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# Gas plasma treatments of polypropylene tape

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This paper highlights the applications of Scanning Probe Microscopy (SPM) and Scanning Electron Microscopy (SEM) to study the effects of argon, nitrogen and oxygen plasma treatments on the topography of polypropylene (PP) tapes. Contrasting surface effects created by the different plasma gases as observed by Atomic Force Microscopy (AFM), Lateral Force Microscopy (LFM) and SEM are discussed in detail with images obtained from both AFM and SEM demonstrating the changes in the surface topography.


## 1. Introduction

Although gas plasma treatment is not a new technology, it is only due to recent technical advancements such as the introduction of large low pressure treatment units and atmospheric plasma that it has now become possible to apply treatments on a commercial scale [1]. The result of this development has been an increase in the use of gas plasma treatment as a viable alternative surface treatment tool to alter the surface characteristics of materials without affecting their bulk properties. A variety of work has been carried out using plasma treatments. However, it has generally been utilised as a process tool without in-depth microscopical analysis into changes in the topography of polymers at the polymer — plasma interface [2]. Work carried out using plasma treatment includes investigation of changes in reactivity [3], changes in mechanical properties [4], contact angle measurements [5], radical analysis [6] and changes in the subsurface chemistry [7]. The nature of this work is to investigate the topographical differences caused as a result of plasma treatment.

To analyse the plasma-treated polymers a combination of traditional and modern microscopy techniques has been used. Electron microscopy, predominantly scanning electron microscopy (SEM), has been used to analyse synthetic fibres and tapes for many years [8]. In contrast over the past two decades major advances have been made in the capabities of surface analytical tools. As an example, the scanning probe microscope (SPM) was developed to facilitate measurement of surface topological features with resolution that can reach the atomic level. One type of SPM technology is Atomic Force Microscopy (AFM), which operates by scanning a micron scale cantilever across a surface in the very near surface region and develops a surface topography map. By measuring the lateral deflection or twist in the same cantilever as it scans the surface, Lateral Force Microscope (LFM) images, which map the near surface frictional effects, can be obtained. The major advantage of SPM is that it can image down to sub-micron levels [9] and the samples do not need any special surface preparation such as gold coating required for SEM. This gives much greater diversity in terms of the types of materials that can be examined. Sequential experiments can be carried out whereby the sample can be imaged at various stages throughout an experiment. The aim of this paper is to utilise both the traditional method of SEM and the modern AFM and LFM techniques to identify the effects of plasma treatments on the surface topography of PP tape. Both these very different techniques have provided detailed images showing that not only does the surface topography change with plasma treatment but also it creates varied surface formations and environments depending on the gas used in the treatment.

## 2. Experimental

### 2.1. PP tape production

The polypropylene raw material used for this work was FINAPRO PPH 9096 from AtoFina Chemicals, with a melt flow index of 25.0 g/10 min as quoted by the

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manufacturer. When tested the MFI was found to be 29.0 g/10 min.

The PP tape was extruded using a bench top labspin extrusion plant for medical polymer research model MBP 25/1 (Extrusion Systems Limited (ESL)), fitted with a single slit die with a width of 8 mm and a depth of 0.4 mm. The tape was extruded under the following conditions: barrel temperatures were 180, 185 and 190°C, respectively for the three zones. The metering pump temperature was 195°C with a speed of 4 rpm. The die head temperatures were 200°C for each zone, with the extruded tape subsequently cooled in a water bath at a temperature of 26°C. The cooled tape was collected by means of a winder with a speed of 10 rpm. For the second section of the work extrusion conditions were varied, in order to assess their effect on the plasma treatment. Three conditions were created, ranging from gravity collection without any draw to fully drawn where the tape was drawn on a separate draw frame to the point at which it started to break. For producing the gravity-spun sample, the metering pump was set at 0.6 rpm. The tape was air cooled and collected by hand. For producing the partially drawn sample the metering pump was set at 4 rpm. The tape was cooled in a water bath at 38°C and was collected using the quench tank winder set at 10 rpm. For producing the fully drawn tape the metering pump was set at 4 rpm. The tape was cooled in a water bath at 38°C and was passed through the quench tank winder at 23 rpm. The tape was subsequently diverted onto a draw frame and cold drawn using three successive rollers, set at 30, 49 and 200 rpm, respectively.

### 2.2. Plasma treatment procedures

The plasma treatment equipment used throughout this work was a surface treatment CD400PC MHz system laboratory scale plasma treatment plant supplied by Europlasma. The treatment plant could be operated manually or automatically using self-developed programmes. To keep the work more consistent the automated mode was chosen. Consequently, an operating procedure was devised to control the plasma treatments. This option also allowed process time, power and process gas to be altered. Three treatment times of 1, 5 and 10 min were used along with two operating powers of 100 and 300 W. The gases used were oxygen, argon and nitrogen. Two methods of sample preparation were employed, both of which utilised perforated metal trays to house the samples. The first method involved mounting the tape (cut into 300 mm lengths) flat onto the surface of the tray using double-sided adhesive tape. The second method involved laying the tape (cut into 300 mm lengths) on its side on the base of the trays. This allowed both sides of the tape to have better contact with the plasma.

### 2.3. SPM procedures

The SPM used throughout this work was a Topometrix TMX 2000 explorer supplied by Veeco Instruments. The X, Y, Z scan range for the scanner head used was $100 \times 100 \times 8$ $\mu$m respectively. However, due to the diverse nature of the tape's topography a maximum scan range of $50 \times 50$ $\mu$m was generally used. Scanning was carried in contact mode and both AFM and LFM images were collected. Silicon nitride tips were used throughout, with a nominal spring constant of 0.03 $Nm^{-1}$. AFM was used to generate a topographical map of the surface. This was generated by laser deflections, created by the vertical and horizontal movements of the cantilever as it scans across the PP tape surface. A laser is deflected off the back of the cantilever and onto a four-quadrant photodetector, which is used to measure the deflections. LFM was utilised to measure any twisting or lateral force encountered by the tip during scanning usually the result of friction and slope variations. All images were taken under ambient conditions and with a set point between 5 and 30 nA. Tape samples were prepared for scanning by mounting small sections (6–8 mm) onto steel AFM stubs using double-sided adhesive carbon discs.

### 2.4. SEM procedures

A Hitachi S530 scanning electron microscope was used throughout this work. The PP tape samples were cut into small sections (6–8 mm in length) and mounted onto steel SEM stubs using double-sided adhesive carbon tabs. Due to the insulating nature of the PP tape, the samples were gold coated for 30 s using a Polaron SC7620 sputter coater to avoid surface charging. Once coated the samples were viewed using accelerating voltages between 15 and 25 kV.

## 3. Morphology of the plasma treated tape

Figs 1a and b are examples taken from a section of untreated PP tape obtained from the SEM and AFM respectively. Although the image shows evidence of grooves in the surface of the tape running parallel to the longitudinal axis of the tape, the surface is relatively smooth. These grooves are likely to be the result of small defects in the die slit formed during the extrusion process to manufacture the tape. Fig 1b shows the tape surface in greater detail. Raised areas on the surface are observed as lighter regions on the image, using the scale on the left-hand side as a reference. Fig. 2a is an SEM image, showing an area of tape, which had undergone argon plasma treatment for 1 min at 300 W. In this case, the surface is covered predominantly with clusters of angular structures, which appear highly crystalline. These formations appear either as individual units or merged to form larger structures. The lengths of the units are ca. 1.8 $\mu$m, but their breadths are in the range, 0.7–1.8 $\mu$m. Fig. 2b shows an AFM topography scan of the treated PP tape. It can be seen that the tape surface is covered with small raised units, the majority of which appear on the ridged sections of the tape.

Figs 3a–c (SEM images) and Fig. 3d (AFM image) show sections of tape that have undergone oxygen plasma treatments for 1 min at 300 W. Two types of structure are observed to be predominant on the tape surface. One type of structure (Fig. 3a) consists of small angular formations, some of which are assembled in small clusters. These angular structures are quite similar to those observed after treatment of the tape with argon plasma (Fig. 2). However, other angular formations

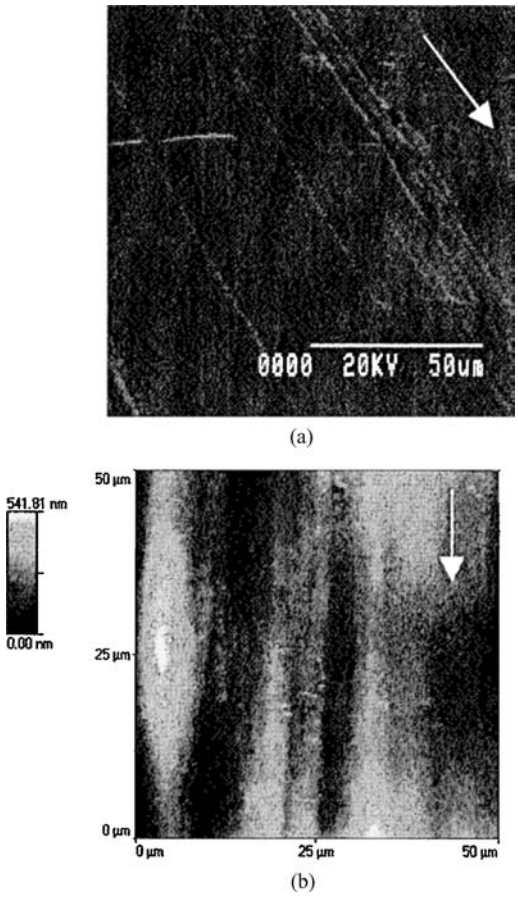


*Figure 1* Images of untreated PP tape. Arrows indicate direction of fibre axis: (a) SEM and (b) AFM.

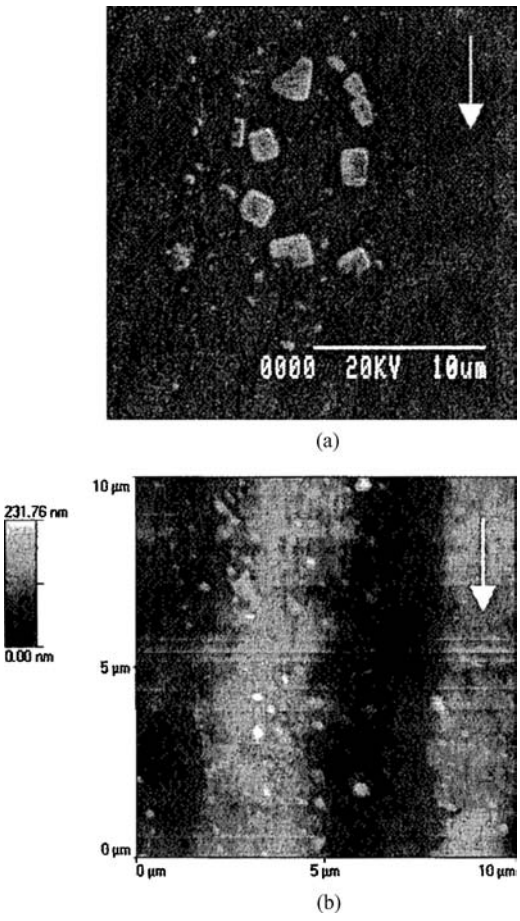


*Figure 2* Images of argon plasma treated PP tape (1 min at 300 W). Arrows indicate direction of fibre axis: (a) SEM and (b) AFM.

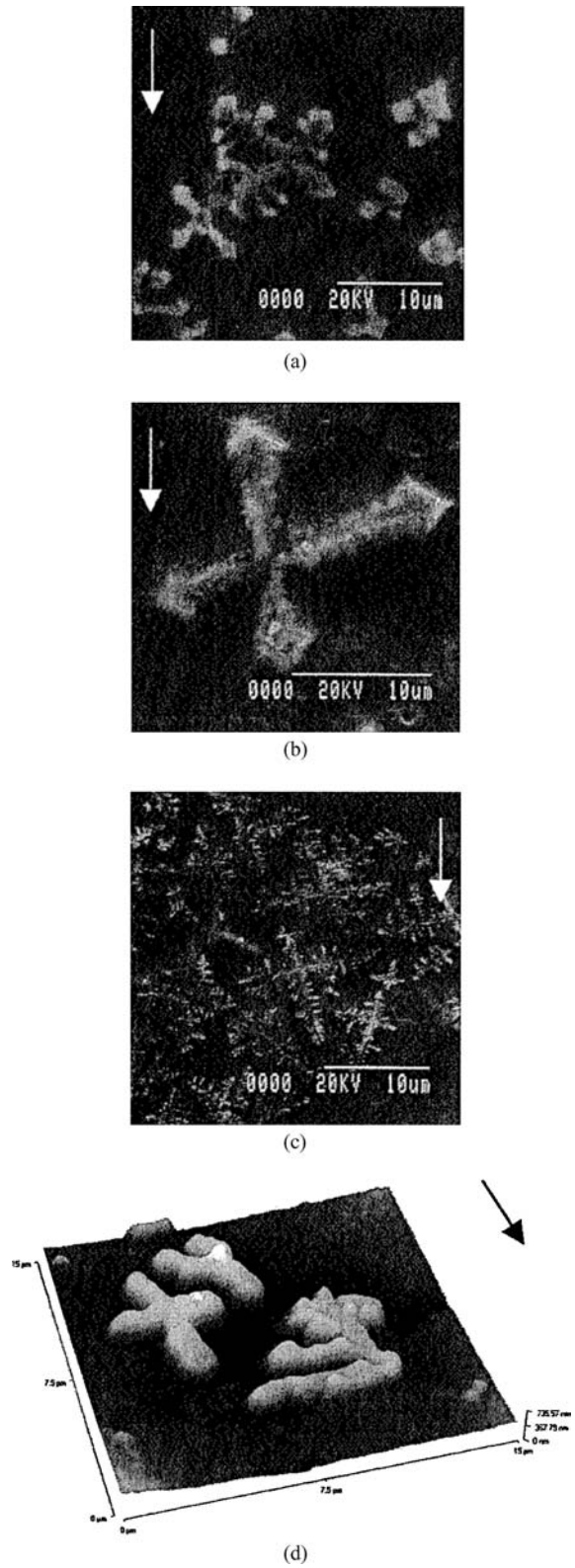


*Figure 3* Images of oxygen plasma treated PP tape (1 min at 300 W). Arrows indicate direction of fibre axis: (a) SEM, (b) SEM, (c) SEM, and (d) AFM: 3D image.

are observed at the tips of small crosses in localised groups over the surface of the tape. The other type of structure observed is also cross-shaped in nature. These cross-shaped structures vary both in size and orientation from large complex structures with multiple cross-hatching (Fig. 3c) to small, simpler structures (Figs 3b and d). None of these features appears uniformly over the surface of the tape: the features are confined within distinct clusters.

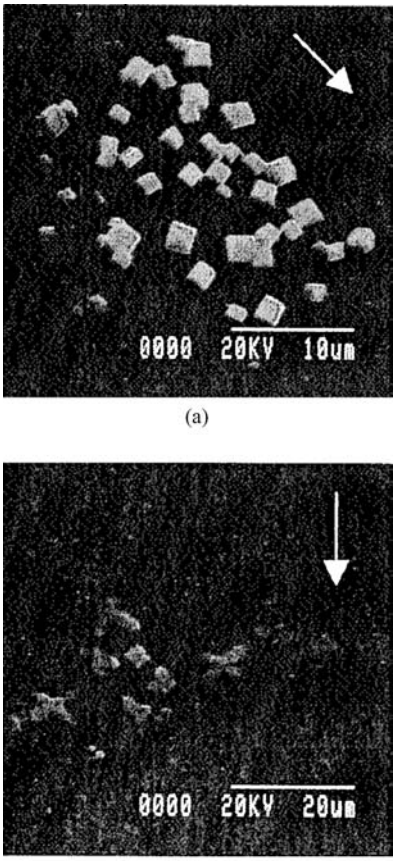


*Figure 4* Images of nitrogen plasma treated PP tape (1 min at 300 W). Arrows indicate direction of fibre axis: (a) SEM and (b) SEM.

Nitrogen plasma treatment produces effects similar to those observed in the samples treated with argon and oxygen plasmas (Fig. 4). Angular structures are visible in large quantities over the tape surface (Fig. 4a). The lengths and breadths of each unit are mostly similar, in the range, 1.4–2.3 $\mu$m. In addition, small cross-shaped structures are also visible (Fig. 4b) which, although similar to those observed in the oxygen plasma treated tape, do not appear to contain side branches.

## 4. The effects of varying extrusion parameters

### 4.1. Untreated PP tape

Fig. 5 shows an AFM image of an untreated gravity-spun PP tape. Spherulites of a hill type are observed, in which the spherulitic centre is raised relative to its immediate surroundings. The spherulites are ca. 20 $\mu$m in diameter and are quite closely packed together. Some hill type spherulites have been observed previously in gravity-spun PP fibres [9].

Fig. 6 is a collection of AFM images of the partially drawn PP tape. Both spherulites and microfibrils are now present (Fig. 6a), with the microfibrils aligned in the direction of the tape axis. Moreover, the spherulites are the commoner valley type, in which the spherulitic centre is lower than its surroundings. The spherulites are present as individual entities and in short chains oriented along the tape axis (Figs 6a–c). The chains of spherulites appear to be linked in the axial direction by fibrillar structures.

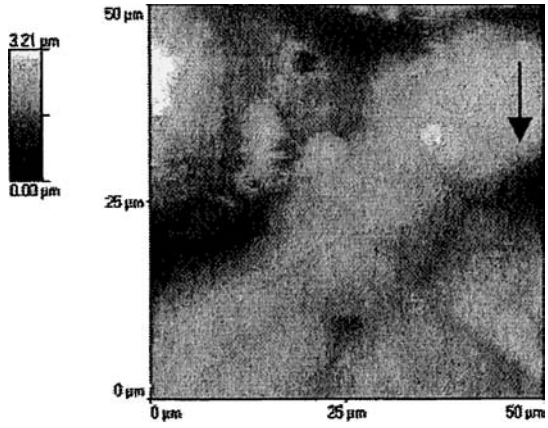


*Figure 5* AFM image of untreated gravity spun PP tape. Arrow indicates direction of fibre axis.

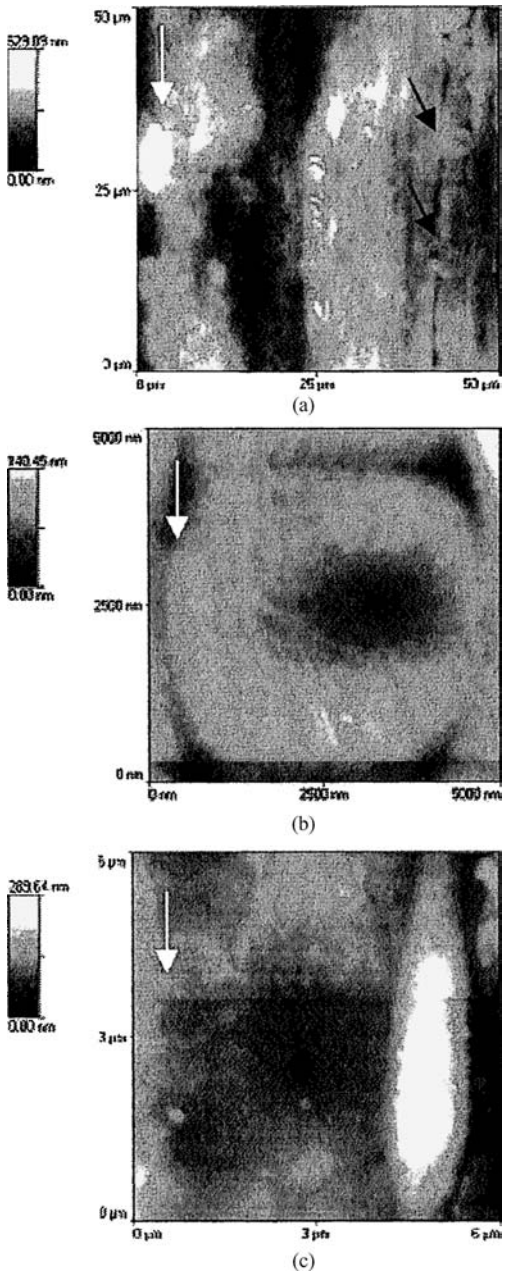


*Figure 6* AFM images of untreated partially drawn PP tape. White arrows indicate direction of fibre axis. Black arrows indicate location of spherulites within the microfibrillar structure: (a) Image showing both spherulites and microfibrils, (b) Close up of a spherulite within the microfibrillar chain, and (c) Close up of a deformed spherulite.

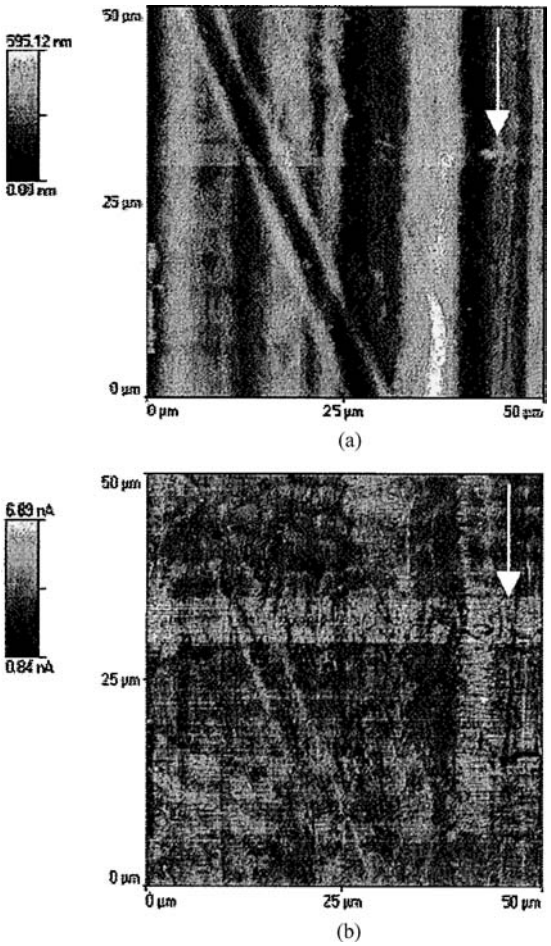


*Figure 7* Images of untreated fully drawn tape. Arrows indicate direction of fibre axis: (a) Topography and (b) Lateral Force.

Fig. 7 shows AFM images of fully drawn PP tape. The scored groove running at just over 20° to the tape axis is a defect in the tape caused during extrusion. The tape surface is dominated by microfibrils, and no spherulites can be discerned.

## 4.2. Treated PP tape

Fig. 8 shows an area of the gravity-spun tape which has been exposed to oxygen plasma for 5 min at 300 W. After the gas plasma treatment, the boundary between the spherulites is far less clear, giving the impression

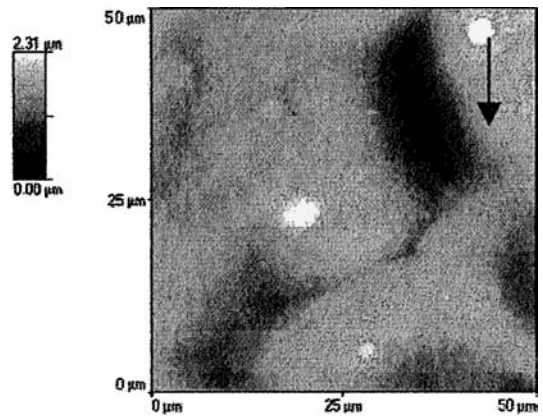


*Figure 8* AFM image of oxygen plasma treated gravity spun PP tape (5 min at 300 W). Arrow indicates direction of fibre axis.

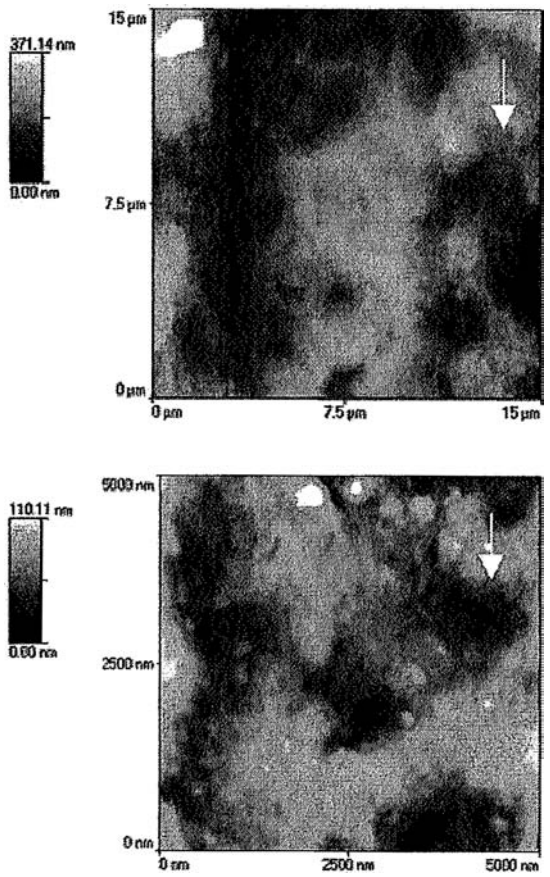


*Figure 9* Images of oxygen plasma treated partially drawn tape (5 min at 300 W). Arrows indicate direction of fibre axis.

that the spherulites seem to be adhering to one another. The surfaces of the spherulites are no longer smooth, and appear pitted. This is evident by the number of light speckles on each of the spherulites. Oxygen plasma treatment of the partially drawn tape also damages the spherulites (Fig. 9). The boundaries between the spherulites are less well defined, and their shapes appear distorted. Here too, the spherulites are pitted. In contrast, the fibril structure remains intact with little apparent damage. Oxygen plasma treatment of the fully drawn tape has apparently had little effect on it (Fig. 10). The fibril structure is still clearly defined, with only the surface slightly roughened.

## 5. Discussion

### 5.1. Effects of gas plasma treatments

Two principal types of feature arise on the PP tape surface as a result of these treatments: angular structures, some of which appear at the tips of small crosses, and cross-hatched structures.

The formation of angular structures is common to all three gas plasma treatments applied. Whereas the images reveal the structures from nitrogen plasma treatment to possess square cross-sections, the structures arising from argon plasma treatment possess similar lengths but varying breadths. After oxygen plasma treatment, the angular structures appear smaller. All the angular structures are likely to be crystalline, in that their shapes are well defined, especially after nitrogen plasma treatment.

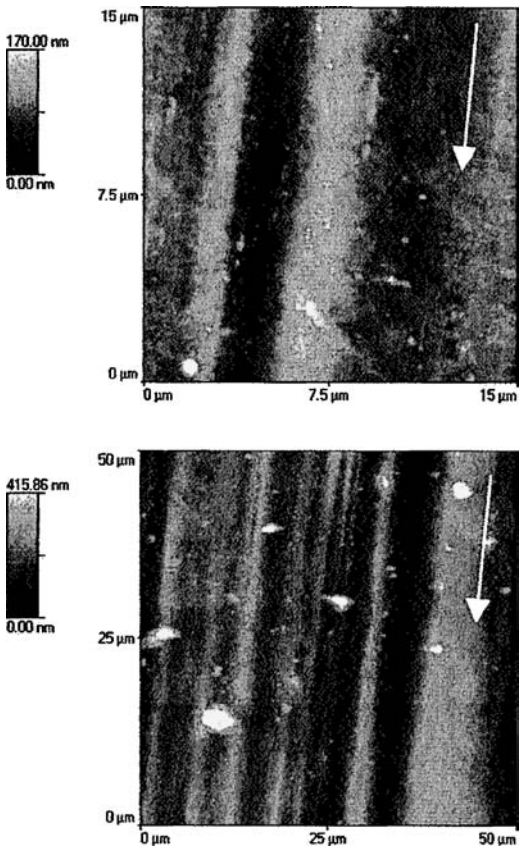


*Figure 10* Images of oxygen plasma treated fully drawn tape (5 min at 300 W). Arrows indicate direction of fibre axis.

The origin of the structures needs to be considered. They may become visible in the images, as a result of their exposure on the tape surface, arising from gas plasma treatment. They may instead be the result of a recrystallisation process induced by gas plasma treatment. They may alternatively be composed of an additive present in the original grade of PP to enhance its performance in application. Most of these additives will be compatible with PP, and hence it is unlikely that they will appear as structures of cross-section of the order of magnitude of 1 $\mu$m. One additive that will be present in crystalline form, however, is titanium dioxide rutile pigment, incorporated as delustrant. The unit cell of the rutile crystal lattice is tetragonal, a feature consistent with the appearance of some of the angular structures observed. However, a typical median cross-section is as low as 0.2 $\mu$m, and the pigment crystals are less angular in appearance [10]. In addition, gas plasma treatment is unlikely to affect the size and shape of the pigment crystals, given that the melting point of the pigment is as high as ca. 1830°C. The angular structures are, therefore, likely to consist of PP, most probably in the $\alpha$-form.

A striking feature of the oxygen plasma treatments is the appearance of cross-shaped structures on the tape surface. In Fig. 3a, both angular and cross-shaped structures can be observed. Indeed, it appears from Fig. 3a that the angular structures may be instrumental in the formation of the cross-shaped structures. Each branch of a cross is thicker at its tip than at the centre of the cross. However, it is noteworthy that the angles formed between adjacent branches of the crosses appear to be at ca. 80 and 100°. These angles are also observed in the spherulites of $\alpha$-PP [11], where the angle between the directions of growth of mother and daughter lamellae is 80°. Nitrogen plasma treatments also produce some structures on the tape surface (Fig. 4b), but they are far less dominant than those produced as a result of oxygen plasma treatments. This observation is consistent with the lower reactivity of nitrogen plasma in comparison with oxygen plasma [2].

The cross-hatched structures observed in some regions of the oxygen plasma treated tape are also intriguing. In contrast to the cross-shaped structures in Figs 3a and b, there is no evidence of the broadening of each branch towards its tip. The fronds emanating from each branch (Fig. 3c) appear to be at approximately right angles to the branch. Again, this branching is to some extent redolent of the growth of daughter lamellae from mother lamellae in spherulites of $\alpha$-PP. A more detailed discussion of these structures is planned for a later paper.

### 5.2. Effect of drawing conditions

The gravity-spun PP tape consists of hill type spherulites, in contrast to the more usual valley type spherulites (Fig. 5). It has been tentatively suggested previously that hill type spherulites are composed of $\beta$-PP, with radial lamellae [9]. There is no branching of daughter lamellae in $\beta$-PP spherulites. The presence of $\beta$-PP in the gravity spun tape has yet to be investigated.

On drawing, the spherulitic structure on the tape surface is, as expected, progressively deformed into a microfibrillar structure (Figs 6 and 7). It is interesting to note that in contrast to the gravity-spun tape the spherulites present on the partially drawn tape surface are valley type. It should be noted, however, that, whereas the gravity-spun tape was cooled in air, the drawn tapes were cooled in a water bath. It is also noteworthy that short chains of these valley type spherulites have been observed to be oriented along the fibre axis (Fig. 6a). These chains of spherulites are sandwiched between adjacent microfibrils and are even linked along the fibre axis by a fibrillar type of structure (Fig. 6a, indicated by the black arrows). Some evidence has, therefore, accrued that the spherulites are converted directly into microfibrils without the intermediate formation of shish-kebab structures. The surface of the fully drawn tape (Fig. 7) consists solely of microfibrils.

Treatment of PP tape with oxygen plasma for 5 min at 300 W appears to have little effect on microfibrillar structure at the tape surface but does induce pitting of spherulites. In addition, the boundaries between the spherulites become blurred, indicating that the difference in densities between the spherulites and regions between them may have been reduced.

## 6. Conclusions

Gas plasma treatments of PP tape produce profound changes in morphology at the tape surface. Of the three types of treatment we applied, oxygen plasma

treatment is the most powerful and argon plasma treatment is the mildest under identical treatment conditions. This observation is in common with those of other workers [2]. Argon plasma treatment leads to the formation of angular structures on the tape surface. These structures are thought to be essentially $\alpha$-PP crystals. More powerful gas plasma treatments can induce the formation of cross-shaped structures, some of which include cross-hatching. These structures have been tentatively explained in terms of the formation of mother and daughter lamellae of $\alpha$-PP. The level of draw applied to the tape not only affects the surface structure of the untreated tape but also affects the sensitivity of the tape surface to oxygen plasma treatment.

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## References

1. M. LIEBERMAN and A. LICHTENBERG, in "Principles of Plasma Discharges and Materials Processing" (John Wiley and Sons, New York, 1994).
2. C. D. RADU, P. KIEKENS and J. VERSCHERUREN, "Surface Characterisation of Fibers and Textiles," edited by C. M. Pastore and P. Kiekens, (Marcel Dekker Inc., New York, 2001) p. 203.
3. F. PONAN-EPAILLARD, B. CHEVET and J. C. BROSSE, "Plasma Surface Modification of Polymers Relevance to Adhesion," edited by M. Strobel, C. S. Lyons and K. L. Mittal, (VSP BV., Netherlands, 1994).
4. N. INAGAKI, S. TASAKA and M. MAI, *J. Appl. Poly. Sci.* **48** (1993) 1963.
5. P. WITTENBECK and A. WOKAUN, *ibid.* **50** (1993) 187.
6. R. WILKEN, A. HOLLÄNDER and J. BEHNISCH, *Sur. Coat. Techn.* **116–119** (1999) 991.
7. A. HOLLÄNDER, R. WILKEN and J. BEHNISCH, *ibid.* **116–119** (1999) 788.
8. J. W. S. HEARLE, J. T. SPARROW and P. M. CROSS, in "The Use of the Scanning Electron Microscope" (Pergamon Press Ltd, Oxford, 1972).
9. O. K. RISNES, R. R. MATHER and A. NEVILLE, *Polymer* **44** (2003) 89.
10. W. A. KAMPFER, in Pigment Handbook, Vol.1 Properties and Economics, edited by T. C. Patton, (John Wiley and Sons, New York, 1973) p. 1–36.
11. F. L. BINSBERGEN and B. G. M. DE LANGE, *Polymer* **9** (1968) 23.

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