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Comparing the surface and internal structure of polypropylene fibres using advanced microscopy techniques

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This paper highlights the importance of both surface and internal (bulk) structure of polypropylene (PP) melt extruded monofilament fibres and the dependence of structure on processing conditions. Gravity spun and as-spun fibres showed similar spherulitic surface structure but Wide Angle X-ray Scattering (WAXS) results indicated that the overall fibre crystallinity was contrasting for the two fibre types. From analysis of longitudinal and transverse fibre cross sections using Scanning Probe Microscopy (SPM) and Environmental Scanning Electron Microscopy (ESEM) it was found that gravity spun fibres showed a shish-kebab type structure in contrast to the macrofibrillar internal structure of the as-spun variant. *In situ* tensile testing gave powerful evidence to suggest that deformation in the necking region for the gravity spun fibres was due to the composite behaviour of the spherulitic surface and the internal shish-kebab structure.

1. Introduction

The characterisation of synthetic textile fibres has traditionally employed techniques such as optical and electron microscopy, X-ray diffraction and mechanical and thermal analysis. Over the past two decades, considerable progress has been made in the development of new surface analytical tools. Two of the most significant advances for polymer scientists have been the invention of SPM, in particular Atomic Force Microscopy (AFM), and a development in electron microscopy in the form of the ESEM. Despite the relative maturity of these techniques and the success of SPM in the characterisation of a range of polymeric materials, neither of them has so far been utilised to any great extent in the study of textile fibres. For PP fibres specifically, only a handful of papers have been published to date [1–4]. The SPM offers the potential to image and characterise a range of materials at submicron level. The ESEM has the ability to image at relatively low vacuum compared to a standard SEM, thus enabling analysis on non-conducting materials without the need for carbon or gold coating and also, importantly, dynamic experiments on these materials. The installation of a tensile stage into the chamber of an ESEM makes feasible *in situ* observations of structural and morphological changes at high magnification. As with SPM, the published research involving ESEM in textile fibre research is also limited, despite its many advantages over conventional SEM for textile research, as pointed out as early as 1994 by Tao and Collier [5].

The authors have, in a previous publication [6], demonstrated how SPM, in the form of AFM and Lateral Force Microscopy (LFM) in contact mode, is suitable for fibre analysis. More specifically, SPM was successfully applied to the investigation of changes in the morphology of PP monofilaments during melt-extrusion and subsequent drawing. A gradual deformation at the fibre surface from a spherulitic structure to a shish-kebab type structure was observed for the gravity spun (no previous mechanical stretching) and as-spun variants. In the drawn PP filaments, the surface morphology was predominantly fibrillar in character, though the nature of the fibrillar structure was found to be influenced by the drawing conditions. WAXS diffraction patterns of the same PP filaments gave, in conjunction with the SPM analysis, indications of contrasting features in the structural development of bulk and surface crystal structure both at the as-spun and

drawn stages of production [6]. In an attempt to understand more fully the differences in surface and internal (bulk) structure as reported in [6], longitudinal and transverse cross-sections of the PP filaments have been prepared and have been analysed using both SPM and ESEM imaging. In addition, *in situ* surface structural developments between filaments of similar surface morphology, but with contrasting bulk morphology, have been investigated using a new ESEM methodology. PP fibres have been drawn inside the ESEM chamber and real time images have been collected as the drawing process proceeds. To our knowledge, this is the first report of the application of a tensile stage inside an ESEM for real-time studies of PP fibre morphology.

To control production parameters more closely, in the case of synthetic textile fibres, it is necessary to gain as much information as possible about the fibre microstructure at all stages of production and hence better define structure/property relationships. This paper presents the results from ESEM and SPM analysis of the PP cross-sections, as well as observations made *in situ* of the drawing of PP filaments inside the ESEM sample chamber. The results are discussed in relation to the authors' previous publication on PP morphology [6] as well as to the existing literature on morphology development for PP filaments.

2. Experimental

2.1. Melt extrusion

The type of PP raw material used was polypropylene HF445J B2-9037 from Borealis, with a melt flow index (MFI) of 19.0 g/10 min quoted by the manufacturer. Our tested MFI of the PP raw material was found to be 20.5 g/10 min, as determined by a Ceast 100 plastometer at Beckton Dickinson UK Ltd. in accordance with the ASTM D1238 procedure.

The PP monofilament was spun on a Labspin extruder (Extrusion Systems Limited (ESL), with a 2.5 cm^3 metering pump and a single hole spinneret with a diameter of 0.50 mm. Barrel temperatures were 210/215/225°C respectively for the three barrel zones. Metering pump temperature was 230°C with a pump speed at 1 rpm^{-1}, corresponding to an extrusion rate of 4.0 m min^{-1}. The die head temperature was 235°C and the extruded filament was cooled in an air chamber at 23°C (±1°C) with airspeed set to zero to minimise nonuniform cooling [7]. The gravity spun filaments were collected 1.5 metres below the die-head in the air-quench chamber. The as-spun filaments were spun on to a winding roller with a winding speed (take-up speed) varying from 100 m min^{-1} to 400 m min^{-1}. No spin finish was applied.

2.2. SPM procedures

The SPM used in this work was a Topometrix TMX 2000 Explorer (TM Microscopes). The scannerhead had a maximum scan range in x, y, z direction of 100 × 100 × 8 μm respectively. Scanning was carried out in contact mode AFM and LFM using a silicon nitride cantilever with a nominal spring constant of 0.03 N m^{-1}. The vertical and lateral deflection of the cantilever, which are used respectively to obtain topographic (AFM) and lateral force images (LFM), are detected by a quadrant photodetector via laser light reflected from the back of the cantilever. The measured cantilever deflection in AFM is generated into a surface topography map of the sample. For LFM scanning, the twisting or lateral forces experienced by the cantilever are usually caused by variations in surface friction and changes in slope. LFM scanning should be carried out simultaneously with AFM to separate one effect from the other. Constant force was employed by the cantilever during scanning with a set point in the range of 5 nA to 35 nA. All images were obtained at ambient conditions. Fibre samples used for scanning of surface morphology were mounted onto doublesided SEM tape on magnetic AFM sample stubs. Cross-sections were prepared by embedding the fibres in wax with subsequent microtoming.

2.3. ESEM procedures

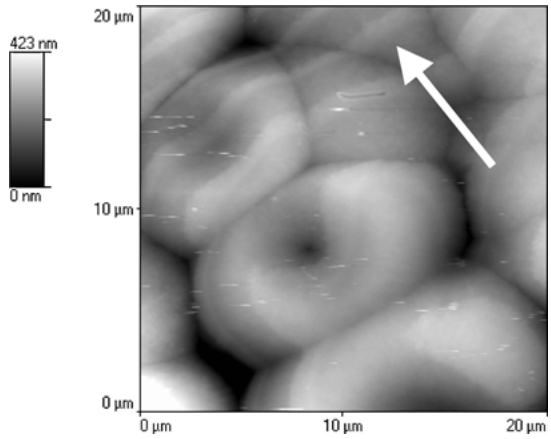
The ESEM used was a Philips XL 30 operated under low vacuum. An environmental secondary electron detector specifically designed to function within a low vacuum gaseous environment was used as the source for imaging. A purpose built tensile stage (Ernest. F. Fulham, 100 lb), fitted within the ESEM, was used to draw the PP filaments. Drawing was carried out at room temperature with a rate of 5.7 mm min^{-1} for both the gravity spun and as spun samples.

3. Results and discussion

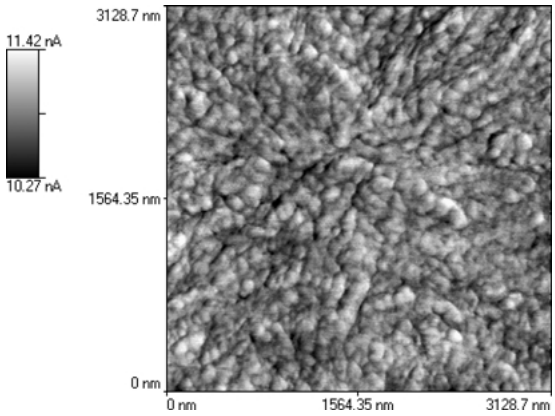
3.1. Surface and internal structure characterisation

Fig. 1a and b are examples of the spherulitic surface morphology found for the gravity spun PP filament. The nodular substructure (Fig. 1b) has also been observed by other workers using SPM [2–4]. The nodes may indicate cross-hatching between lamellae, as previously reported for α-type monoclinic crystalline structures present in PP spherulites [8]. WAXS results on the same gravity spun sample show that the bulk structure is also of the α-form (Fig. 2a). ESEM analysis of the longitudinal cross-sections, indicates a relative inhomogeneous morphology, with the presence of spherulites and a shish-kebab type structure in the bulk of the gravity spun filament (Fig. 3). Both shish-kebabs and spherulites are crystalline features. The ESEM observations are therefore in agreement with the WAXS diffraction pattern for this fibre showing a high degree of crystallinity (Fig. 2a) [6].

The surface morphology for the as-spun 100 m min^{-1} filament was found to be similar to that of the gravity spun, with well-defined spherulites containing a nodular subspherulitic structure. However, it can be seen from Fig. 2b that the WAXS diffraction pattern has changed from an α-type monoclinic structure, in the case of the gravity spun fibre, to a transitional, almost paracrystalline form for the as-spun 100 m min^{-1}. The increase in draw-down ratio for the as-spun filaments from 100 m min^{-1} to 400 m min^{-1} has been shown to

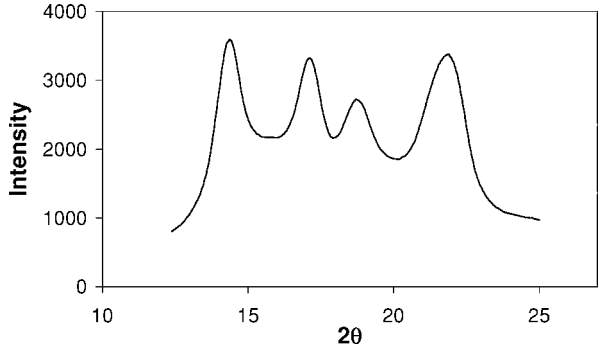


(a)



(b)

Figure 1 (a) Topography of gravity spun PP scanned by AFM in contact mode. (Arrow indicating longitudinal direction). (b) LFM scan of α-spherulite centre.



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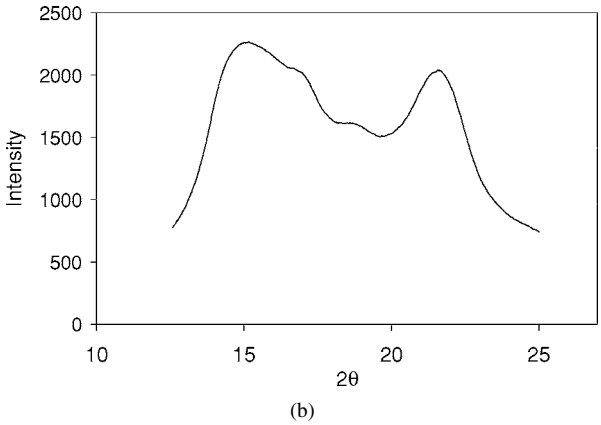


(b)

Figure 2 (a) WAXS diffraction pattern of gravity spun PP. (b) WAXS diffraction pattern of as-spun 100 m min^{-1} PP.

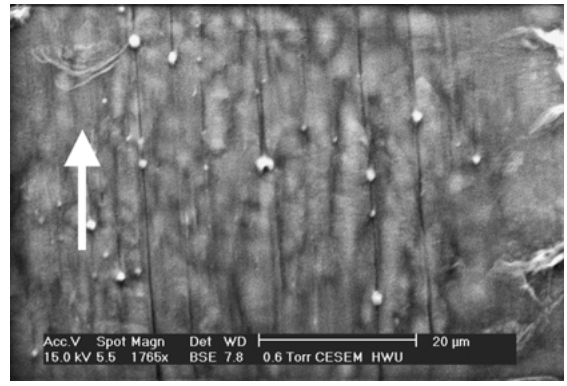


Figure 3 Longitudinal cross section of gravity spun PP scanned by ESEM.

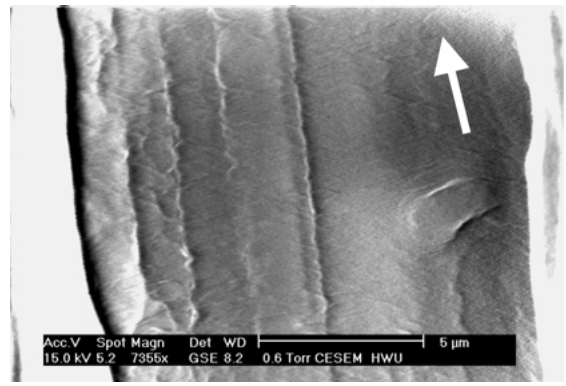
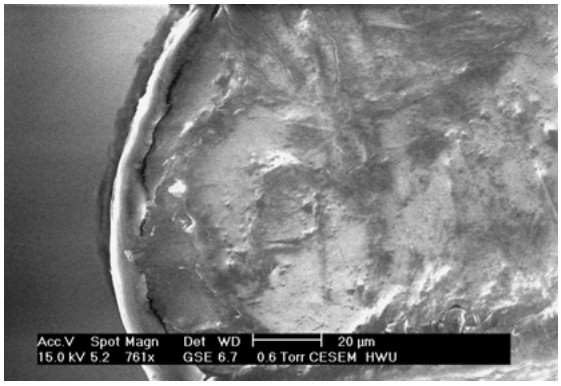


Figure 4 Longitudinal cross section of as-spun 100 m min^{-1} PP scanned by ESEM.

have only minor effects on the bulk crystalline structure compared to the significant changes in surface morphology [6]. Fig. 4 shows the longitudinal cross-section of the as-spun 100 m min^{-1} filament. The morphology is more compact and featureless compared to the gravity spun variant. Comparing transverse cross-sections of the gravity spun and as-spun fibres (Fig. 5a, b) it would appear that the as-spun sample has a more homogeneous bulk structure than the gravity spun variant. SPM analysis confirms the presence of a shish-kebab type bulk morphology in the gravity spun filament (Fig. 6a, b). The undulations along the fibrils are indicative of a shish-kebab structure with the epitaxially grown crystals (Shish) protruding. This is in contrast to the smooth profile observed for the as-spun variant (Fig. 7a, b), which suggests the presence of macrofibrils. These have probably developed due to stretching of the epitaxially grown crystals in the shish-kebabs present in the gravity spun filament. The importance of shish-kebabs to the study of essential issues in polymer crystallisation has been highlighted by Monks *et al.* [9]. It would therefore be of interest, for future work, to investigate the transformation of the shish-kebabs in real time for PP filaments.

3.2. *In situ* tensile testing

As mentioned previously, both types of filament have a very similar surface morphology and are mainly distinguished by their differing bulk crystalline structure.



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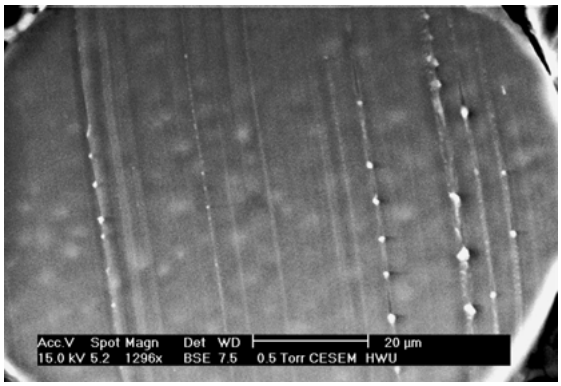
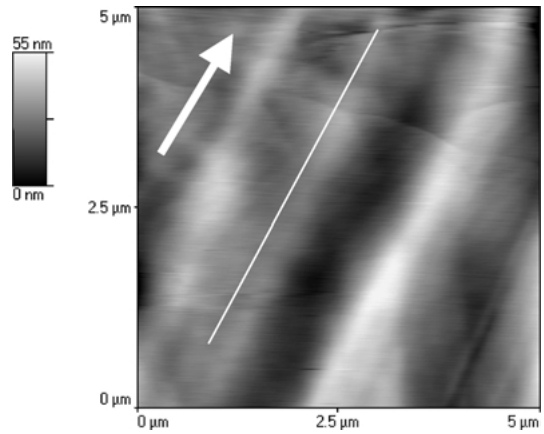


(b)

Figure 5 (a) Transverse cross section of gravity spun PP scanned by ESEM. (b) Transverse cross section of as-spun 100 m min^{-1} PP scanned by ESEM.



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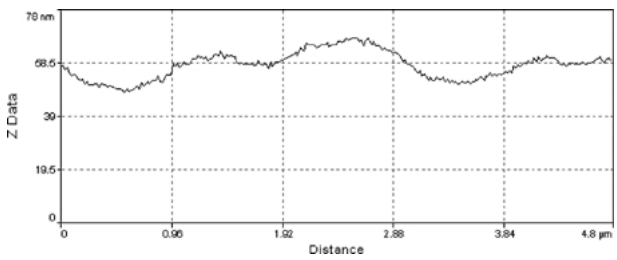
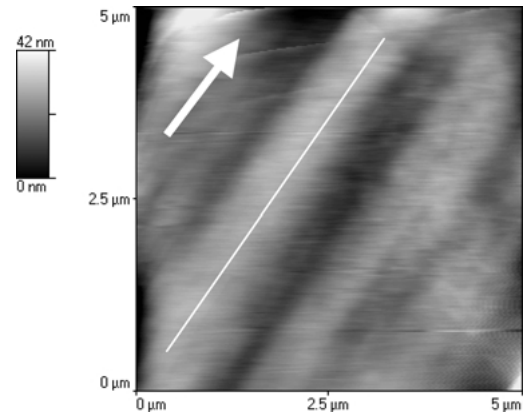


(b)

Figure 6 (a) Longitudinal cross section of gravity spun PP scanned by AFM in contact mode. (b) Line profile from longitudinal cross section of gravity spun PP, indicated by white line in Fig. 6a.



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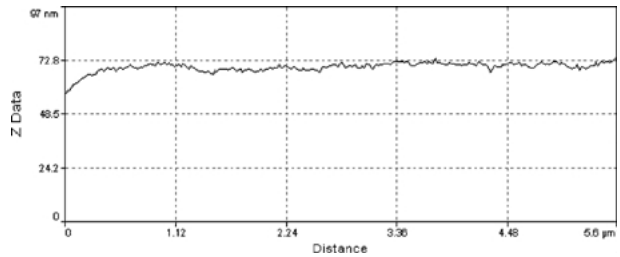
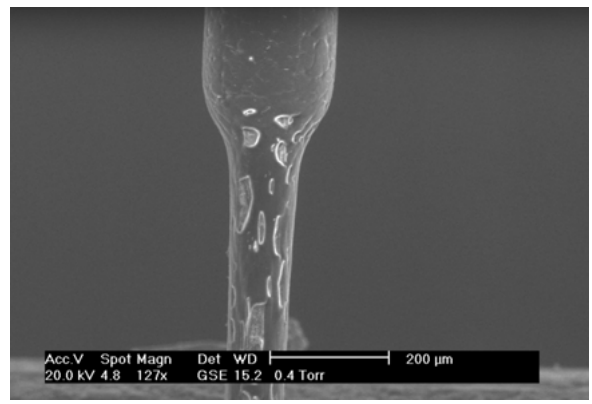


(b)

Figure 7 (a) Longitudinal cross section of as-spun 100 m min^{-1} PP scanned by AFM in contact mode. (b) Line profile from longitudinal cross section of as-spun 100 m min^{-1} PP, indicated by white line in Fig. 7a.



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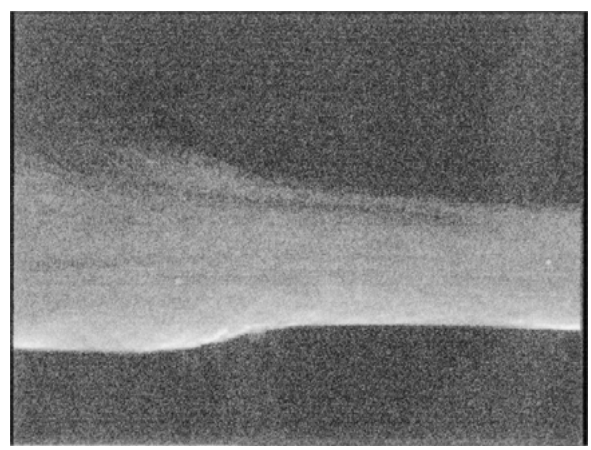

(b)

Figure 8 (a) *In situ* image of gravity spun PP during cold drawing. (b) *In situ* image of as-spun 100 m min^{-1} PP during cold drawing.

Fig. 8a shows the gravity spun filament at a point in time during cold drawing, before rupture in the tensile stage. The structural development in the necked region, in the form of cavities, took place while neck propagation was still in process. This observation is in contrast to the expected sequence of events for a semi-crystalline material during necking, where a resistance to further deformation is present in the necked region until neck propagation has finished [10]. It can be seen from Fig. 8b, however, that the result from the drawing of the as-spun 100 m min^{-1} fibre concurs with the generally accepted changes which occur during necking for a semi-crystalline material, with no apparent deformation on a macroscale in the necked region while necking is in progress [10]. One explanation for the difference in behaviour between the two types of PP filament stems from the difference in overall crystalline properties between the surface and the fibre bulk. The gravity spun fibre has a high degree of crystallinity and may therefore possess properties more like that of a crystalline material during necking. However, other factors have also to be considered. The α-spherulites present on the surface of both the gravity spun and as-spun 100 m min^{-1} fibres have been reported as having a brittle behaviour during tensile loading [11]. Aboulfaraj *et al.* found that the α structure deformed less than the global deformation and that plastic slide was very difficult in this phase [11]. Therefore, if the deformation in the necked region is caused by the surface structure alone, one would expect the same cavities to appear for the as-spun variant. Both the core and surface of the gravity spun filament are made up of mainly α-type crystalline structures, whereas in the as-spun variant, α-structures are much less prominent. It is therefore likely that the cavities observed are caused by deformation in the bulk of the gravity spun filament as well as on the surface.

3.3. Practical implications for fibre processing

Both surface and bulk morphology play fundamental roles in governing some key technical properties of PP fibres, and these properties are, to a large extent, related to the processing conditions [12]. The contrast in structural development between surface and bulk morphology during processing suggests that for the purpose of optimising processing parameters both should be monitored. It is not possible to make conclusions about surface structure based on observations of bulk structure and vice versa. Both are, however, important for understanding the ultimate properties of the fibre. The conditions for drawing used in this work are, of course, far from those used in industry. The combination of high speed combined with a higher temperature within the bulk of the filaments at such an early stage of the fibre processing will have a different effect on the global deformation of the polymer structure than what is yet possible to replicate inside an ESEM chamber. Also, the fibre diameter in this work is larger than typically handled in fibre processing and this can be expected to induce more variation in surface and bulk structure. However, contrasting features between surface and bulk crystalline structure have previously been found for drawn PP monofilaments produced under conditions closer to those found in industry [6]. It should also be considered that this effect, if present, will be even more prominent in multifilaments due to the higher ratio of surface to bulk. It clearly demonstrates the need to consider the fibre as a 3-dimensional entity with key properties that can not simply be analysed in two dimensions.

4. Conclusions

1. Similar surface but contrasting bulk structures have been observed on gravity spun and as-spun PP fibres using advanced surface analysis of longitudinal and transverse cross sections.

2. WAXS results have been confirmed through direct observation of the internal fibre structure.

3. The gravity spun fibre in tensile tests does not behave as expected for a semicrystalline material. This is probably due to the internal shish-kebab structure and external spherulitic structure having an α type structure, thereby imposing overall behaviour more similar to crystalline material.

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