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Atomic force microscopy and Fourier transform infra-red studies of the influence of a highly oriented poly(tetrafluoroethylene) substrate on poly(ethylene terephthalate) overlayers

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Atomic force microscopy (AFM) and Fourier transform infra-red spectroscopy (*FT*i.r.) were used to investigate the nature of poly(ethylene terephthalate) (PET) films formed on the surface of a highly oriented poly(tetrafluoroethylene) (PTFE) substrate mechanically deposited on silicon wafers. PTFE films have been previously shown to be highly effective substrates for the growth of oriented overlayers; such materials often have unique properties. In this study we report *FT*i.r. observations of an increase in crystallinity of a PET film formed on such an oriented substrate when compared to a film formed on the untreated silicon wafer. AFM imaging is used to show the deeply contrasting surface of the PET film formed on each substrate.

(Keywords: atomic force microscopy; i.r. spectroscopy; PET films)

Introduction

The growth of highly oriented overlayers on mechanically deposited poly(tetrafluoroethylene) (PTFE) films was first demonstrated by Wittmann and Smith[1], who reported that a wide range of organic and inorganic materials undergo induced orientation in the PTFE draw direction. In a later study it was found that other polymers were also able to form orienting substrates, most noticeably high density polyethylene, although in each case the performance was inferior to PTFE films so prepared[2]. Poly(n-di-alkylsilylene) films have been reported to show similar orientational growth on mechanically deposited PTFE substrates[3]. Microscopy and polarized infra-red spectroscopy are among the more popular techniques for characterization of such overlayers[1–3]. The structure of the PTFE films has been found to consist of a ribbon-like morphology with long strands of PTFE approximately 100 nm wide, separated by regions of exposed substrate of similar width, aligned in the draw direction of the film[4–7]. Atomic force microscopy (AFM) has been used not only to demonstrate the existence of the extended ribbon morphology but also to show that the high degree of alignment is reproduced on a molecular level[4,5,7]. Several recent studies have shown that the individual polymer molecules also align in the film draw direction with a highly regular chain spacing of 0.55 nm in agreement with X-ray diffraction studies[4,5,7,8]. Angle resolved high resolution X-ray photoelectron spectroscopy studies have also been employed to demonstrate the extended ribbon morphology, and reached the same conclusions concerning the bulk structure of the film[7]. Poly(ethylene terephthalate) (PET) was chosen as an overlayer for this study as a partially crystalline polymer which has already been shown to form oriented overlayers on such PTFE films[1] and which is known to undergo significant changes in crystallinity depending upon the processing conditions used [9–11]. Crystallinity is difficult to induce in PET due to a relatively high T_g (358 K) and as a result crystalline products require significant processing effort. The crystallinity is dependent to a large extent upon the conformation adopted by the $-CH_2-CH_2-$ group in the polymer repeat unit[12–15]; the *trans* isomer which produces a relatively straight chain is associated with crystalline polymers due to its greater regularity. The *gauche* isomer on the other hand presents a greater degree of disorder in the system and is therefore the structure associated with amorphous polymers. Unless care is taken with the processing conditions the *gauche* isomer tends to dominate, resulting in mainly amorphous products. The *gauche* and *trans* isomers of PET are easily distinguished by infra-red spectroscopy[12–15], making it an effective technique for comparing crystallinity, even in largely amorphous materials.

Experimental

Preparation of PTFE tribological films. Highly oriented PTFE films were prepared by the friction transfer method which has been described in detail elsewhere[7] but briefly consists of sliding a loaded PTFE bar across the desired substrate at a known temperature. A specially designed friction transfer apparatus was used with a knife-edge PTFE bar under load of 750 g, substrate (Si wafer) temperatures of 543 K and sliding speed 0.6 mm s^{-1}. A single sliding pass was made for each sample and the regularity of the deposited layer was examined by AFM measurements over several regions.

Growth of PET overlayers. PET was deposited onto the prepared PTFE substrates and untreated Si wafers as a control experiment by spin-casting from a 1% solution in hexafluoroisopropanol. Following spin-casting the

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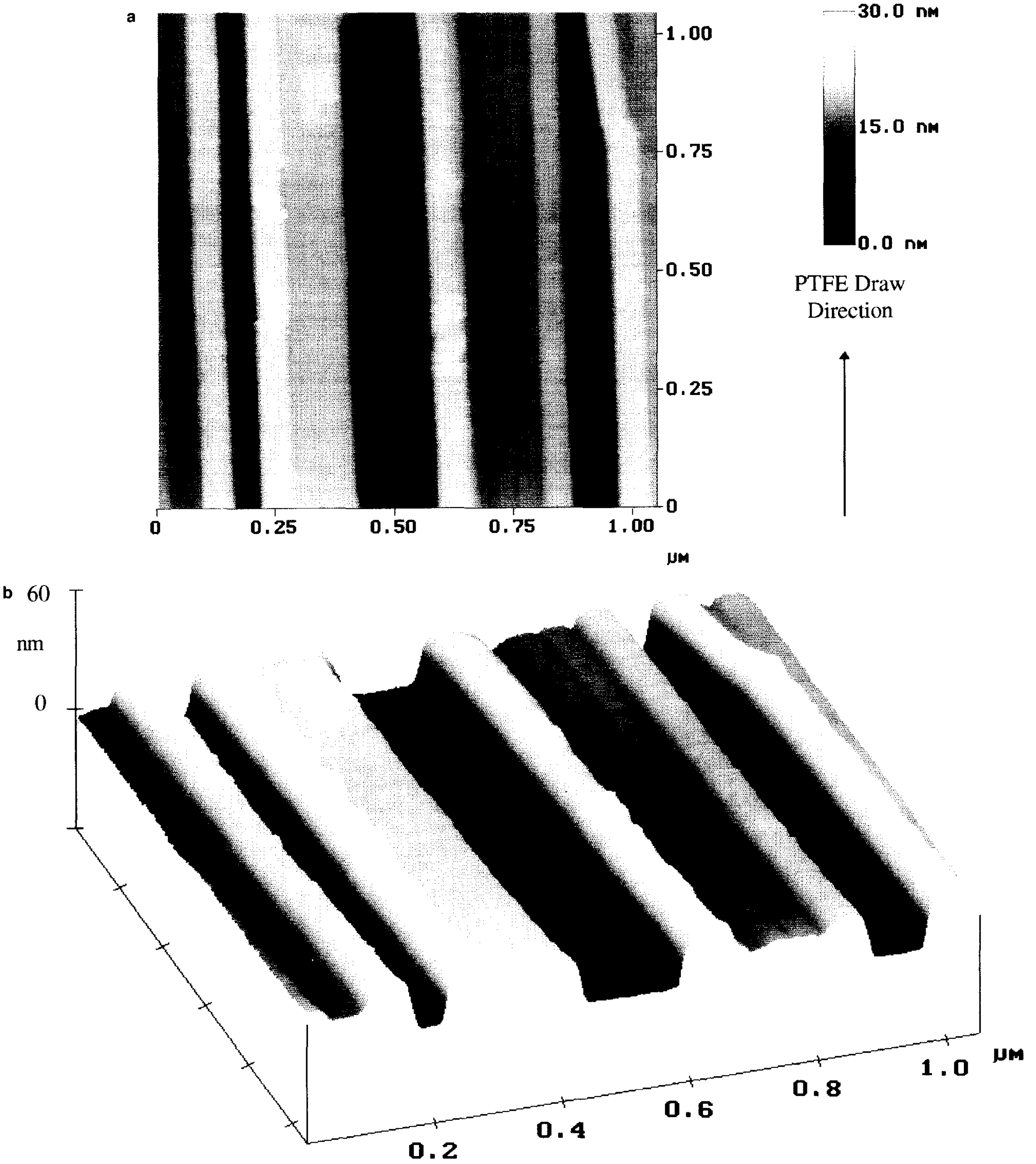

Figure 1 AFM images showing (a) the PTFE/Si substrate viewed from above, and (b) the surface contour of the PTFE/Si substrate

PET films ($T_m = 538$ K) were melted at 558 K for 1 h and then rapidly quenched to room temperature; the films were then annealed for 5 h at 483 K to allow the development of crystallinity.

AFM measurements. The films were imaged using a Digital Instruments Nanoscope III AFM system, fitted with a 'D' type scanner having maximum scan size of 20 μm. AFM images were obtained using 'height mode', which maintains the force at a constant level. To obtain the best images without damage, the applied force was minimized by adjusting the cantilever height (set point voltage) for each sample.

FT *i.r. spectroscopy.* The PET films prepared as described above were examined by transmission Fourier transform infra-red spectroscopy using a Bomem DA3 spectrometer. Prior to preparation of the PET films, background spectra were collected of the untreated Si and the PTFE/Si substrates. The spectra of the PET films were collected, using the relevant background spectrum in each case, after the annealing

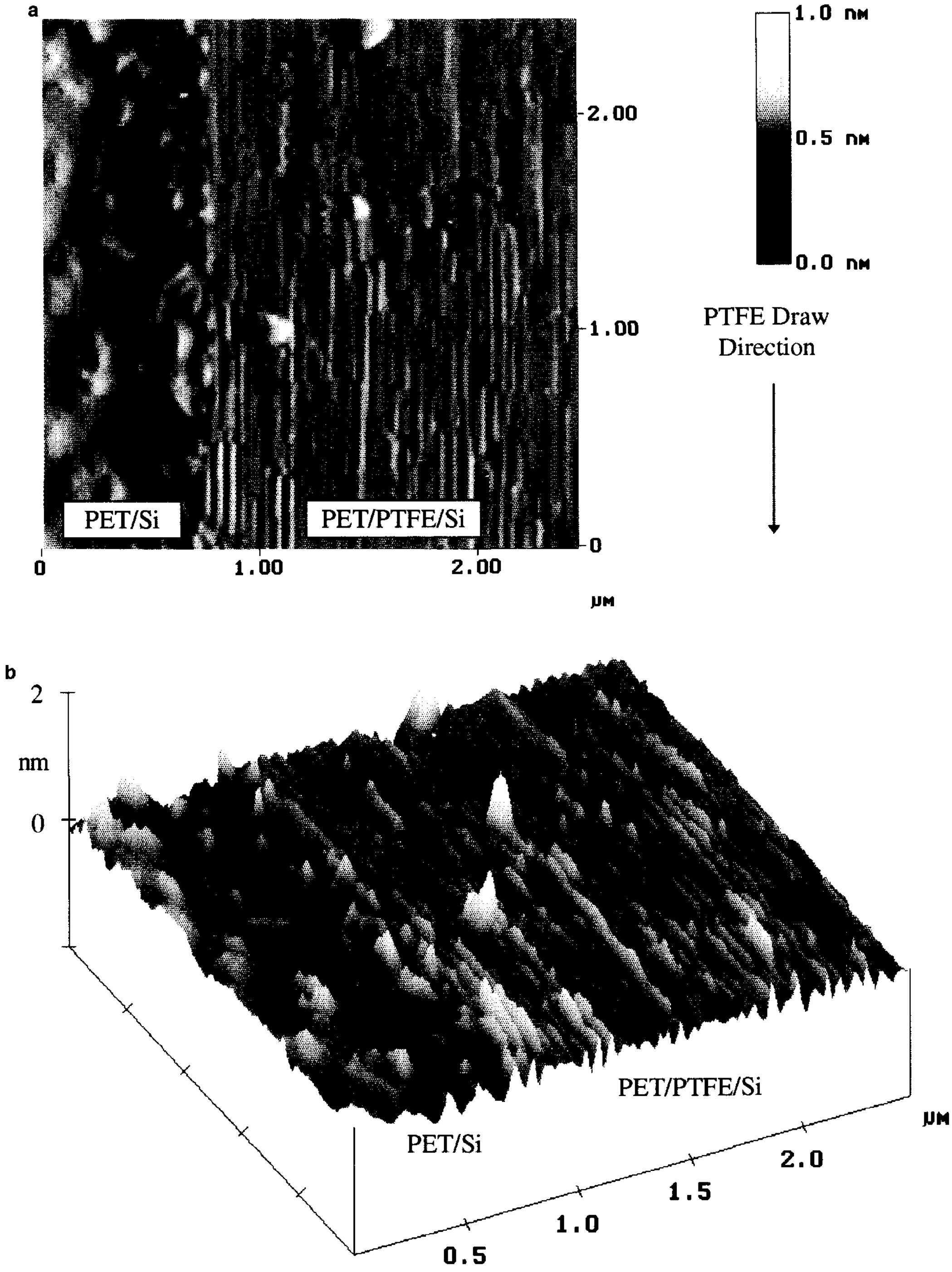

Figure 2 AFM images. (a) PET overlayers on Si (left-hand side) and PTFE/Si (right-hand side) after annealing for 5 h at 483 K viewed from above. (b) Surface contour of PET overlayers on Si (left-hand side) and PTFE/Si (right-hand side) after annealing for 5 h at 483 K

period of 5 h. All spectra were collected over 25 scans at a resolution of 4 cm^{-1} in the region 800–2000 cm^{-1}.

Results

AFM imaging. AFM images of the PTFE/Si substrate are presented in *Figures 1a* and *b*, clearly illustrating the ribbon-like morphology of the PTFE film The PTFE ribbons were found to align with the draw direction of the friction transfer apparatus, as previously observed[4–7]. No changes were observed in the PTFE/Si substrate following annealing at 483 K for 5 h. The contrasting nature of the PET overlayers on untreated Si and PTFE/Si substrates is illustrated in *Figures 2a* and *b*, showing the clear boundary between the regions in the AFM images. It is immediately obvious that the PET overlayers behave very differently on either side of the substrate boundary: on the untreated Si surface, as represented by the left hand side in *Figures 2a* and *b*, there is little or no apparent ordering of the overlayers. In contrast, where the PET overlayer covers the PTFE/Si substrate, as represented by the right-hand side of *Figures 2a* and *b*, there is significant ordering of the overlayer. The PET film apparently aligns with the PTFE draw direction running from top to bottom of *Figure 2a*.

These images show good agreement with the optical microscopy results of Wittmann and Smith[1], who also observed well defined boundaries for overlayers on PTFE/Si substrates. The PET overlayer was observed to form a channelled surface structure, reflecting the ribbon-like morphology of the PTFE substrate, following annealing. Annealing PET is known to induce crystallinity with which there would be an expected shrinkage as the polymer molecules pack closely in a more ordered structure[9-11]; this could account for the observed surface channelling. As the PET film contracts into more ordered regions constrained by the PTFE substrate, cracks appear in the surface where material is lost.

FT *i.r. spectroscopy*. The infra-red absorption spectrum of PET contains a number of bands which are influenced by the conformation of the polymer, which may adopt either a *trans* or *gauche* isomerism of the $-CH_2-CH_2-$ group in the basic repeat unit[12-15]. The *trans* isomerism is associated with the crystalline polymer whereas the *gauche* isomerism is typical of the amorphous polymer[12-15]. In this study we have used the bands at 1344 cm^{-1} and 1410 cm^{-1} to compare the crystallinity of the PET overlayers deposited on PTFE/Si or untreated Si substrates; the band at 1344 cm^{-1} is assigned to the γ_{w} CH_2 of the *trans* isomer[12-15] and the band at 1410 cm^{-1} is assigned to the aromatic ring vibration which is insensitive to conformational changes.[15]. This pair of bands was chosen owing to their relatively close proximity, with the ring vibration providing a standard measure of sample thickness against which the 1344 cm^{-1} band could be normalized. *Figure 3* shows the resulting spectra in the region 1300–1450 cm^{-1} for PET overlayers on both the PTFE substrate (A) and the Si substrate (B). It can be clearly seen that the intensity of the 1344 cm^{-1} vibration is much greater for the PTFE substrate than for the Si substrate when compared to the internal standard band at 1410 cm^{-1}. Integration of the 1344 cm^{-1} peak area and normalization with the area of the 1410 cm^{-1} vibration reveals the ratio $A/B = 3$ for the 1344 cm^{-1} band. The PET overlayer grown on a PTFE substrate therefore has considerably higher *trans* content than the equivalent overlayer grown on untreated Si. Greater *trans* content in turn implies a higher degree of crystallinity for the PET film on the PTFE substrate. Several workers have reported that the amorphous regions of the polymer also have some *trans* content[13,15-17] but this is generally thought to comprise less than 20% of the total *trans* isomers present[13]. Such observations are in keeping with the findings of the AFM experiments where an oriented channel structure was found for the same sample. A simple model explaining these observations would be that PTFE substrates induce a high degree of orientation in the PET film upon melting/quenching, which on annealing between T_g and T_m allows the formation of ordered crystalline regions through molecular rearrangement. The process may be considered similar to that used to prepare biaxially oriented films in which the PET film is stretched in two perpendicular directions above T_g and then annealed at ~ 503 K[9-11], achieving the desired orientation necessary to prepare a film of appreciable crystallinity.

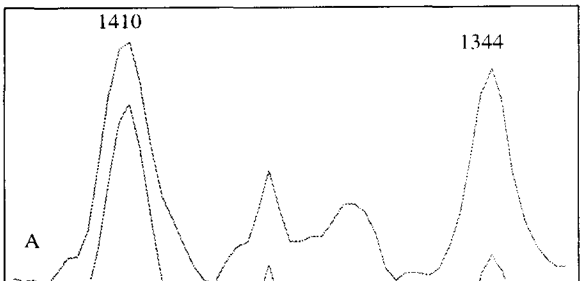

Figure 3 *FT*i.r. spectra (A) PET/PTFE/Si and (B) PET/Si after annealing for 5 h at 483 K

Conclusion

The influence of highly oriented PTFE substrate on PET overlayers is to induce a high degree of orientation in the PET film which on annealing above T_g results in significantly enhanced crystallinity over films prepared on an untreated Si substrate. The highly oriented PET film produced by deposition on such a PTFE substrate can be considered in many ways similar to the orientation induced during the biaxial stretching process used commercially to prepare crystalline PET films.

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