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The mechanism of PTFE and PE friction deposition: a combined scanning electron and scanning force microscopy study on highly oriented polymeric sliders

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The mechanism of friction deposition of polytetrafluoroethylene (PTFE) and polyethylene (PE) was studied by scanning electron (SEM) and scanning force microscopy (SFM) on the worn surfaces of PTFE and PE sliders that were used in friction deposition on glass substrates. These surfaces exhibited a fibrillar morphology which was oriented in the sliding direction. The molecular order of the PTFE and PE chains on the surface of thin microfibrils on the slider could be readily imaged with molecular resolution using SFM. The SEM and SFM images present direct evidence of an orientation of the slider on both a fibrillar *and* a molecular level and thus support the orientation mechanism postulated by Pooley and Tabor (*Proc. R. Soc. London A*, 1972, **329**, 251). The orientation occurs during shearing of the material that sticks to the glass surface due to the high adhesion between the first layer of PTFE and the glass. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polytetrafluoroethylene (PTFE) is an example of a typical high performance polymer. PTFE is chemically resistant and has found widespread applications owing to its low surface energy and extraordinary frictional properties[1,2]. Its frictional properties have been attributed to its ‘smooth’ molecular profile rather than to its chemical composition. In their pioneering work, Pooley and Tabor investigated the tribological properties of PTFE[3]. These authors attributed the low coefficient of dynamic friction to the sliding of an *oriented* slider. During sliding, a thin film of PTFE is formed by friction transfer of the polymer onto the solid substrates. Similar observations were reported for polyethylene (PE)[3]. Pooley and Tabor attributed this similarity to the ‘smooth’ molecular profile of both polymers because polymers with bulky side groups did not show the same behaviour.

These friction deposited PTFE films have found application as substrates for the orientation of a diversity of materials, ranging from polymers to liquid crystals[4]. Early scanning force microscopy (SFM) investigations showed that the transferred films were indeed highly oriented and could be imaged with molecular resolution[5,6]. The friction anisotropy of surfaces of the transferred films of PTFE as well as the sliders has been the subject of several recent SFM studies[7–10].

In this paper, we report on a combined scanning electron microscopy (SEM) and SFM study on the surfaces of worn PTFE and PE sliders used for friction deposition of PTFE or PE onto glass substrates. This study gives insight into the mechanism of the friction transfer process and ultimately proves that the surfaces of worn PTFE and PE *sliders* are highly oriented. Thus, the results support the mechanism postulated by Pooley and Tabor.

EXPERIMENTAL

Sample preparation

Samples were machined from PTFE (Teflon) rods which were obtained from Warehoused Plastic Sales Inc. (Toronto, Canada). The orientation of the sample surface was achieved by manually sliding the PTFE specimens over a cleaned glass slide in a Mettler FP 82 HT microscope hot stage at a specific temperature. Samples were prepared at temperatures between 20°C and 250°C. PE specimens were prepared in a similar manner from HDPE samples (BASF, trade label HDPE 6031 HX). The sliding was performed at 120°C.

Scanning electron microscopy

A thin layer of gold was sputtered onto the polymer specimens in a Balzers SCD 040 sputtering machine at an argon pressure of 0.1 mbar. The SEM images were obtained with a Jeol JSM-T 220A electron microscope at a voltage of 20 kV.

Scanning force microscopy

The SFM measurements were carried out with a NanoScope II and a NanoScope III multimode SFM (Digital Instruments (DI), Santa Barbara, CA, USA) in contact mode. SFM scans were performed both in air, utilizing cantilevers with a nominal spring constant of 0.38 N m^{-1} (Si_3N_4, DI), and in ethanol (p.a., Merck), utilizing a liquid cell (DI) and cantilevers with nominal spring constants of 0.38 N m^{-1} and 0.12 N m^{-1} (Si_3N_4, DI). All images shown in this work correspond to *unprocessed raw* data.

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The high resolution SFM images were evaluated by calculating the average interchain distance from cross-sectional plots. Up and down scans were averaged in order to eliminate effects of the thermal drift. The instrument was recalibrated by imaging a sample of mica with exactly the same height after each set of experiments[11].

RESULTS AND DISCUSSION

The surface of all the investigated PTFE sliders showed uniaxial orientation in the sliding direction in the micrometre and nanometre scale. In low magnification SEM images, oriented features in the sliding direction could be seen on the slider surface (*Figure 1A* and *B*). Furthermore, individual fibrils and bundles of (micro)fibrils could easily be distinguished. The surface of worn sliders frequently contained lumps of polymer material from which fibrils and microfibrils had been torn (*Figure 1B*). These lumps of material could also be found on the glass surface (*Figure 1C*). Apparently the fibres and fibrils were pulled from the corresponding piece of PTFE.

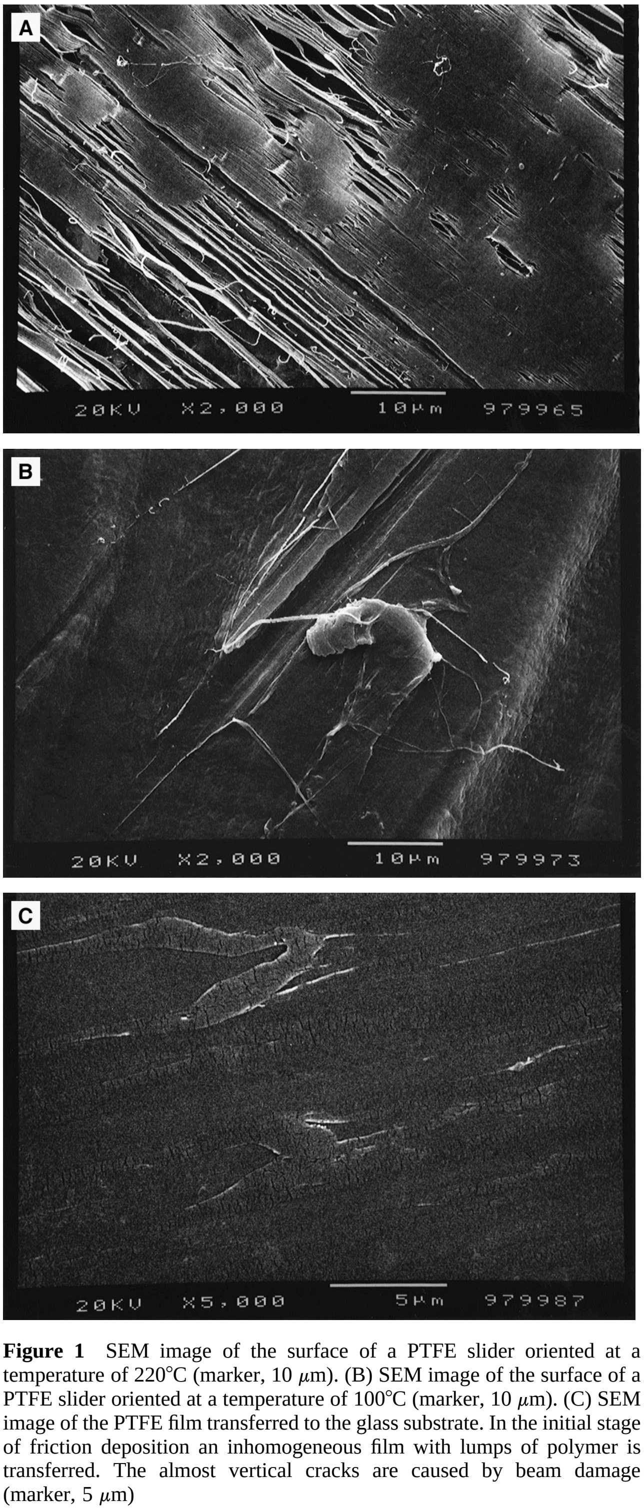

Figure 1 SEM image of the surface of a PTFE slider oriented at a temperature of 220°C (marker, 10 μm). (B) SEM image of the surface of a PTFE slider oriented at a temperature of 100°C (marker, 10 μm). (C) SEM image of the PTFE film transferred to the glass substrate. In the initial stage of friction deposition an inhomogeneous film with lumps of polymer is transferred. The almost vertical cracks are caused by beam damage (marker, 5 μm)

Pooley and Tabor[3] observed the deposition of lumps mainly at the beginning of the sliding process. During later stages of the sliding process a coherent film was deposited onto the glass substrate. These films were used by Wittman and Smith[4] as substrates which have remarkable orienting properties. Polymers, liquid crystals, and other materials can be oriented when friction deposited PTFE is used as a substrate.

The region on the slider where the unoriented bulk is transformed to a fibrillar morphology can be seen in *Figure 2*. This transition is reminiscent of the (micro)necking region described by Peterlin[12]. Note that the bulk PTFE is easily damaged by the electron beam (compare the ‘cracks’ which are perpendicular to the orientation direction).

The ordered surface could be imaged with higher resolution using SFM. In *Figure 3a–c*, a sequence of images of the fibrillar morphology can be seen. These micrographs were captured in air.

The rather perfect order of the PTFE fibrils and microfibrils on a molecular scale could be routinely detected by SFM. The crystal structure of the PTFE could be resolved. The nanograph presented in *Figure 4* was obtained in ethanol. The imaging in a liquid allows one to reduce the imaging forces to very small values (*ca.* 0.5–5 nN). Thus, deformation of the sample surface is minimized. Note that the lateral force image (right) shows the same periodicities as the simultaneously captured height image (left). The contrast in the lateral force mode corresponds to a molecular stick–slip process[7,8].

The observed interchain distance of 5.56(± 0.25) Å corresponds very well with the crystal structure of the hexagonal IV phase of PTFE (5.55 Å)[13]. The high degree of orientation of the worn PTFE sliders was also proved in measurements of the friction anisotropy of the surface. The friction force between the tip and the polymer surface

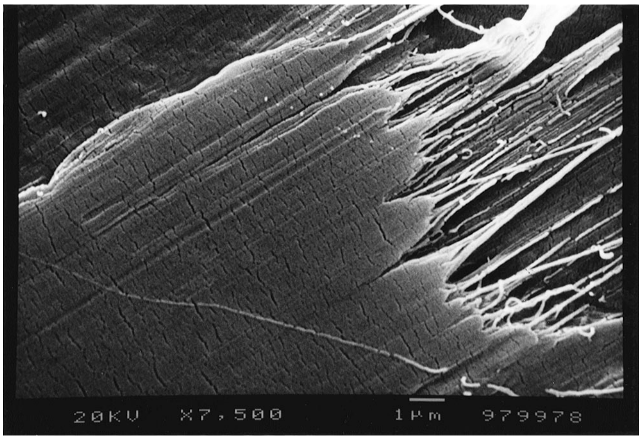

Figure 2 SEM image of the surface of a PTFE slider oriented at a temperature of 50°C (marker, 1 μm)

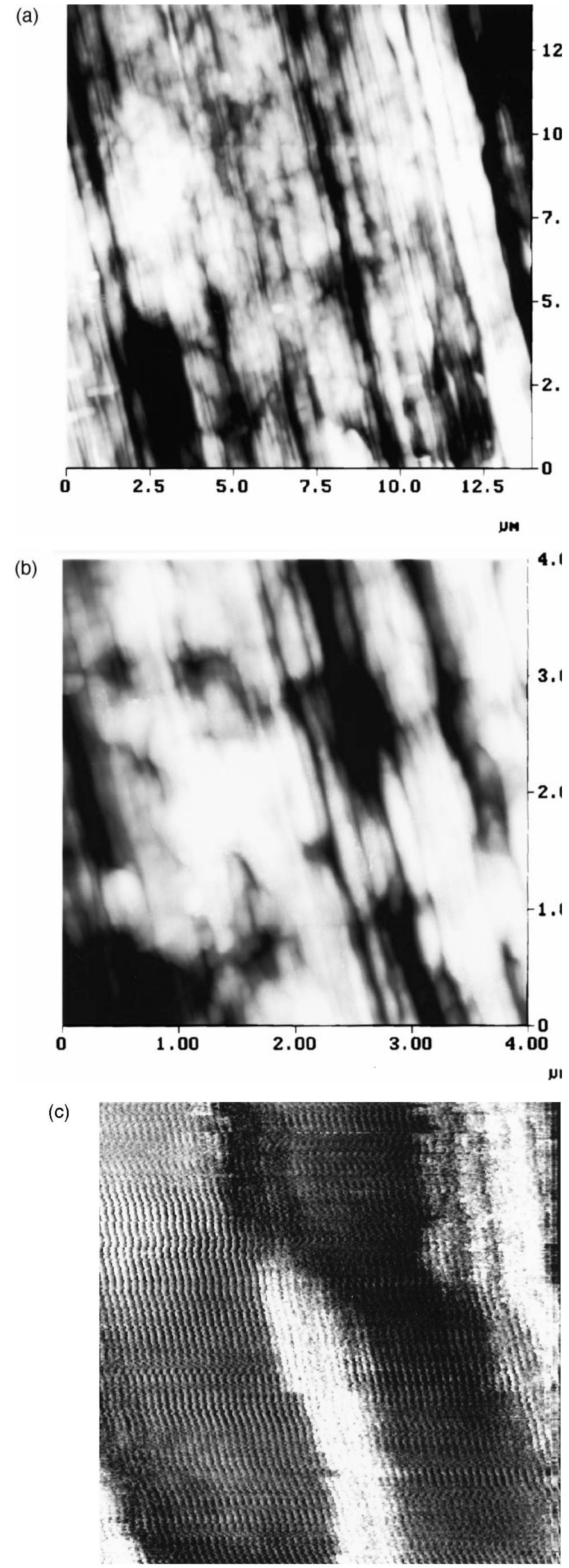

Figure 3 SFM image of the surface of a PTFE slider oriented at a temperature of 220°C. (b) SFM image of the surface of a PTFE slider oriented at a temperature of 220°C. (c) Friction force micrograph of the surface of a PTFE slider which has been oriented at a temperature of 220°C imaged in air (35 nm × 35 nm). The parallel lines correspond to tightly packed PTFE chains oriented in the sliding direction

depends (a) on the normal force applied to the surface and (b) on the orientation of the polymer chain with respect to the scan direction. The friction measured during scans perpendicular to the polymer chain direction is significantly higher than the friction measured during scans parallel to the chain direction. The orientation of the polymer chains with respect to the fixed scanning direction (perpendicular to the cantilever's long axis) was adjusted manually by turning the sample. The friction anisotropy has been previously reported for SFM experiments performed in air[7,8]. The results shown in *Figure 5* were obtained in ethanol. Due to the absence of capillary forces, the friction force versus normal force dependence can be measured accurately to very small imaging forces.

The orientation of the worn surface of the slider could also be observed for high density polyethylene (HDPE) specimens that were oriented by sliding on glass at a temperature of 120°C. On these surfaces, *both* the *ac* and *bc* crystal facet of orthorhombic polyethylene could be imaged with molecular resolution (*Figure 6*)[10]. The interchain distances of 4.94 ± 0.35 Å (*bc*) and 7.44 ± 0.35 Å (*ac*) agree very well with the crystallographic repeat lengths found in orthorhombic PE ($a = 7.418$ Å; $b = 4.946$ Å) (the surface crystal structure of highly oriented orthorhombic PE has been previously imaged with SFM)[14,15].

The explanation by Pooley and Tabor[3] for the observed low dynamic coefficient of friction for PTFE (and PE) is the sliding of an *oriented* slider which transfers a thin film of highly oriented PTFE (PE) by friction transfer of the polymer onto the solid substrate. The adhesion between the glass and the closest polymer chains is larger than the interfacial shear strength. Upon continued sliding the polymer is sheared and then is deposited as a thin highly oriented film. The initial value of the friction coefficient is high, but if the sliding continues, the value of the friction coefficient drops significantly because of the above-mentioned sliding of an oriented slider. Pooley and Tabor assumed in their explanation that the surfaces of the PTFE (PE) sliders were oriented. The reduction in friction could be explained based on the smooth molecular profile.

The experimental results presented here clearly support the assumption of the oriented slider and thus support the original explanation by Pooley and Tabor[3]. Even at room temperature, fibres, fibrils, and microfibrils are formed by shear forces acting on the polymer. Independent of the temperature at which the samples were prepared, the surface of the sliders is highly oriented. The orientation of the polymer chains in the sliding direction can be imaged by SFM on a molecular scale.

CONCLUSION

A combined SEM and SFM study proved that the sliding of PTFE and PE specimens over glass substrates results in the orientation of the sliders' surfaces as well as in the known transfer of a highly oriented polymer film onto the substrate. The orientation of the worn surface of polymeric sliders could be visualized on different length scales: fibres, fibrils, microfibrils and the polymer crystal structure could be observed. The polymer chain direction on top of the microfibrils corresponded to the sliding direction. Our results strongly support the validity of the mechanism of the friction deposition and the explanation of the low coefficient of friction of PTFE and PE by Pooley and Tabor.

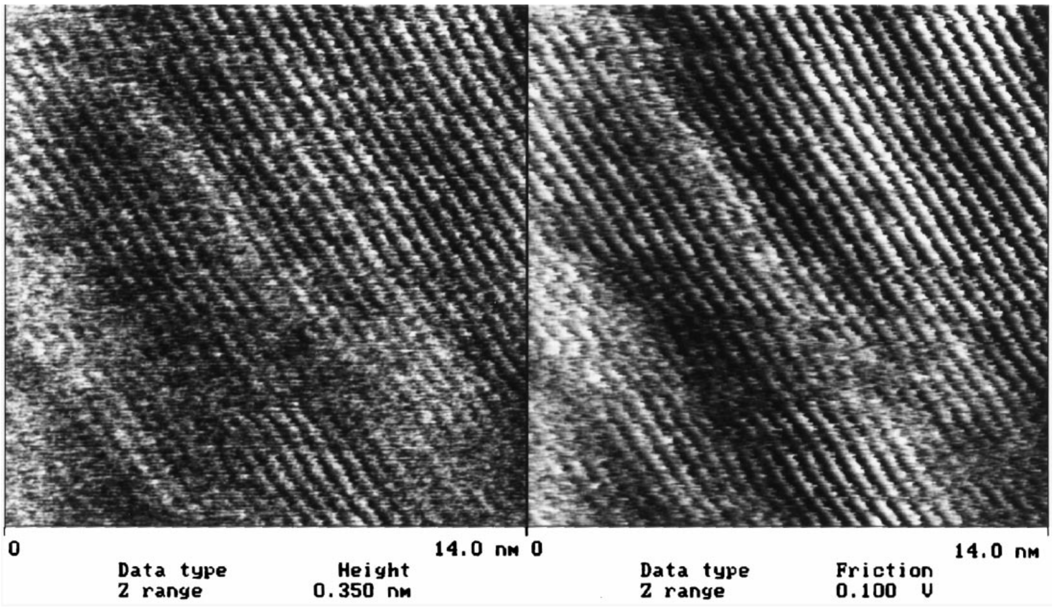

Figure 4 Dual height (left) and lateral force (right) nanograph of the highly oriented surface of a PTFE slider imaged in ethanol

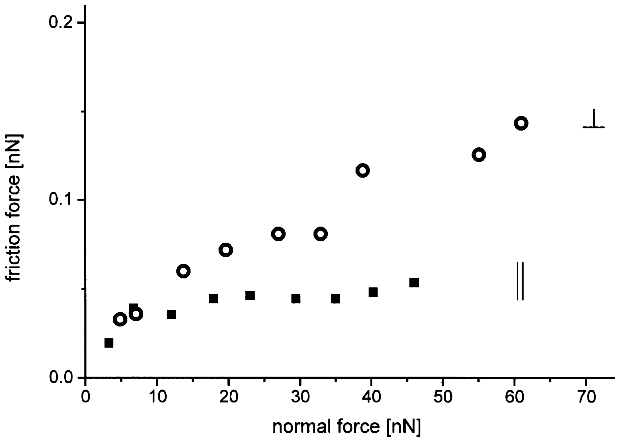

Figure 5 Friction force between a Si_3N_4 tip ($k = 0.12\ N\ m^{-1}$) and highly oriented PTFE in dependence of the normal force and the scanning direction measured in ethanol. The data was obtained by evaluating so-called friction loops[6]

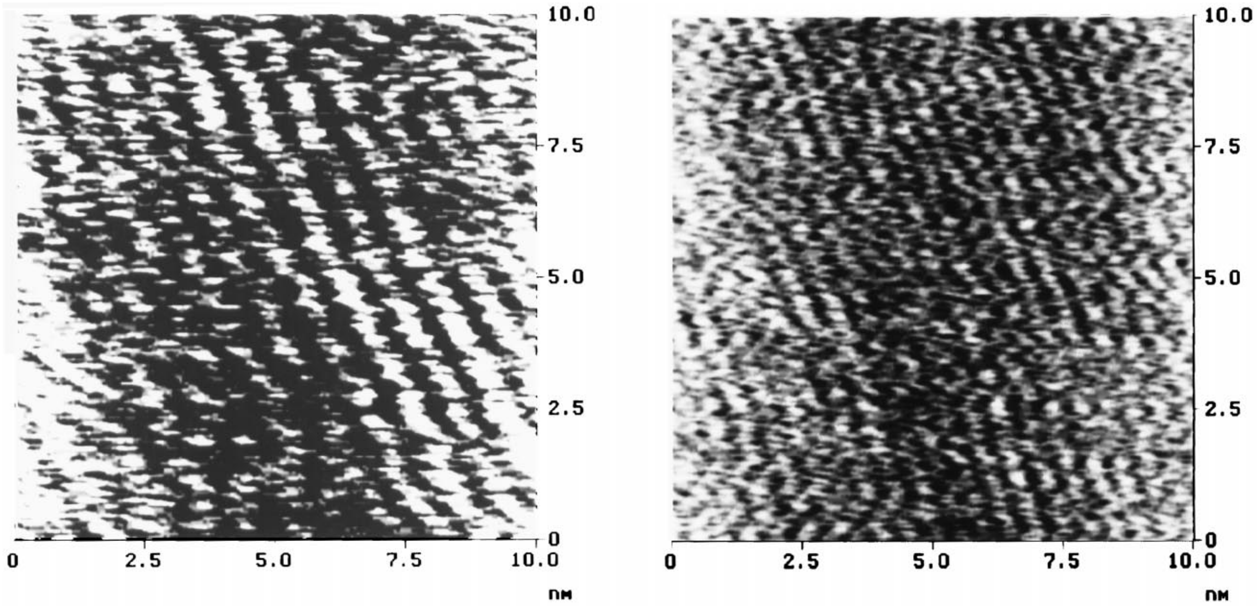

Figure 6 Height images of *ac* (left) and *bc* (right) crystal facets of orthorhombic polyethylene on the highly oriented surface of a PE slider imaged in air

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