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Scanning force microscopy of bulk-filled uniaxially oriented poly(ethylene terephthalate) films

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Abstract

Bulk-filled uniaxially oriented poly(ethylene terephthalate) film surfaces have been investigated by scanning force microscopy. Comparison with additive-free films shows that the addition of filler particles during manufacture increases the final surface roughness of the films. Filler particles at or near the surface are accompanied by deep depressions aligned in the direction of draw. Raised plate-like features oriented diagonally to the draw direction are present on all the films. Lateral Force Microscopy shows that this overlayer region is of lower friction and phase imaging shows that it is of higher phase shift than the surrounding polymer. The observations imply that the raised material is more crystalline than the surrounding background.

Keywords: Scanning force microscopy; Uniaxial orientation; Bulk-filling

1. Introduction

Recently, the advent of scanning probe microscopic methods has led to significant advances in the elucidation of surface structure, chemical and mechanical properties of commercial polymeric materials at the nanoscale [1–7]. Traditionally electron microscopic techniques have been widely used to investigate the topography of polymer surfaces. However, there are certain drawbacks to techniques such as Scanning Electron Microscopy (SEM). For example, polymers are susceptible to electron beam damage and their poor conductivity often requires a coating stage before imaging which can alter the surface topography. In contrast, scanning probe microscopic techniques, such as Scanning Force Microscopy (SFM) and Chemical Force Microscopy (CFM) allow access to high-resolution topographic data and facilitate the comparison of surface structure with other local properties such as friction, adhesion and compliance [8–13].

We have previously investigated the surface topography and frictional properties of biaxially drawn polyester films by SFM [14–16]. These were either additive-free (Melinex 'O') or had been treated to incorporate silicate additives at regular heights and intervals across the surface (Mylar D). The bulk-filled materials studied in this publication represent a commercially important type of polymer material. Many different types and shapes of filler particles have been incorporated into polymeric films before the drawing process [17]. Carbon black particles are added to impart the insulating polymer with electrical conductivity, whilst the fillers used in this study (glass beads, silica, clays) are added to enhance surface mechanical properties including, in particular, the reduction of "blocking" (the adhesion of adjacent surfaces) [17,18].

In this study we were interested to see what information SFM techniques could reveal about the surface morphology and mechanical properties of experimental unaxially drawn films which had been bulk-filled with particles of different types, sizes and distributions. By using a combination of contact and intermittent contact SFM methods we have been able to investigate the relationship between surface roughness and topographic features and their local properties such as friction and compliance. We have used Lateral Force Microscopy (LFM), to investigate frictional differences on the surfaces of the composite films. In LFM the twisting motions of the cantilever are recorded with high contrast, and are indicative of significant frictional interactions between tip and sample [4,5,19]. To increase the sensitivity of LFM to frictional differences, probe tips were employed that had been previously chemically

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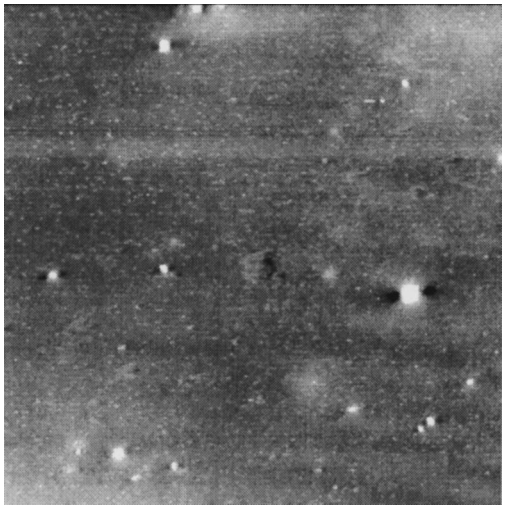

Fig. 1. Topographic image of unfilled uniaxial film. Image size 20 μm × 20 μm. Contact mode with MUA-functionalised probe tip. *Z*-scale range 0–20 nm.

modified by the attachment of a self-assembled monolayer of hydrophilic carboxylic acid-terminated alkanethiol molecules.

The lateral forces that allow clear differentiation between regions according to their frictional characteristics can also cause surface damage that is detrimental to image quality [14,20], particularly when a region is rescanned at higher magnification. To eliminate these lateral forces, we have used an intermittent-contact SFM technique, Tapping Mode, to obtain high resolution topographic data. Phase detection imaging was also performed at high resolution and allowed detailed analysis of the surface features. Phase shift maps, which are a measure of energy dissipation on contact of the tip with the surface, are thought to probe differences in stiffness/adhesion across the surface [12,13,21–24].

2. Experimental

Six different poly(ethylene terephthalate) film surfaces were investigated by SFM and SEM. These were experimental materials kindly supplied by Dr D.H. MacKerron of ICI Films Division, Wilton, UK. They were all uniaxially oriented with a draw ratio of 3.3. One was unfilled (UF) and the other five were filled with China Clay (CC), China Clay Supreme (CCS), Silica (S), P2 glass beads (GB2) and P4 glass beads (GB4). Average particle sizes were 1.7, 0.5, 0.5, 2 and 4 μm respectively. Squares of size 1 cm × 1 cm were cut from reels and the inner surfaces examined by SFM imaging. Topographic SFM images were obtained in ambient conditions either with a Nanoscope IIIa MultiMode scanning probe microscope (Digital Instruments, UK) or a TopoMetrix Explorer (TopoMetrix Corporation, Saffron Walden, UK). Contact mode imaging was performed using silicon nitride cantilevers (nominal normal force constants 0.06 N m^{-1}, NanoProbes from Digital Instruments or 0.064 N m^{-1}, TopoMetrix). The applied load was about 10 nN for the contact mode imaging. A flatten procedure has been applied to some of the images (Figs. 4 and 8(a)). This was occasionally deemed necessary as all the samples were cut from reels of film, and minimises the effect of sample slope/curvature on image quality. Surface roughnesses were always measured before applying this procedure.

Friction force imaging was performed simultaneously with the topographical imaging. The Scope Mode of the NanoScope IIIa microscope was used to provide friction loops and thus obtain (relative) friction-load plots.

NanoProbe SFM tips (Digital Instruments) were modified [9] with alkanethiol SAMs terminated with hydrophilic (carboxylic acid) groups. All glassware was cleaned with "Piranha" solution before use. (Great care should be exercised in handling Piranha solution, a 3:7 mixture of 30% hydrogen peroxide and concentrated sulphuric acid; it is an

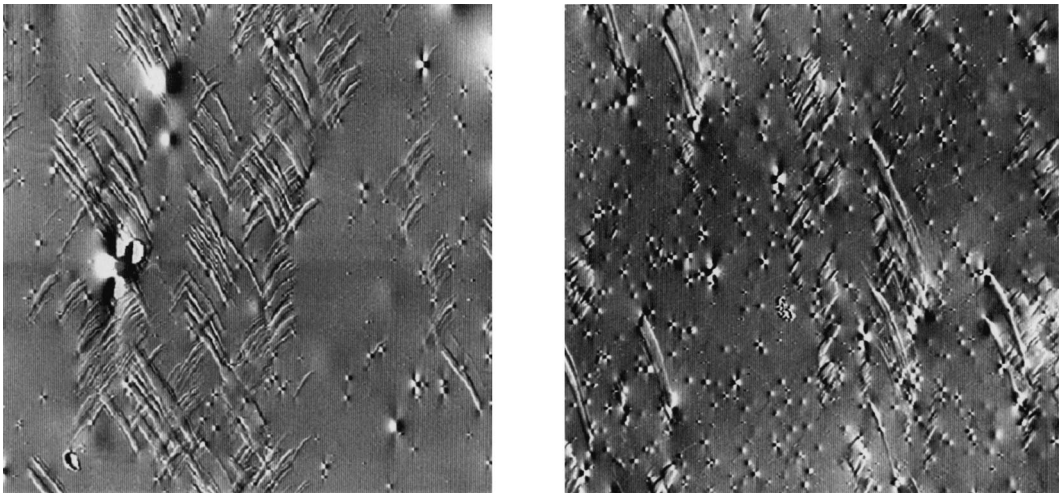

Fig. 2. Topographic images of (left) GB2 film and (right) GB4 film. Image size 150 μm × 150 μm and *Z*-scale range 0–0.5 μm for both films. Contact mode with silicon nitride tips.

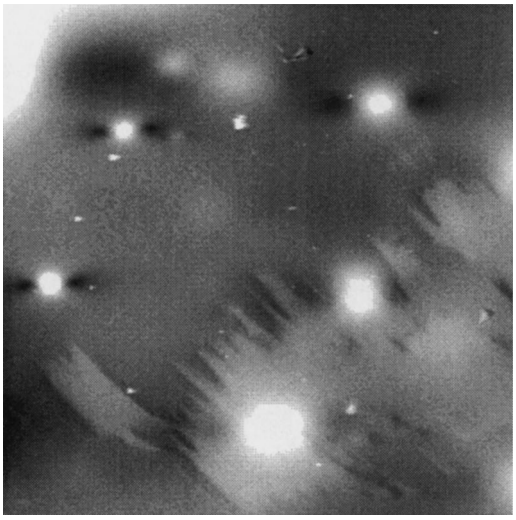

Fig. 3. Tapping mode image of CCS film. 20 μm × 20 μm. *Z*-scale range 0–100 nm.

extremely strong oxidising agent and has been known to detonate spontaneously on contact with organic material.) An Edwards bell jar vacuum coating system was used to modify the tip-cantilever assemblies and slides, as follows; deposition of 2 nm of chromium as an adhesion promoter was immediately followed by deposition of 20 nm of gold. The evaporation rate for the gold was always below 0.03 nm s^{-1} to ensure that the cantilevers did not bend during heating [9,25]. Once cool, the cantilevers were immersed in 1 mM solutions of mercaptoundecanoic acid (MUA) in degassed ethanol for at least 18 h for the self-assembly process. MUA was synthesised according a procedure adapted from the literature [26]. The functionalised tips were kept in the alkanethiol solutions until use.

Tapping Mode and Phase images of the film surfaces were acquired using the NanoScope IIIa. A silicon cantilever with a resonant frequency of 300 kHz was used, with the ratio of the amplitude of set-point oscillation to the free oscillation (ca. 40 nm) at about 0.4.

SEM was performed using a Jeol 6400 SEM on films coated with a thin (ca. 4 nm) overlayer of gold.

3. Results and discussion

3.1. Characterisation of surface topography

The unfilled unaxial film material was very flat, with a RMS roughness typically about 4 nm over a 20 μm × 20 μm area (Fig. 1). A few small particles can be seen in the film surface, and there is evidence of some modification of the surface (deep depression) in the draw direction due to the presence of the particles. It is probable that the presence of these few additive particles on the surface is the result of contamination by residual particulate material left in the extruder following manufacture of bulk-filled film. There are also much smaller circular features that are quite regularly spaced over the surface.

The addition of filler particles to the films during manufacture had a noticeable effect on their final surface roughness. RMS values are typically 20–25 nm over a 20 μm × 20 μm area for all of the bulk-filled materials examined, apparently independent of the average diameter of the filler particles. It should also be noted that the final particle distributions and aggregation behaviour probably vary between the films.

In regions that have a lower density of particles the roughness decreases, approaching that on the unfilled material. Fig. 2 shows contact mode images of GB4 and GB2 films at 150 μm × 150 μm scale; the draw direction is from top to bottom of the images. Tapping Mode (or intermittent contact mode) images are very similar.

Fig. 3 shows a 20 μm × 20 μm topographical image of the CCS film. The approximate draw direction is from left-to-right across the image. It can be seen that the China Clay particles exhibited a range of dimensions and also appear to be present at varying distances from the geometric surface. Particles that were covered with a significant amount of polymeric material were observed as bumps in the film surface, which is deformed in order to accommodate the underlying particle. Often the particles appeared more exposed at the surface, and these were accompanied by depressions on either side of the additive and aligned in the direction of draw. Particles of all sizes appeared to be covered by a polymeric overlayer and exhibited the depressions in the drawing direction. It thus appears that the surface topography for a particular filler is a reflection of the statistical distribution of the depths of particles below the geometric surface, rather than being dependent specifically on the size or geometry of the particulates.

Fig. 4 shows the deformation of the film surface in the presence of CCS additives. The deep depressions on either side of the particle aligned in the draw direction (left to right across the image) can be clearly seen. It appears that the strain in the film surface increases with the proximity of the additive to the geometric surface, until some critical point where the film withdraws from the particle under the stress applied during drawing. Similar observations were made for the other film types, too, which also exhibited additives at varying distances from the geometric surface.

In Figs. 2 and 3, “plate-like” features can be seen running diagonally to the direction of draw. These features are present on all the bulk-filled film surfaces, and to a lesser degree on the unfilled material. Fig. 5 shows a high resolution image of a region containing these plate-like features. We have termed these features “plate-like”, as they are usually very flat, extending over micron distances with heights typically only 5–8 nm above the background phase. However, high resolution topographical images, such as the one shown in Fig. 5, hint at a more detailed substructure, and this was investigated using phase imaging (see below).

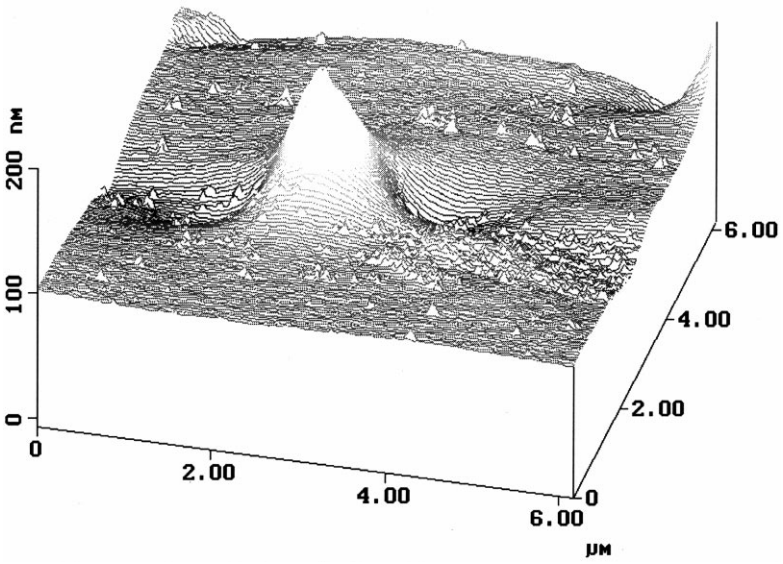

Fig. 4. Tapping mode image of CC film. 6.16 μm × 6.16 μm. *Z*-scale range 0–100 nm.

In some regions, for example near the bottom of Fig. 3, the plate-like features are coincident with the filler particles. Generally the presence of additives does not significantly affect their form, except that the surface exhibits greater curvature and the plate-like features must curve to follow the surface contour. Larger scale images show that these features orient diagonally to the draw direction in two different directions leading to a "herringbone" pattern. For example, on GB4 film, the angle between the long axes of the features was consistently close to 73°, meaning that the average orientation was 36.5° with respect to the draw direction. The angle between the two orientation directions varied slightly for the other samples.

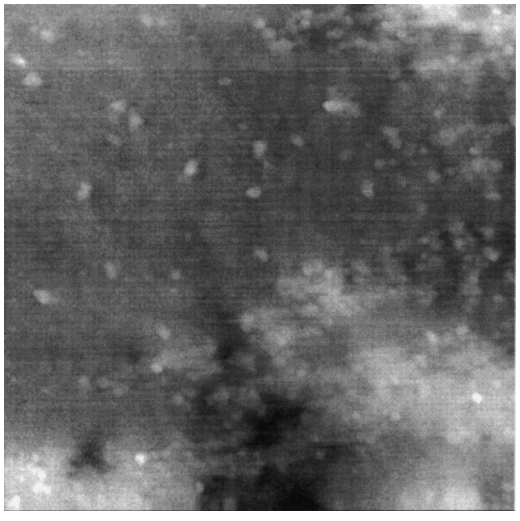

Fig. 5. Topographic image of unfilled uniaxial film showing detail of a region exhibiting a plate-like feature (bottom right-hand corner). Image size 2 μm × 2 μm. Contact mode with MUA-functionalised probe tip. *Z*-scale range 0–20 nm.

The raised features (plates and isolated circular regions) being only ca. 5 nm high are not always clearly visible in topographical images; their small size means they are not clearly resolved against the background roughness due to the presence of large filler particles at/near the surface. Consequently, we have used Friction Force Microscopy and phase imaging to further investigate these features.

3.2. Friction force microscopy

In Lateral (or Frictional) Force Microscopy (LFM or FFM), the torsional or twisting motions of the cantilever are recorded with high contrast, and are indicative of significant frictional interactions between tip and sample. To increase the sensitivity of LFM to frictional differences we have employed tips of low spring constant ($0.06\ N\ m^{-1}$) which had been previously chemically modified by the attachment of a self-assembled monolayer of carboxylic-acid-terminated alkanethiol molecules. Other experiments in our laboratory have shown that these tips are sensitive to small changes in surface composition. Typical LFM images of S film are shown in Fig. 6. The raised phase exhibits an inversion of image contrast compared to the background phase on reversing the scan direction. This inversion is indicative of a frictional difference between the two regions. It is necessary to obtain a frictional line profile [16,19] or a friction map to see whether the biggest change in friction is over the higher or lower phase as shown below.

When there are variations in surface topography the LFM signal contains a component due to the normal force acting through the local slope [19,27]. Since the lateral force is determined from the difference between signals reaching the left and right halves of a four-segment photodetector, in principle (ignoring piezoelectric drift) the topographic contribution to the LFM image may be eliminated by

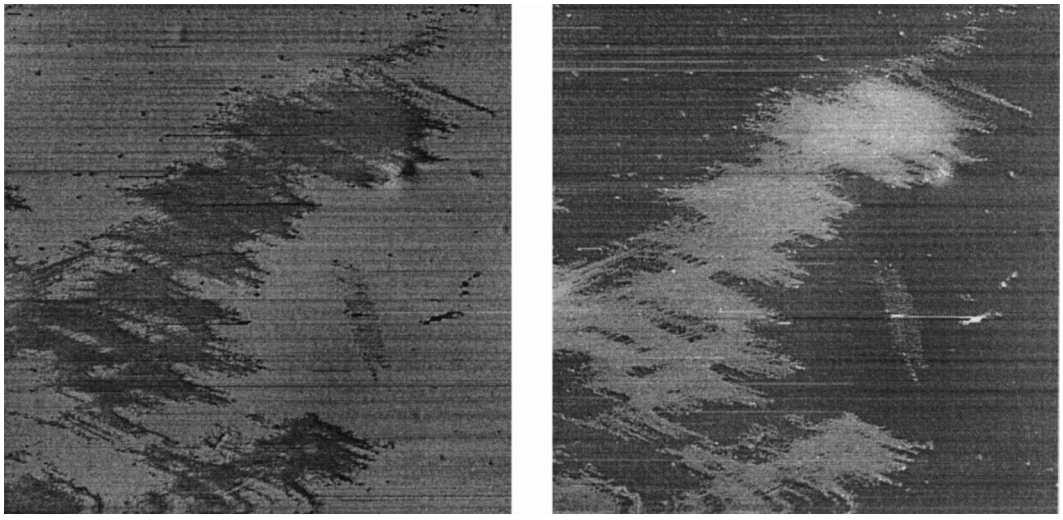

Fig. 6. Lateral force images of S film recorded in the forward (left) and reverse (right) scan directions. Image size 14.4 μm × 14.4 μm. MUA-functionalised probe tip. *Z*-scale range: friction signal 0–0.5 V.

subtracting images recorded in the forward and reverse directions. The subtraction of forward and reverse scans to produce a friction map that accurately reflects the frictional force acting between tip and sample was done using the software of the NanoScope IIIa. A typical friction map produced by subtraction of forward and reverse LFM images is shown in Fig. 7 for S film. The friction map shows that the higher phase is of lower friction. As a consequence of this, although the higher phase is quite sharply resolved, there is a reduction in image quality over the lower phase; the higher friction force between this region and the MUA-functionalised tip is detrimental to image quality. We have also investigated the wear characteristics of these unaxial films and have found that the higher friction force regions are also more susceptible to tip-induced wear than the raised regions [28]. Tapping Mode, which minimises the lateral or shear forces, has been employed to obtain the high resolution topographic images in Figs. 4, 8 and 9.

We have also used LFM to investigate whether the particles are exposed at the surface or whether they remain covered by a polymeric layer. Our previous studies of Mylar D, a biaxially drawn polyester film treated during manufacture to incorporate additives solely at the surface, showed that the friction force over the additives, deduced from friction line profiles, was lower than over the surrounding polymeric regions. However, the bulk-filled uniaxial films here generally do not show a contrast inversion over the additives, indicating that they exhibit similar frictional characteristics to the surrounding polymeric material. This suggests that the majority remain covered by a thin polymer film, even if they protrude from the geometric surface by up to 100 nm.

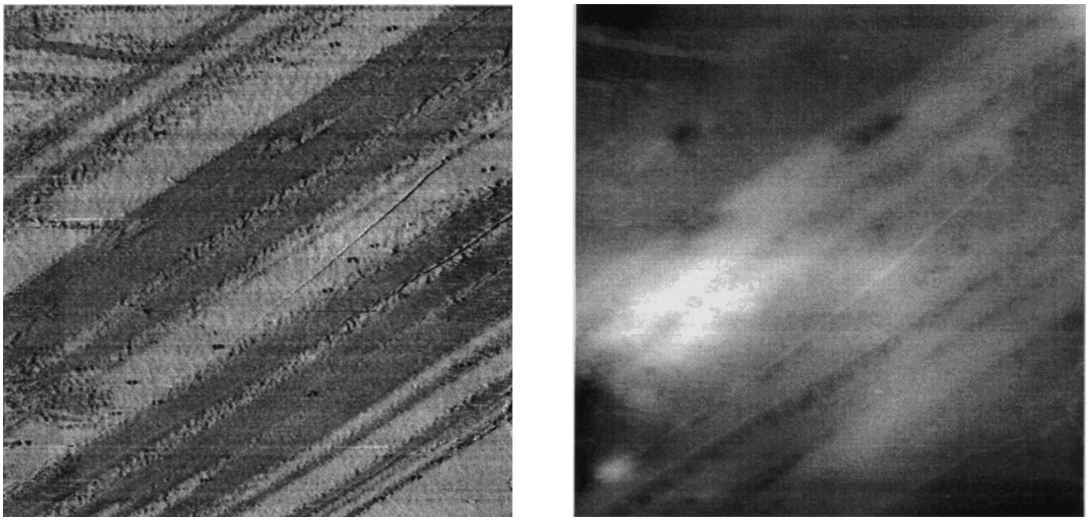

Fig. 7. Friction (left) and topography (right) of S film. Image size 10 μm × 10 μm. MUA-functionalised probe tip. *Z*-scale ranges: friction signal 0–1 V, height 0–60 nm.

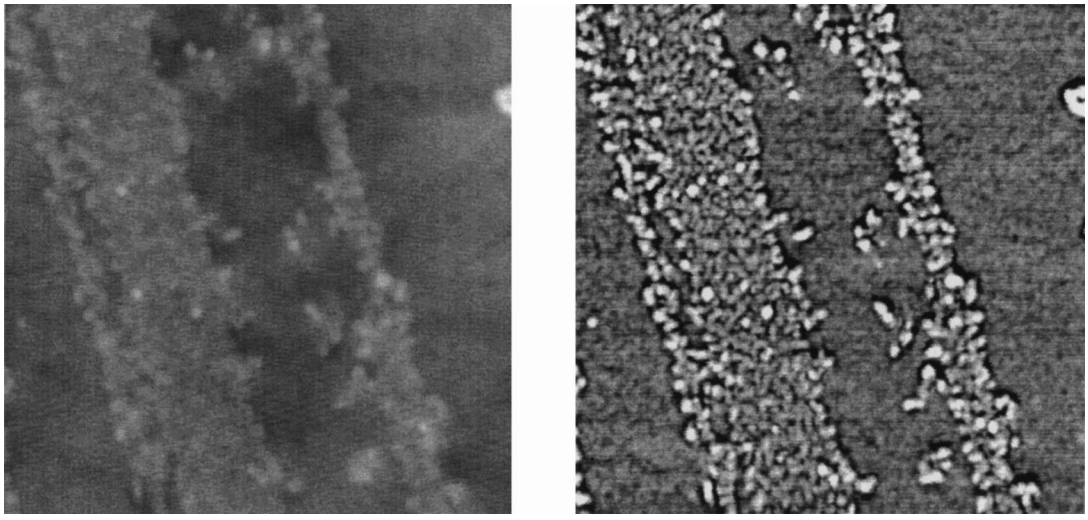

Fig. 8. Tapping (left) and phase mode (right) images of GB4 film. Image size 0.91 μm × 0.91 μm. *Z*-scale covers 0–15 nm height variations in the tapping mode image and 0–20° phase differences in the phase image.

3.3. Phase imaging

The conclusion from the LFM study, that most of the additive particles are not exposed at the surface, was supported by phase imaging data. Apparent phase shifts at scan speeds over 1 Hz were found to be illusory. They were directional, being high on one side of the additive and low on the other, and underwent a reversal of this contrast on changing the scan direction; they can be considered to be of topographic origin. This dependence of the phase signal on local topography could be effectively eliminated by the use of much reduced scan speeds (0.1–0.5 Hz). Under those conditions the vast majority of particles showed very little phase shift difference to the surrounding polymer. Occasionally however, particulates were observed to have more positive phase shifts (~20°) than the surrounding polymer, which itself had a buckled appearance, as might be caused by wear from an adjacent film surface. In these circumstances it was thought that the additive particles protruded through the film overlayer.

Phase shift maps, which are a measure of energy dissipation on contact of the tip with the surface, are thought to probe differences in stiffness/adhesion across the surface. Under conditions of moderate tapping [23] (the ratio of the amplitude of set-point oscillation to the free oscillation (ca. 40 nm) was set to ~0.4), a feature with a more positive phase shift than the surrounding material is thought to be of higher stiffness than the surrounding material [22–24]. For our bulk-filled films, the Young's modulus of all the additive materials are higher than the surrounding polymer, explaining the much higher phase shifts observed when the harder particles protrude through the film.

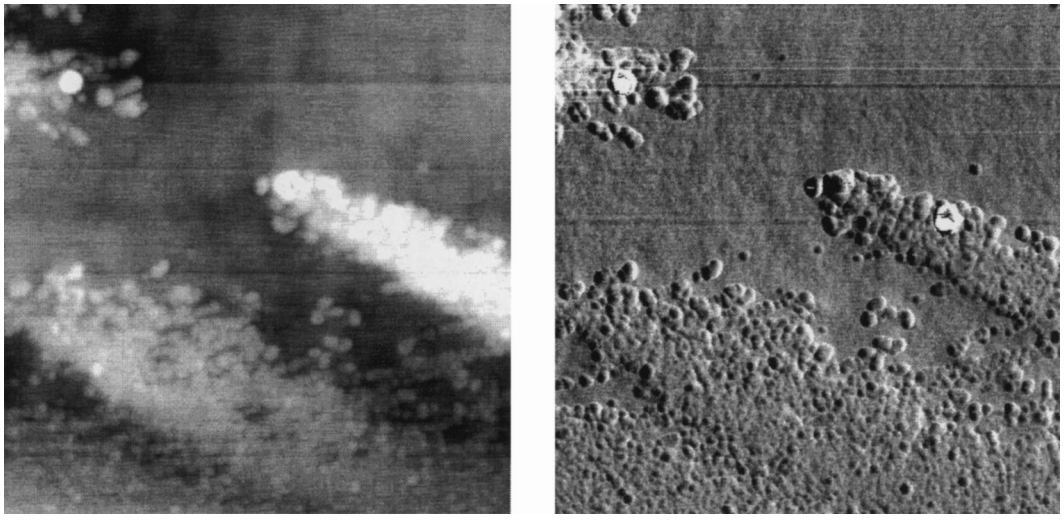

Fig. 9. Tapping and phase images of S film. Image size 1.37 μm × 1.37 μm. *Z*-scale covers 0–15 nm height variations in the tapping image (left) and 0–5° phase differences in the phase image (right).

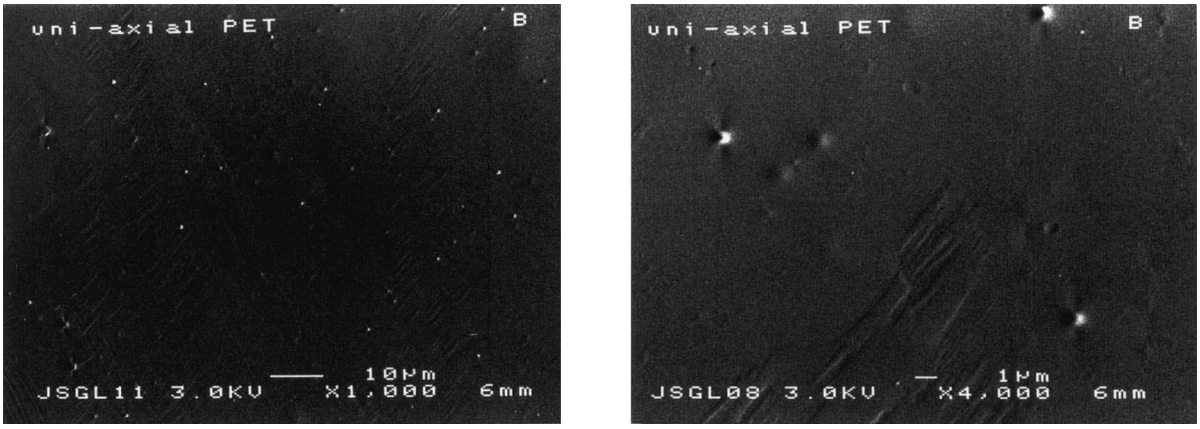

Fig. 10. SEM images of GB2 film.

Tapping Mode with phase detection imaging has also been used to investigate the nature of the raised features shown in Fig. 7. Fig. 8 shows that the raised regions exhibit higher phase shifts (~2°) than the surrounding background. Less energy is dissipated over the raised regions, as would be expected for a material of lower friction (from the LFM) than the background.

Fig. 9 shows clearly that the raised regions are composed of small circular domains. These domains are of very similar dimensions (and LFM contrast and phase shifts) to the small isolated circular regions which can be seen over large areas of the surfaces (see Fig. 5); it is reasonable to conclude that they are composed of the essentially the same material.

Phase imaging and LFM have shown that there are at least three separate regions of dissimilar energy dissipation on the film surface. The filler particles, where they protrude through the polymer surface exhibit very high phase shift as expected for materials of very low friction, low adhesion and high Young's modulus. The identity and orientation of the other phases is less simple to deduce. On the basis of the evidence it seems to us very likely that the raised features (for example in Fig. 7) are PET regions that are more crystalline than the background phase. This would explain (a) the enhanced protection against tip-induced wear; (b) the lower energy dissipation (high phase shift) in intermittent contact mode and (c) the lower frictional dissipation on sliding contact (LFM). The orientation of these features, diagonally to the draw direction in two different directions leading to a "herringbone" pattern, implies a level of ordering. Perhaps during drawing there exist biaxial or shear stress fields in the draw gap at about 45° to the direction of draw, which are capable of aligning and ordering the raised material.

Haugstad and co-workers have shown that the presence of similar raised regions of low friction and high phase on the surface of cast polyvinyl alcohol films on mica can be rationalised in terms of crystallinity differences; on annealing their films to produce greater crystallinity the proportion of the low friction component increased [12,13].

3.4. Comparison with SEM

We have performed SEM on gold-coated specimens of all the films and have compared the results with the SFM data described above. Fig. 10 shows illustrative SEM images for GB2 film. Many of the essential features of the SFM images, such as the plate-like features and filler particles with depressions aligned in the draw direction, are evident. However the resolution is significantly poorer, and the density of particles resolved in the SEM images is lower than that in the SFM images, presumably because some bumps at the surface due to concealed particles are resolved by SFM but not by SEM. The exposed particles show up as bright points in the SEM, indicating that the scattering is more effective from the glass beads than from the polymer, even after the film has been coated with ca. 4 nm of gold. However the brightness of these particles in the SEM micrographs is out of proportion to the extent that they protrude from the geometric surface in the SFM images. SFM data show that concealed particles (which have much lower contrast in the SEM images) often form raised features of comparable height to more exposed additive particles. In agreement with previous work in our laboratory, SFM provides a significantly more comprehensive analysis of surface structure than SEM of gold-coated polymer films.

4. Conclusions

We have investigated several bulk-filled uniaxially drawn PET films by SFM and SEM. SFM provides a significantly more comprehensive analysis of surface structure than SEM of gold-coated polymer films. Quantitative measurements of the nanoscale surface roughness of the films have been obtained by SFM; comparison with additive-free films shows that the addition of filler particles during manufacture markedly increases the final surface roughness. SFM techniques have revealed other interesting features of the topography of these filled films. Filler particles at or near the surface are accompanied by deep depressions aligned in the

direction of draw. Raised plate-like features oriented diagonally to the draw direction are present on all the films. LFM shows that these raised regions are of lower friction and phase imaging shows that they exhibit a higher phase shift than the surrounding polymer. The observations suggest that the raised material is more crystalline than the surrounding background.

Acknowledgements

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