Nanometer-Scale Tribological Properties of Highly Oriented Thin Films of Poly(tetrafluoroethylene) Studied by Lateral Force Microscopy

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ABSTRACT: Lateral force microscopy (LFM) studies of poly(tetrafluoroethylene) (PTFE) films obtained by pressing and sliding a block of polymer on a clean heated glass surface are reported. The sample preparation process utilized, invented by Wittmann and Smith, resulted in samples of thin, well-oriented films and fibers of PTFE which were deposited on the glass. The formation of such oriented PTFE films was confirmed by dual LFM/AFM images. During LFM/AFM scanning, PTFE molecules were picked up by the nanoscope tip probe, which clearly reduced the frictional force differences measured between glass and PTFE. This observation is in line with the model of Tabor, which assumes strong interfacial tension between PTFE and glass during sliding friction. LFM experiments performed on the PTFE films at scan directions between ca. 40 and 90° with respect to the polymer main chain orientation showed a "stick−slip" type frictional motion at the molecular level. This phenomenon allowed us to obtain LFM images of a synthetic polymer with molecular resolution. Chain−chain packing distances obtained by LFM and contact-mode AFM were identical to within the experimental error and had a value of 5.78 Å at 25−30 °C imaging temperature. Dual-mode contact AFM/LFM imaging was also performed by scanning in the chain direction. Here LFM nanographs showed no measurable "stick−slip" phenomenon; i.e., basically a featureless, flat image was obtained. The contact-mode AFM images, however, exhibited clear molecular resolution with the expected chain−chain periodicity. The disappearance of the "stick" component in scans performed in the chain direction is a result of the smooth surface of PTFE on the molecular scale.

Introduction

Poly(tetrafluoroethylene) (PTFE) is one of the most remarkable synthetic high polymers, combining a large range of different useful chemical and physical properties.[1] Even though PTFE is one of the "older" commodity polymers (its synthesis was first reported by Plunkett in 1941; see ref 2), its fascinating properties are still the subject of many recent investigations.[3] PTFE is highly crystalline with a very high molecular weight and very little cross-linking and branching. In its commercially available form, it consists of cold-fused material with a low degree of entanglements.

The properties of interest for this work are the unique tribological characteristics of PTFE. This polymer has a very low surface tension and coefficient of friction over a wide temperature range. Pioneering studies of the frictional properties of PTFE were done by Tabor[4,5] long ago. The molecular explanation of the low coefficient of friction of PTFE, however, is still a subject of some controversy. Initially, it was assumed that the weak interfacial bonding of PTFE at the free surface was responsible for the low sliding frictional coefficient. This was explained by the low molecular adhesion at the PTFE interface, which can be attributed to the screening effect by the relatively large F atoms on the positive charges on the C atoms of the polymer backbone. In contrast, the work of Pooley and Tabor[5] showed that, during dynamic friction of a PTFE slider on a glass surface, polymer chains are transferred from the moving slider to the glass surface. This indicates the presence of strong interfacial interactions between glass and PTFE. The low frictional coefficients observed in re-

peated sliding experiments were explained by the deposition of a thin, well-oriented PTFE layer on glass which consists of smoothly profiled macromolecules at the surface.[5] The low value of the frictional coefficient, according to this explanation, would paradoxically arise from the high adhesion between glass and PTFE.[6]

The transfer of a well-ordered PTFE layer during the sliding motion of the polymer on glass allowed Wittmann and Smith[7] to prepare ordered PTFE films for use as substrates in oriented epitaxial crystallization. Various polymeric materials which have a remarkable degree of alignment were epitaxially crystallized[8] on these surfaces.[7]

The PTFE film itself, obtained by the technique described in ref 7, was the subject of several atomic force microscopy (AFM) studies.[9,10] These papers unveiled that the deposited PTFE consisted of thin single-crystal-like layers with a high degree of molecular order. AFM images with clear molecular resolution were captured with an intermolecular spacing of 5.8 Å.[10] This value is in reasonable agreement with typical chain axis separation distances for the chain separation in the phase IV hexagonal structure. The value obtained for the chain−chain distance by X-ray diffraction for this structure is 5.55 Å.[11]

The discovery and commercialization of LFM opened up an exciting era in force microscopy. LFM is the key technique for the emerging new discipline of nanotribology, which is of great practical importance. Early frictional force microscopy studies demonstrated that sliding friction on graphite at the atomic level is discontinuous. It was shown that the friction of the LFM tip on graphite can be best described by a stick−slip process with a periodicity that corresponds to the atomic periodicities at the sample surface in the direction of the sliding motion.[12] Other studies at surfaces of polymer lamellar crystals unveiled anisotropic friction at the surface of lamellar polymer crystals, including

poly(oxymethylene)[13] and polyethylene.[14] These experimental studies are complemented by recent theoretical work[15,16] which discusses the molecular origins of friction. Dual lateral force and contact-mode AFM measurements yield information about the topography of the sample surface as well as the chemical composition of heterogeneous materials.[17] Thus, LFM can be used to complement contact-mode AFM experiments. AFM tips can also be functionalized, e.g., by coating them with a single layer of molecules which have a given functional group at the free surface of the tip. If such functionalized tips are used in LFM measurements, the nanographs obtained can selectively unveil the spatial distribution of the chemical composition of certain types of chemical groups at the sample surface.[18]

In this paper, we report on lateral force microscopy (LFM) studies of thin PTFE films obtained by moving a PTFE bar on surfaces of heated glass or heated muscovite mica. We focus our attention on dual LFM/contact-mode AFM imaging on the micrometer scale as well as at the molecular level. The objective is to study tribological properties of the PTFE film, with special emphasis on the "stick–slip" phenomena on the molecular scale.

Experimental Section

PTFE blocks used in this study for film deposition were machined from Teflon rods which were obtained from Warehoused Plastic Sales Inc., Toronto, Canada. The static coefficient of friction on steel for this PTFE had a value of 0.02, as specified by the distributor. For PTFE film deposition, precleaned microscope slides and freshly cleaved muscovite mica were used. The glass slides were obtained from Baxter Canlab. They had a thickness of 1 mm and were used without further cleaning. The muscovite mica was obtained from J.B. EM Services Inc., Québec, Canada. PTFE films were prepared on these substrates by using a Mettler FP 82 HT microscope hot stage. The substrate (glass or mica) was first placed in the hot stage which was heated to the temperature at which deposition took place (150, 200, and 250 °C, respectively). After reaching the set temperature, the hot stage and the substrate were allowed to equilibrate for ca. 5 min. A small block of PTFE was machined from the commercial rod for polymer deposition. The sliding surface was cut by a Sorvall MT 6000 ultramicrotome utilizing glass knives. After temperature equilibrium was established in the hot stage, its cover was opened. The PTFE block was then manually pressed against the hot substrate and pulled over once.

A NanoScope III setup manufactured by Digital Instruments was used for AFM/LFM imaging. The instrument was equipped with an A scan head which was calibrated in the x- and y-directions by using images of muscovite mica as described in ref 19. All scans were performed in air with Si_3N_4 NanoProbe integrated microcantilevers with a nominal force constant of 0.38 N m^{-1}. The scan rates selected were between 7 and 9 Hz. Scanning was performed at 90° with respect to the direction of the long axis of the cantilever spring, as is usual for LFM/AFM dual imaging.

Results and Discussion

Dual LFM/AFM images of highly oriented PTFE films obtained on glass are displayed in Figures 1a,b, and 2a,b. The LFM images are shown on the left, and the contact-mode AFM images (captured in the constant-force mode) are shown on the right. The dual LFM/AFM image in Figure 1a corresponds to the first scan, obtained by using a freshly mounted cantilever, over an area of (9.5 μm)^2. The third dual scan obtained over the same area is captured in Figure 2a,b. The AFM and LFM scans show the microfibrils and strips of oriented films which were deposited on the heated glass sub-
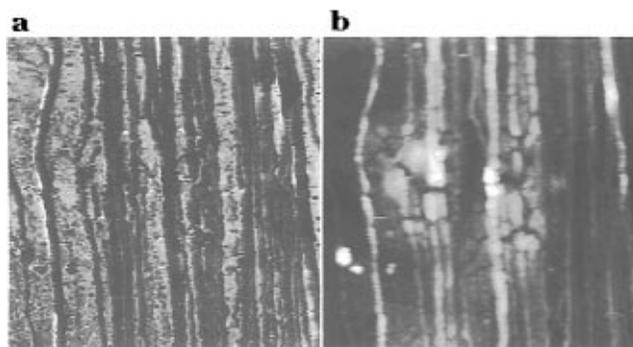

Figure 1. Lateral force microscopy (a) and contact-mode (height) atomic force microscopy (b) images of PTFE deposited on glass. The same area of 9.5 μm × 9.5 μm is depicted on both micrographs; first scan.
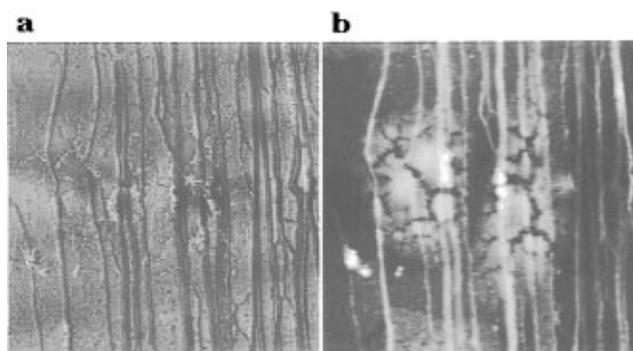

Figure 2. Lateral force microscopy (a) and contact-mode (height) atomic force microscopy (b) images of PTFE deposited on glass (same area that is shown in Figure 1;, third scan). Scan size: 9.5 μm × 9.5 μm.

strate while the PTFE block was sliding. The typical height of the PTFE fibers, obtained from a cross-section analysis of the AFM images, was 8–12 nm. A comparison of Figure 1a with Figure 1b shows that the contrast change is nearly inverse in the AFM image compared to the LFM image; i.e., AFM micrographs of the fibers have a bright tone while the corresponding areas on the LFM image have a dark tone. This observation means that the friction over the PTFE fibers is lower than the friction on glass because (in these LFM experiments) darker colors correspond to lower friction. As mentioned, the nanographs shown in Figure 1a,b were obtained during the very first scan of a freshly prepared cantilever. The difference between the frictional forces on glass and on PTFE was occasionally significantly reduced during subsequent scans, a typical example being the nanographs captured in Figure 2a,b. A cross-section analysis, obtained at a ca. 2 μm distance from the bottom of the LFM images, displayed in Figures 1a and 2a, is shown in Figure 3. The minima on these cross-sectional plots correspond to the LFM signal on PTFE (low friction), while the maxima are related to the LFM signal on glass (high friction). The average amplitude of the oscillating signal, in a first-order approximation, can be interpreted as a result of the difference between the friction on glass and on PTFE. A visual comparison of the two cross-sectional profiles displayed in Figure 3 shows that the difference in the frictional coefficients of glass and of PTFE is reduced during repeated scans. To give a possible explanation for this effect, we assume that PTFE chains get transferred to the probe tip and cover the tip surface during scanning. This PTFE coat on the tip acts as a "lubricant" reducing the frictional differences between glass and PTFE fibers. In an independent study, Güntherodt
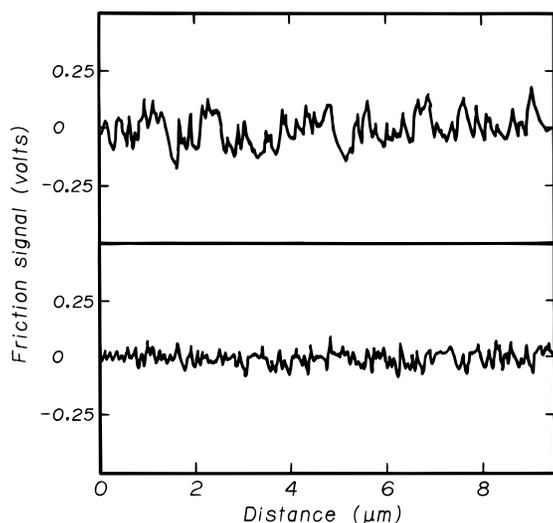
Figure 3. Cross-section plots of the lateral force microscopy signal shown in Figures 1a and 2a at a distance of ca. 2 μm from the bottom edge of the LFM images, obtained in the horizontal ($\times$) direction. Top figure: first scan; bottom figure: third scan.
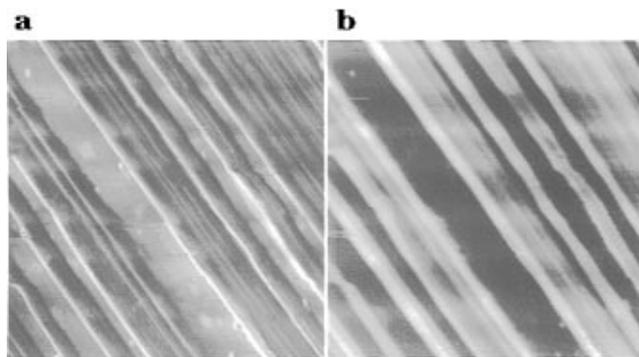

Figure 4. Lateral force microscopy (a) and contact-mode (height) atomic force microscopy (b) images of PTFE deposited on muscovite mica. The same area of 1 μm $\times$ 1 μm is depicted on both micrographs.

et al.[20] showed that the transfer of PTFE chains to AFM tips can reduce adhesion forces and allow one to image surfaces which are highly sensitive to contact forces. In ref 20 this was demonstrated in a scanning force microscopy study of the Si(111)7$\times$7 surface reconstruction. Images of the reconstructed Si surface with atomic resolution were obtained in this work only by using PTFE covered tips.

The surface of the glass slides used was quite uneven, as can be clearly seen on the micrographs shown in Figures 1 and 2. In order to have a molecularly smooth surface for PTFE deposition, we repeated the sliding experiments of PTFE on heated mica platelets. The temperature of mica during these experiments was varied and had values of 150, 200, and 250 °C, respectively. A typical dual LFM/AFM scan showing a 1 (μm)^2 area of a PTFE sample deposited on mica at 250 °C is displayed in Figure 4a,b. The oriented features, captured in this micrograph, are aligned at an angle of ca. 35° counterclockwise with respect to the vertical direction. The features imaged correspond to thin, long polymer films and fibers which were obtained during the PTFE deposition process on mica. Again, dark tones on the LFM micrograph correspond to low friction (PTFE surface), while bright tones indicate areas with high friction (mica). At preselected locations on the PTFE film, we zoomed in, in an attempt to obtain
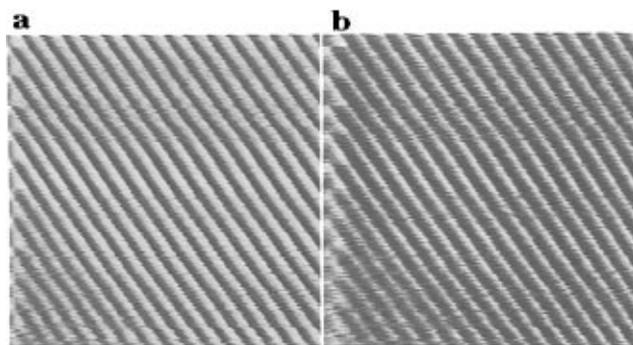

Figure 5. Dual-mode lateral force microscopy (a) and contact-mode (height) atomic force microscopy (b) images of PTFE deposited on muscovite mica showing molecular resolution. Scan size: 10.7 nm $\times$ 10.7 nm; the same area is shown in both images. Scan direction: 55° with respect to the chain direction.

nanographs with molecular resolution. A typical dual LFM/AFM image capturing an area of (10.7 nm)^2 is displayed in Figure 5a,b. The AFM and LFM nanographs show regularly packed rowlike features on the angstrom scale, aligned in the direction of the PTFE deposition on mica. This orientation direction corresponds to the expected direction of the macromolecules.[5] The average distance between the features obtained during imaging at a temperature between 25 and 30 °C was found to be 5.78 ($\pm$ 0.2) Å. This is in reasonable agreement (to within the experimental error) of the expected chain–chain separation distance in the phase IV hexagonal structure of PTFE.[11] Based on the feature alignment and on the separation, we concluded that the nanographs displayed in Figure 5a,b correspond to images of PTFE molecules. It is worth mentioning that no structure could be resolved in the macromolecular direction; i.e., it was not possible to image the helical conformation of PTFE chains in our experiments. A comparison of these LFM and AFM nanographs shows that the lateral force signal captured in the LFM experiment is synchronized with the normal force signal measured in the contact-mode AFM. This suggests that the LFM signal originates in a stick–slip type motion at the molecular level. Dual LFM/AFM nanographs with similar molecular resolution (shown in Figure 5a,b) were obtained also on PTFE films deposited at 200 °C and at 300 °C. The chain–chain distance measured was the same to within the experimental error of ca. $\pm$4% for all PTFE samples, regardless of the film deposition temperature. Occasionally, significant differences between "down" scans and "up" scans in the dual LFM/AFM imaging mode were observed. These differences are related to the apparent macromolecular orientation and the interchain separation distance. The differences disappeared after replacing the probing tip. A possible explanation for this observation might be that PTFE molecules were picked up by the tip during scanning and were then dragged over the sample surface. Obviously, this would result in an extra force which pulls the tip to one side and thus distorts the images. This distortion clearly depends on the scan direction.

A simple phenomenological model, suggested by Mate et al.,[12] which explains atomic-scale friction observed while scanning a tungsten tip on graphite, assumes that the frictional force consists of a periodic conservative component and a dissipative, constant component. These forces can depend on the direction of the microtip asperity (which actually provides the dominant force of interaction with the sample surface during imaging) with respect to the two-dimensional surface lattice.
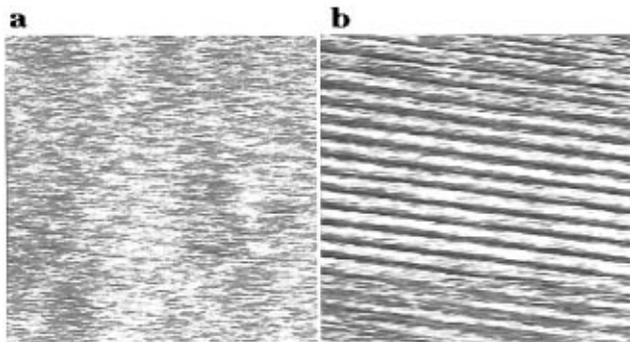
Figure 6. Dual-mode lateral force microscopy (a) and contact-mode (height) atomic force microscopy (b) images of PTFE deposited on muscovite mica. Scan size: 10 nm × 10 nm; the same area is shown in both images. Scan direction: 6° (nearly parallel) with respect to the chain direction.

Figure 7. A typical LFM scope trace showing a friction loop. Scanning proceeds from left to right on the top line (trace) and from right to left following the bottom line (retrace). One division on the y axis corresponds to 0.02 V friction signal. Scanning was performed at 66.3° with respect to the chain direction.

Obviously, in order for stick−slip type motion to occur, periodic forces must be present. In order to investigate the anisotropy of the relative contribution of the periodic forces with respect to the conservative component, we performed LFM/AFM experiments also by scanning parallel to the expected chain direction. A typical dual LFM/AFM image obtained by scanning at an angle of ca. 6° with respect to the chain direction is shown in Figure 6a,b. These scans were obtained by manually rotating the sample until an approximately parallel position of the PTFE film orientation direction with respect to the scan direction was obtained. It is obviously very difficult to obtain an orientation of the film exactly in the scan direction in this manner. A scanning angle of 6° therefore can be considered a good attempt. As the LFM image displayed in Figure 6a shows, the effect of the change in the scan direction with respect to the marcromolecular alignment is dramatic. Even though the sensitivity of the torsion signal measurement in this LFM scan was set to a value which was 10 times higher than the scale used when the image shown in Figure 5a was measured, the periodic features in the LFM signal practically disappeared. The contact-mode AFM signal (see Figure 6b) shows a nearly horizontal alignment of the macromolecules, with a spacing that agrees with the average value obtained in scans at 65° with respect to the chain direction. This observation demonstrates that, while scanning (practically) parallel with the chain direction, continuous sliding dominates the friction process and no periodic "stick" can be observed. This means that the periodic conservative component of the frictional force in the scan direction virtually disappears for this scanning geometry, which can be explained by the very smooth surface of the PTFE molecular helix in the chain direction at the atomic level.

The friction force signal for a trace−retrace loop, observed in a typical LFM scan, is shown in Figure 7. This scope trace was obtained by performing a line scan at an angle of 66.3° with respect to the chain direction. The stick−slip process is obvious in this figure. The appearance of the friction loop is similar to that discussed by Mate et al. in ref 12. A decrease of the scanning angle in our case decreases the difference between the maxima of the top curve (trace) and the minima of the bottom curve (retrace) at a constant normal force. This corresponds to a decrease of the frictional coefficient with decreasing scanning angle. A detailed analysis of the friction loops observed is presented in a separate paper.[21]
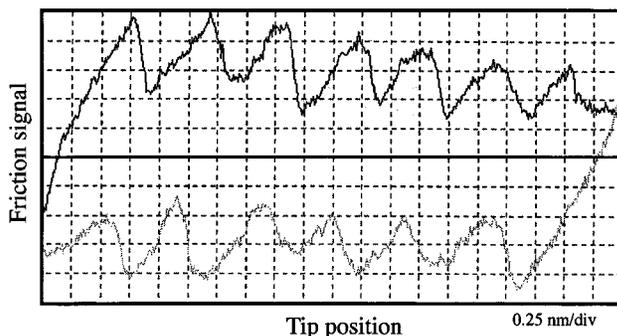
In conclusion, the dual LFM/AFM images discussed in this paper on highly oriented PTFE films demonstrated the importance of interfacial tension in explaining the low frictional coefficient of PTFE. Systematic quantitative tribological studies in the micrometer range are underway to fully clarify the role of interfacial tension and the formation of thin, oriented PTFE films by using different sliders. Nanometer-scale LFM/AFM studies showed "stick−slip" type motion on the molecular scale if scanning was performed at an angle significantly different from zero with respect to the chain direction. As a result, high-quality nanographs with clear molecular resolution were obtained by LFM. The values obtained for interchain packing distances correspond to the values expected from X-ray data. If scanning was performed in the chain direction, the periodic "stick" component disappeared, which was explained by the smooth molecular surface of PTFE chains. Our scanning force microscopy studies on PTFE demonstrated that dual LFM/AFM experiments will eventually lead to a better understanding of the dynamics of friction on the molecular level.

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