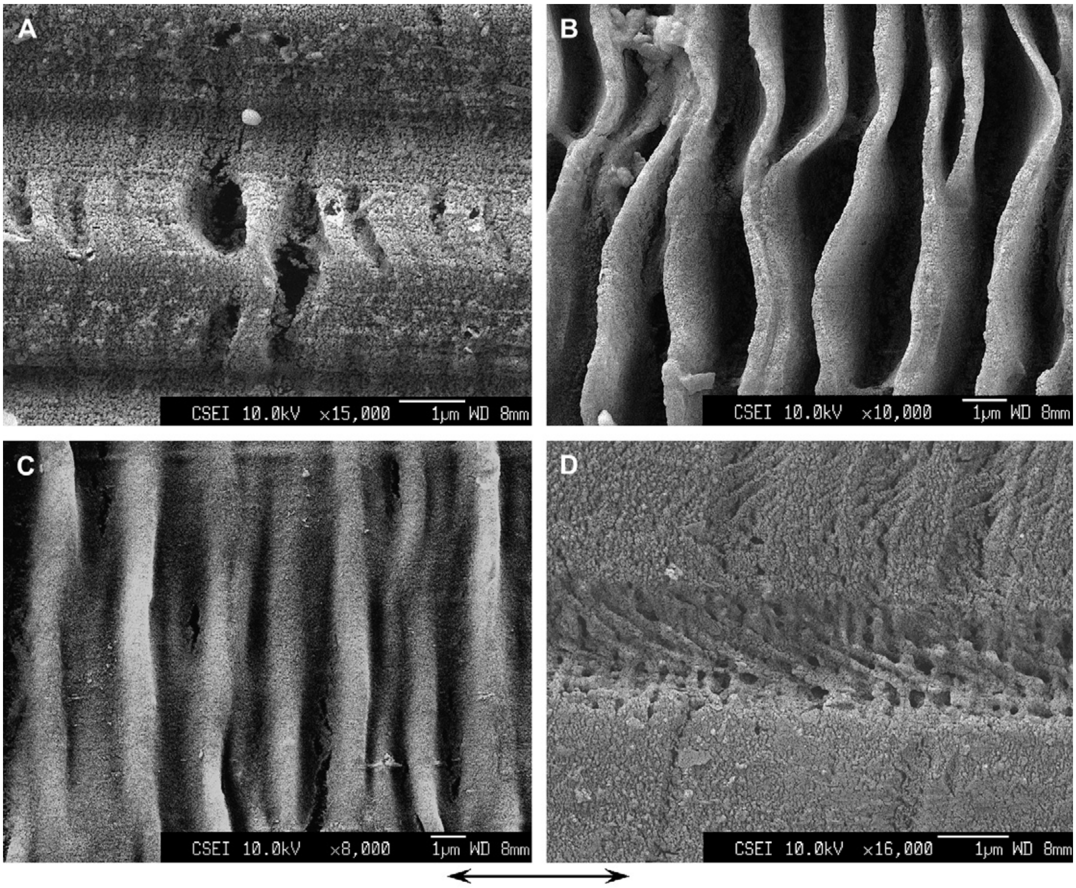


Fig. 8. Electron micrographs of oriented crystalline 50% PET/PEN taken at different magnifications after etching with methylamine for 8 (A), 16 (B) and 24 h (C) and electron micrograph of oriented crystalline annealed 50% PET/PEN after etching with methylamine for 16 h (D). The double-headed arrow represents the direction of the draw.

period obtained from the SAXS results is about 160 Å. Exact SAXS measurements are already documented and will be published soon [26].

3. In order to better reveal the structure and to be able to highly resolve it, methylamine is found to be the most suitable etch that can be used with the 50% PET/PEN random copolymer. It is a selective etch that preferentially removes the amorphous regions of the sample through aminolysis and affects the ordered and crystalline regions to a lesser extent.
4. The banded structure observed is always perpendicular to the draw direction and, in the case of 50% PET/PEN, it is also observed inclined with an angle of 30° to the draw direction. It must be noted here that the angle between the meridian and the line going through two diagonally situated points in the two point pattern is approximately double this value (70°) as shown in Fig. 10 which is also consistent with that observed for PET [26,27].
5. The structure observed in the SEM is on a much larger scale than the actual lamellar thickness obtained from the X-ray results. The results also suggest that the bands are those regions of the polymer that contain the crystalline and the highly oriented material, together with some highly entangled polymer chains too, that are not being removed by the etch.

5. Conclusion

In conclusion, the banded or ribbon-like structure is the portion of the sample that contains the oriented and the crystalline material, otherwise it should have been removed by the etch. The banding itself should not be considered as a consequence of crystallisation but can only be considered as a result of the ordering process itself.

The origin of these bands can be explained using a simple model suggesting that the sample is composed of layers of polymer sheets stacked on top of each other. In an earlier publication Hanna et al. [28] studied sequence segregation in molten liquid crystalline random copolymers, and how this would lead to the observation of a banded structure perpendicular to the shear direction of the polymer. Fischer et al. [29] explained the banded structure taking place in liquid crystalline polymers as being due to the buckling for the polymer chains as a result of their being acted upon by a force in a confined space.

It is clear that PET, PEN and the 50% PET/PEN random copolymer systems exhibit liquid crystalline like behaviour on crystallisation of the oriented polymer during annealing [4–6] and during drawing [9,30–32]. If we adopt the same behaviour here but for a whole sheet of polymer and by drawing the polymer film in the vertical direction, a transverse

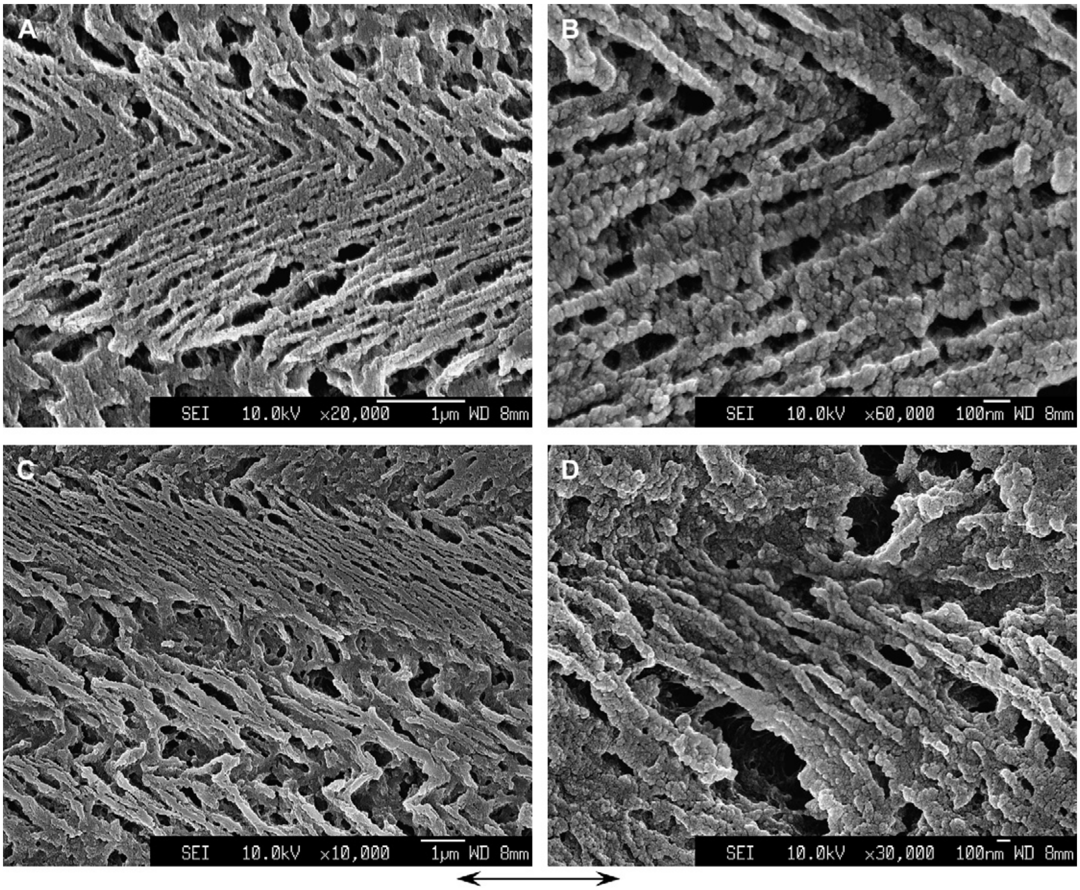


Fig. 9. Electron micrographs of oriented crystalline annealed 50% PET/PEN taken at different magnifications after etching with methylamine for 24 h (A and B) and electron micrographs of oriented crystalline annealed 50% PET/PEN taken at different magnifications after etching with methylamine for 48 h (C and D). The double-headed arrow represents the direction of the draw.

compressive force will act on the other two dimensions of the polymer sheet, causing it to buckle in the direction of that transverse force.

This is schematically represented in Fig. 11. The observed structure will vary depending on the direction from which the sample is examined. The bands or ribbon-like structure will be

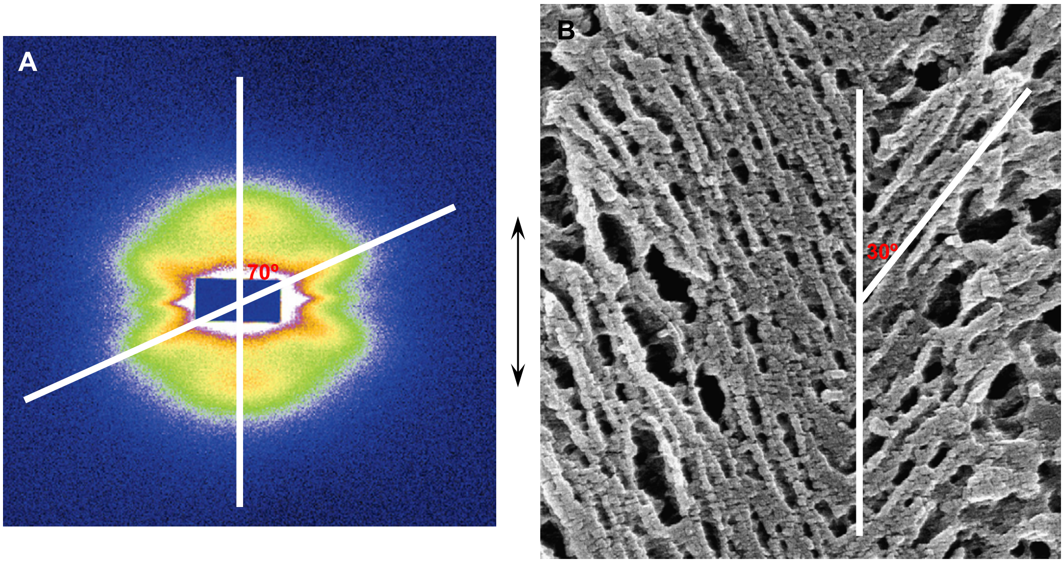


Fig. 10. (A) SAXS pattern of 50% PET/PEN taken at 125 °C showing an angle of 70° between the meridian and the four-point streaking. (B) Electron micrograph of oriented crystalline annealed 50% PET/PEN showing an angle of 30° between the draw direction and the direction of the bands. The double-headed arrow indicates the direction of the draw.

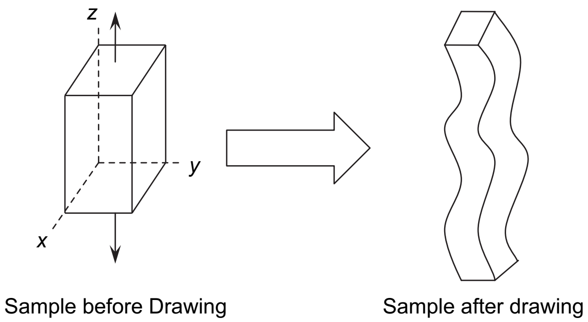


Fig. 11. A schematic representation of buckling that might take place during the drawing of a polymer film due to the transverse contraction strain in the direction perpendicular to the drawing force. The left hand side represents the sample before drawing. The drawing force in this case is vertical and represented by the dark black arrows, it takes place in the $y-z$ plane. The contraction force accordingly takes place in the other two planes perpendicular to that plane, namely $x-y$ and $x-z$ planes. The Buckling after drawing is schematically represented by the right hand side cartoon. The *normal banding* will be observed if we examine the sample perpendicular to the $y-z$ plane. And the *herringbone banding* will be more obvious if we examine the sample perpendicular to the $x-z$ plane.

observed and the sample surface will appear buckled, if the sample is examined perpendicular to the $y-z$ plane. On the other hand the *herringbone banding* will be more obvious if we examine the sample perpendicular to the $x-z$ plane.

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