

Scanning force microscopy of plasma polymerised hexane: information on the mechanical properties of thin films from tip-induced wear

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Abstract

Scanning force microscopy has been used in contact mode to induce wear of thin plasma polymerised hexane (ppHex) films. The extent of wear observed can be used to qualitatively assess the mechanical properties of such thin films. The wear-resistance of the ppHex films varies greatly with the deposition power. They are harder than conventional polymers when deposited at high power and considerably softer when deposited at low power. On continued scanning, the morphology of the ppHex films is modified, leading to the formation of two parallel ridges that gradually merge into one larger central ridge. This behaviour differs significantly from that observed on tip-induced wear of conventional polymer films where patterns of many ridges and troughs often form. Tip-induced wear was more extensive at higher applied load, lower scan rate and at higher scan line densities. The scan speed dependence is different from that observed for conventional polymers, and may be explained in terms of the viscoelastic behaviour of the materials. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Plasma polymerisation represents a method of synthesising material at the same time as it is deposited as a coating onto a substrate. Plasma polymer (PP) coatings are typically pinhole free and can have a high adherence to a wide range of solids [1]. There has been interest in the use of PPs as adhesion-promoting coatings [2–4]. Recently, the application of chemically functionalised PP for adhesion promotion has been explored [5–9]. These materials rely upon the use of relatively mild deposition conditions to retain an organic monomer functionality, e.g. the carboxylic acid group from acrylic acid [8,9].

In the study of adhesion, the ability to obtain surfaces with no functionalities is complementary to the ability to produce oxygen functionalised surfaces; in combination with the conformal nature of PP deposition this offers a means of delineating the contribution of surface roughness to bond strength [10]. It is in this role that we are interested in plasma polymerised hexane (ppHex), the PP investigated

in this report. Deposits from hexane are hydrocarbon with typical compositions of [C] = 99 at.% and [O] = 1 at.% [11]. Increasing the plasma power increases the cross-link density of the deposit. Thus, coatings may be made which exhibit a range of properties, characteristic of a spectrum of materials from viscous liquids through to solids.

The characterisation of the mechanical properties of PP films represents a considerable challenge because they are formed as thin coatings, 1–100 nm, that are usually well adhered to a substrate. Deposition for longer time periods, to obtain microns of material, results in a deposit with very different mechanical properties to that of the thin films because of degradation of the film by vacuum UV emitted from the plasma [1]. Furthermore, the choice of substrate has been shown to alter the topography of the deposit, suggesting that the properties of the coatings are influenced by interactions between the substrate and plasma [12]. Hence, an in situ measurement of the mechanical properties of the coating is necessary. Measurement of the mechanical properties of such thin films is not possible using conventional methods. Thus, here we investigate the effectiveness of scanning force microscopy (SFM) tip-induced wear in characterising the mechanical properties of a range of ppHex films.

In an SFM wear experiment the probe tip can act as a model single-asperity contact, combining sub-nN control of

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the applied force with in situ microscopic analysis of modified surface regions and thin films. Polymers and other soft materials are easily deformed during contact mode SFM imaging [13–18]. A periodic ridged wear pattern has been observed perpendicular to the direction of the motion of the tip on repeated scanning of a wide variety of surfaces including: polystyrene (PS), poly(methyl methacrylate), poly(vinyl chloride), gelatin, poly(DL-lactide), poly(acetylene), polycarbonate and poly(ethylene terephthalate) [13]. No clear picture has yet emerged regarding the necessary conditions and mechanisms of ridge formation and the significance of their spacing, in part, possibly due to the contradictory findings reported in different studies. An early report by Meyers and co-workers found a strong interdependence between the orientation of the patterns formed by the tip, the applied load and the molecular weight (MW) of their amorphous PS samples, although less clear relationships were observed in other studies and systems [18].

Here, we have investigated the wear patterns induced by contact mode AFM scanning on a range of ppHex films of differing mechanical properties. We have observed how the development of the wear process is affected by the scanning conditions, such as applied load, number of scan cycles, scan rate, scan size and the number of scan lines. From the wear rates we are able to qualitatively rank the compliance of the materials, finding agreement with the hypothesis that higher plasma powers result in the formation of harder materials. In addition, we have compared how the wear process on the ppHex films differs from tip-induced wear observed on conventional polymer films.

2. Experimental

2.1. Plasma polymer deposition

The apparatus used to deposit the PPs has been described in detail elsewhere [8]. A radio frequency power source was coupled via copper bands to a deposition chamber evacuated to a base pressure of approximately 1 Pa. Freshly cleaved mica was used as the substrate because of its flat and atomically smooth surface. Deposition was preceded by a 1-min argon etch (100 W). Four powers were used for deposition in this work; 12.5, 25, 50 and 100 W. Hexane (Aldrich) monomer was degassed using a freeze–thaw cycle prior to use. All PP samples used were produced at a hexane flow rate of $2.0 \text{ cm}^3_{\text{STP}} \text{ min}^{-1}$ and a pre-ignition pressure of 33 Pa (base pressure = 1 Pa). Coatings were deposited to thicknesses greater than 30 nm as estimated by a vibrating quartz crystal microbalance.

2.2. Scanning force microscopy

All the PP samples were analysed by tapping mode and contact mode SFM using a Digital Instruments Nanoscope IIIa scanning probe microscope operating under ambient

laboratory conditions. Tapping mode imaging was performed using a silicon cantilever (Nanosensors) driven at its resonant frequency (280.5 kHz). Root-mean-square (RMS) roughness measurements were determined from $1 \mu\text{m} \times 1 \mu\text{m}$ scan areas imaged at 1 Hz. The imaging in tapping mode was carried out in the “light tapping” [19] regime: the free-amplitude of oscillation was 13–15 nm and the ratio of the set point oscillation to the amplitude of free oscillation was set to 0.9. It was determined that possible sample wear during the tapping cycle did not occur at these very low tapping forces.

Studies of tip-induced wear by SFM were performed in contact mode using silicon nitride cantilevers. The force constants for these cantilevers were determined from measurements of their resonant frequencies by a method implemented in the microscope software. All the cantilevers used were from the same wafer and had resonant frequencies between 16.8 and 16.9 kHz, and a force constant of 0.040 N m^{-1} . The applied loads for the wear experiments were in the range of 2–20 nN and the scan rates were typically 11–18 Hz. All images were acquired with the fast scan direction perpendicular to the axis of symmetry of the cantilever. All figures in this paper are presented with the fast scan direction oriented horizontally.

3. Results

To assess the topography of the samples without surface damage it was necessary to employ tapping mode SFM, which revealed that all deposits were flat and featureless (not shown). However, the RMS roughness measurements were observed to vary with deposit power, i.e. 0.49, 0.45, 0.38, 0.35 nm for the coatings deposited at $P = 100, 50, 25, 12.5 \text{ W}$, respectively. These samples are analysed throughout this paper and will be referred to by the power of the plasma at which they were produced.

Fig. 1 shows how the magnitude of the applied load affected the extent of tip-induced wear in the range of PPs studied. The load was increased from 2.8 (top left) to 11.2 nN (bottom right) in the four $1 \mu\text{m} \times 1 \mu\text{m}$ areas in Fig. 1(a)–(d). After individually wearing these four regions the resultant topography has been examined by imaging over $4 \mu\text{m} \times 4 \mu\text{m}$ (at minimal force). It is apparent that the extent of tip-induced wear increased with the applied load. Wear was particularly pronounced on the films deposited at the lower plasma powers ($P = 12.5$ and 25 W). Material was moved away from the edges of the scan, forming a raised feature at the centre of the scanned area, bounded by depressed regions running down the edges perpendicular to the fast scan direction. If the applied load was increased to beyond 15 nN on these two films, the coating surface was disrupted more dramatically, and often suddenly, during a scan cycle. In contrast, there was virtually no tip-induced wear for $P = 100 \text{ W}$ within the range of applied loads studied. Some slight surface modification could be inferred

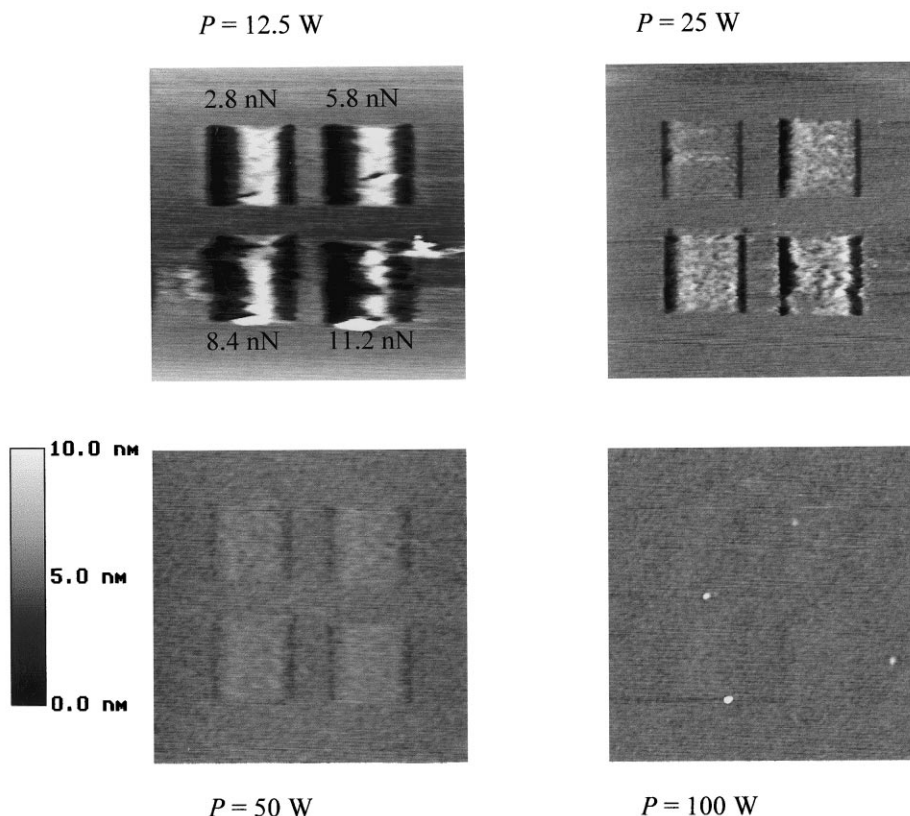


Fig. 1. Contact mode AFM images from $4\ \mu\text{m} \times 4\ \mu\text{m}$ areas (low force). The images include $1\ \mu\text{m} \times 1\ \mu\text{m}$ areas previously scanned at 11 Hz (two passes) using the applied loads annotated on $P = 12.5\ \text{W}$ for each sample.

from lateral force microscopy, which showed higher frictional force over the four previously worn areas than the surrounding polymer (Fig. 2). This frictional force image was determined from subtraction of trace- and retrace-lateral force images.

On the softest coating ($P = 12.5\ \text{W}$), we have investigated the development of the wear morphology by scanning for an extended number of cycles. Fig. 3 shows how a $1\ \mu\text{m} \times 1\ \mu\text{m}$ area was progressively modified by scanning for 10 cycles at 4.2 nN and 11 Hz. After 10 scan cycles the area of the scan was increased to $2\ \mu\text{m} \times 2\ \mu\text{m}$ to allow comparison of the worn regions with the unmodified surface as shown in Fig. 3(f).

Examination of Fig. 3(a) shows that the first scan has begun to move material towards the centre of the scanned region. By the third (Fig. 3(b)) and fifth (Fig. 3(c)) scans, the transfer of material to form ridges running perpendicular to the fast scan axis is clear. These two ridges move gradually towards the centre of the scan and begin to join up in Fig. 3(d). After the ninth scan (Fig. 3(e)) it is no longer possible to distinguish discrete ridges. The RMS roughness may be used as a measure of the development of the wear features. When calculated after each scan an approximately linear relationship was observed between the RMS roughness and the number of scans (not shown).

To determine the influence of the number of scan lines

and scan frequency on the wear process, we varied the scan rate and the number of scan lines per cycle. The result for the softest sample, $P = 12.5\ \text{W}$, is shown in Fig. 4; all four worn regions were scanned at the same applied load. From comparison of the regions worn at a constant scan rate (11 Hz), it can clearly be seen that the extent of tip-induced wear increases markedly with the number of scan lines. Comparison of the regions worn with the same number of lines per scan (512) shows that the efficiency of material transfer is significantly greater at the slower scan rate of 2 Hz.

4. Discussion

Tapping mode SFM showed that all the ppHex films were of very low roughness, as expected with the smooth mica substrate. There was a small increase in the RMS roughness of the ppHex films with P . This trend may be explained by an increase in the etching component of the plasma at higher power causing disruption and hence roughening of the surface.

The clear variation in tribological characteristics between the films in contact mode is evident in Fig. 1: samples deposited at 12.5 W plasma power exhibited severe disruption following just two scans at very modest loads, while

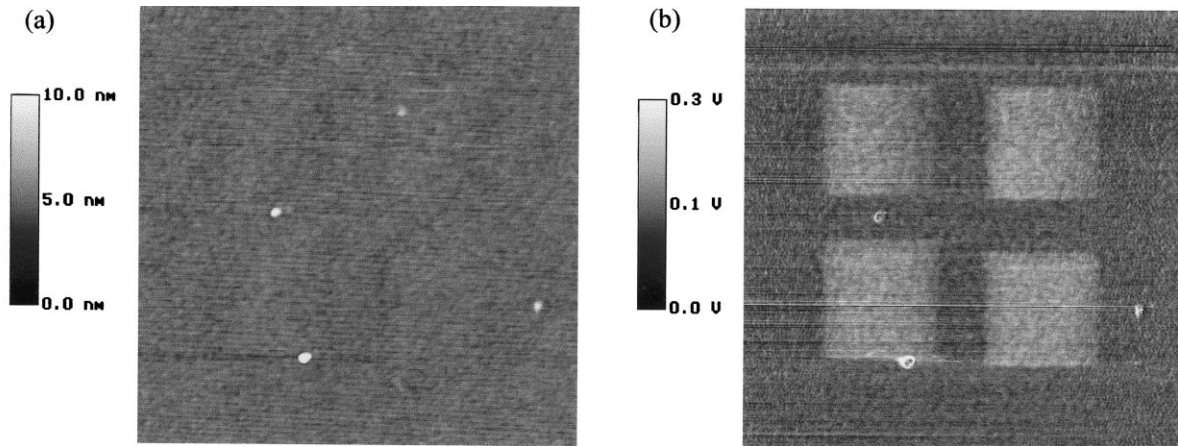


Fig. 2. Topography (a) and friction (b) images of a $4 \mu\text{m} \times 4 \mu\text{m}$ area of the $P = 100 \text{ W}$ ppHex sample. Image acquired at 2 Hz and 512 lines/scan. The images include $1 \mu\text{m} \times 1 \mu\text{m}$ areas previously scanned at 11 Hz (two passes) using loads of 2.8, 5.8, 8.4 and 11.2 nN in the top left, top right, bottom left and bottom right areas, respectively.

samples deposited at the highest power (100 W) exhibited almost no signs of tip-induced disruption. These data provide us with a qualitative measure of the increasing hardness of the ppHex coatings as P increases. If tip-induced wear is due to plastic deformation of the sample, then the

increasing degree of wear resistance observed as the plasma power increases reflects a decreased susceptibility to plastic deformation. Loosely speaking, the materials deposited at low powers behave like soft materials, while those deposited at high powers behave like harder materials. The ppHex

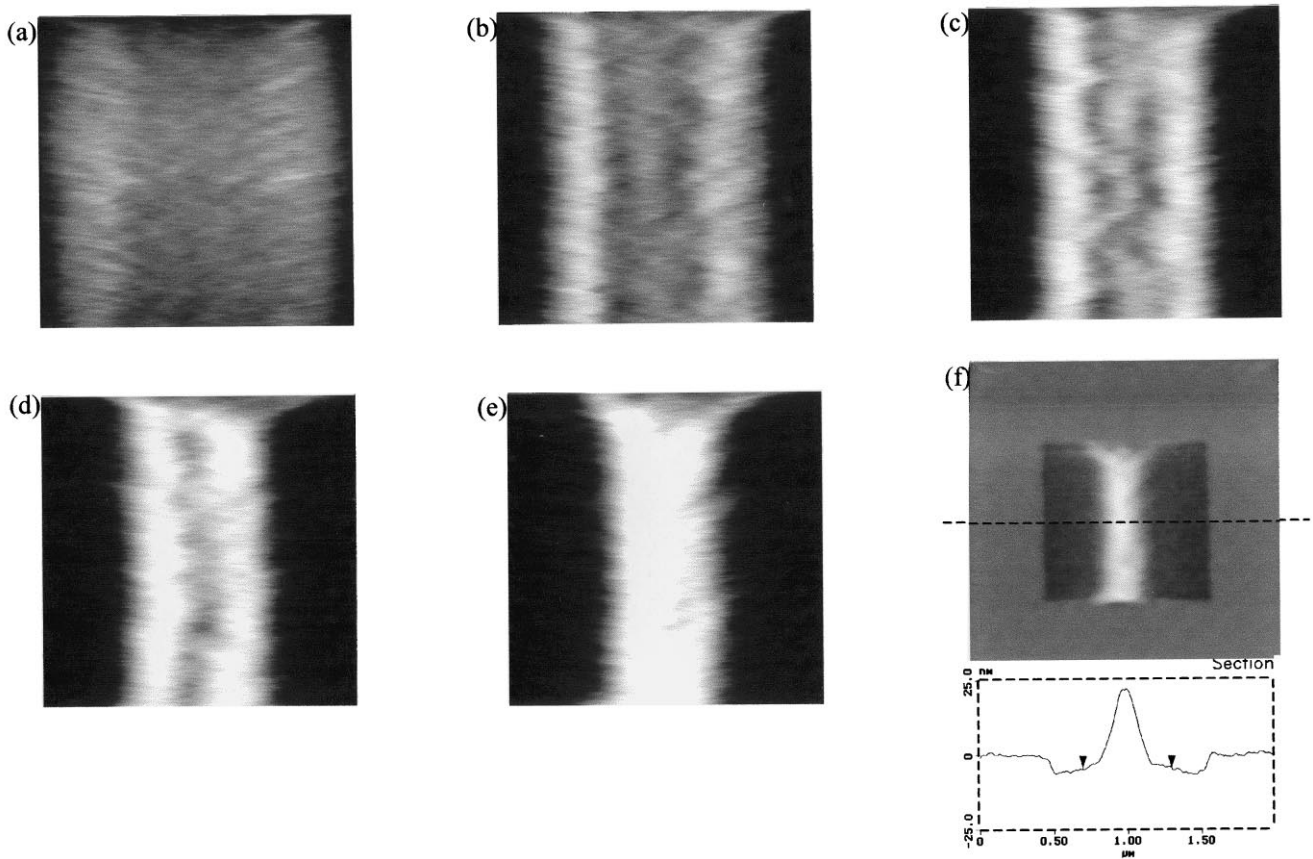


Fig. 3. Topographical images from first (a), third (b), fifth (c), seventh (d) and ninth (e) wear cycles of the $P = 12.5 \text{ W}$ coating. Scan rate = 11 Hz, applied load = 4.2 nN and height range = 0 nm (black) to 20 nm (white). The $2 \mu\text{m} \times 2 \mu\text{m}$ area in (f) was acquired after 10 wear cycles, height range = 0–50 nm and scan rate = 1 Hz.

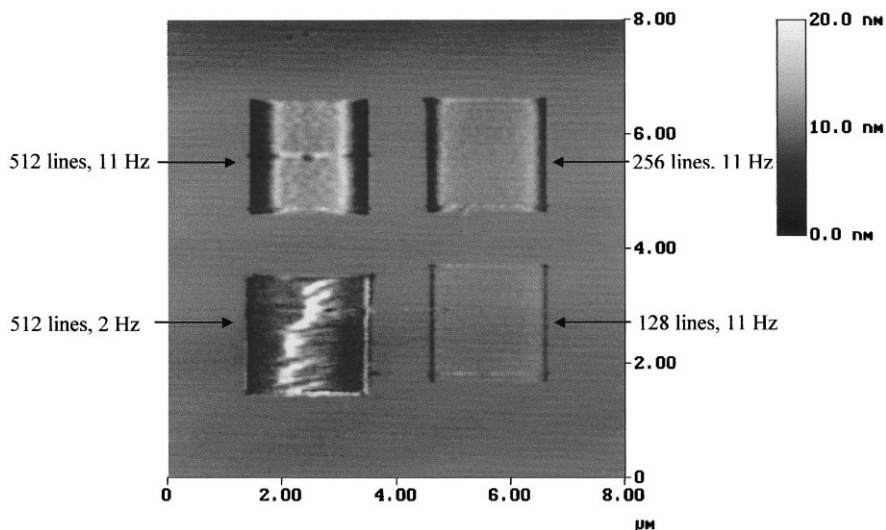


Fig. 4. Topographic low-force $8\ \mu\text{m} \times 8\ \mu\text{m}$ contact mode image of $P = 12.5\ \text{W}$ after three scans of $2\ \mu\text{m} \times 2\ \mu\text{m}$ areas at different combinations of scan lines per cycle and scan rate. Applied load is $64\ \text{nN}$ for all four regions.

films have similar chemical composition (less than 1% O) irrespective of the deposition power, and hence they are all very hydrophobic. The results shown in Fig. 1 reveal dramatic differences in wear-resistance despite the chemical similarities of the ppHex films. The best explanation for these trends is that there are changes in bonding within the PP layer as the power is reduced. It is most likely that the materials deposited at high power are extensively cross-linked, while those deposited at the lowest power are minimally cross-linked and also of low MW. A substantial variation in their mechanical properties would thus be expected, and the trends observed in Fig. 1 reflect this. The most highly cross-linked material is the most resistant to tip-induced wear.

While variations in the chemical composition of a material may lead to variations in the strength of tip-sample adhesive interactions, the molecular structure and organisation of chemically homogeneous materials may have a profound influence on the nature of the tip-sample interaction. The chain length of the adsorbates in a self-assembled monolayer of alkanethiols on a gold substrate influences the coefficient of friction measured. The degree of order in the monolayer increases, from liquid-like short-chain SAMs containing thiols with up to six methylene groups in their alkyl chains up to crystalline monolayers of long-chain thiols (greater than 12 carbon atoms). This gives rise to a decrease in the coefficient of friction [20], probably as a result of the greater deformability of the shorter, disordered layers and the concomitant increase in the tip-sample contact area. We have recently reported that in mixed monolayers of short and long chain thiols, there are also variations in mechanical behaviour that may be attributed to changes in the ordering of alkyl chains within the monolayer [21]. In the light of these earlier results, the present findings suggest that studies of the nanotribological responses of PPs to the

SFM tip may provide a highly sensitive measure of variations in their bonding and structure. By utilising suitable well-defined reference materials, it may be possible to develop a qualitative test for film properties. More usefully, however, if the extent of disruption caused by repeated scanning could be quantified in absolute terms, a powerful characterisation method may result. However, in the present study we have not been able to develop such a quantitative measure. In a previous study [22] the RMS roughness was used to quantify disruption to polyester surfaces caused by repeated scanning. However, in the present study, the range of behaviour exhibited by the different materials was too broad to enable a uniform approach to measurement of the results of wear. Future studies must address this problem. Nevertheless, the potential for probing the properties of nanometre thick polymer films in the simple way shown here is substantial.

It is of interest to compare how the rate and mechanism of the wear process on the ppHex films differs from tip-induced wear observed on conventional thermoplastic polymers. It has been shown previously that low load contact mode SFM imaging induces wear of conventional polymer films within a few scan cycles [13]. Wear patterns on conventional polymer films are often composed of several alternating ridges and troughs aligned perpendicular to the fast scan axis. On repeated scanning, the number of ridges in the scanned region may decrease as lateral movement of material occurs. The rate and extent of wear observed on the ppHex films deposited at low power was significantly greater than that observed on conventional polymer films under similar conditions in our laboratory. In contrast, the ppHex film deposited at $100\ \text{W}$ showed no appreciable topographic modification under the conditions of the experiment shown in Fig. 1. However, a pattern composed of more than two ridges did not form on the ppHex films under

any of the conditions employed in the present study. In contrast with the behaviour observed during tip-induced wear of conventional polymers, we observed the initial formation of two parallel ridges, which subsequently approached each other and combined to form a single central ridge. The development of ridged structures in the centre of the scanned region was accompanied by the formation of troughs along both of the edges of the scanned region perpendicular to the fast scan direction. This implies that material is swept inward from the edges running parallel to the fast scan direction, accumulating to form the ridged structures. This is again in contrast with the behaviour exhibited by conventional polymers, which do not exhibit the formation of such pronounced troughs and for which it is more difficult to unequivocally determine the origin of material that forms ridged features.

It is likely that the tip picks up material as its direction of motion is reversed, possibly due to a transitory increase in load, or an increased lateral force. This material is dragged across the scan area. Continued accretion of material under the moving tip would be expected to lead to a gradual transfer of material to the periphery of the scanned region; the concentration of material at the centre of the scanned area, as observed here, suggests that material is deposited as the tip traverses the scanned area. Deposition from opposing directions leads to the formation of the approximately symmetrical structures observed here.

Fig. 4 reveals that the relaxation time for the perturbed material is long compared to the time taken for the tip to complete a single scan line. As the numbers of scan lines increases, the extent of surface modification becomes more severe. An increasing number of scan lines means that the spacing between successive scans is decreasing. Consequently, the degree of overlap between the areas modified by the tip on successive sweeps of the scanned area increases, leading to cumulative effects. We have previously observed similar relationships between wear and the separation between scan lines in studies of conventional polymers.

To our knowledge, the kind of wear behaviour reported here has not been observed previously for conventional polymers, although similar behaviour has been reported by Schmidt et al. in studies of PS melts at temperatures above 140°C (i.e. significantly above the glass transition temperature) [23]. Below this temperature they observed wear behaviour that was qualitatively similar to that observed at room temperature. However, there are differences between the morphologies created after wear in the present study and those reported by Schmidt et al. In particular, they observed sharply defined ridges under some conditions, and such features were not observed in the present study. While the PPs deposited at high powers in the present study may be resistant to wear, those deposited at low powers probably have low MWs and may be more similar in their mechanical properties to polystyrene above its glass transition temperature (T_g) than to glassy polymers below T_g . However, their MWs are possibly substantially

smaller than that of the PS used by Schmidt et al. (110 000) and they thus exhibit even greater mobility, even at room temperature. The similarity between the morphologies reported in the present study and those described by Schmidt et al. is nevertheless significant, and supports the conclusion that mechanisms of tip-induced wear are strongly dependent on the polymer mechanical properties.

It is significant that for a given number of scan lines, the degree of disruption increases with decreasing scan speed for ppHex. This is in contrast with our previous observations for PET surfaces. It is possibly due to an increase in the effectiveness with which the tip picks material up as the scan speed decreases, although it is also possible that viscoelastic effects are relevant here, with the PP behaving in an increasingly viscous fashion as the scan speed is decreased, with the result that tip-induced damage is increased. There are differing reports on the scan speed dependence of tip-induced wear on conventional polymer films. On PS for example, Woodland and Unertl [15] found that the wear rate increased with scan speed, whilst Vansco and co-workers [14] found it independent of speed, and at temperatures above 140°C (PS melt) Schmidt et al. [23] reported a similar dependence to that found here. In general, for conventional polymers at moderate loads, the consensus seems to be that there is little variation in the tip-induced wear behaviour as the scan speed varies. Woodland and Unertl utilised somewhat higher speeds and loads than have been used in many of the other studies, possibly explaining why they observed different behaviour [13]. Schmidt et al. explained the behaviour they observed in terms of the viscoelasticity of their samples: they found that decreasing the scan rate or increasing the temperature led to similar changes in the wear behaviour [23]. Qualitatively, higher temperatures or lower scan rates tended to produce wear features (ridges) that were less sharp, and caused the orientation of the features to change from perpendicular to parallel to the scan direction. In the present study, it is possible that the more extensive disruption caused at lower scan speeds is also a result of increasingly viscous liquid-like behaviour.

5. Conclusions

SFM has been used in contact mode to induce wear of thin plasma polymerised hexane films. The extent of wear observed can be used to qualitatively assess the mechanical properties of such thin films. The wear-resistance of the ppHex films varies greatly with the deposition power. They are harder than conventional polymers when deposited at high power and considerably softer when deposited at low power. This is explained in terms of the increased level of cross-linking at higher power. The morphology induced by tip-induced wear is radically different from that observed on conventional polymers. As wear develops, two parallel ridges form, and as wear develops, gradually join up to

form one larger central ridge. On the PP deposited at lower powers, tip-induced wear was more extensive at higher loads, lower scan rates and at higher scan line densities. The dependence on scan rate is different from that observed for conventional polymers and possibly indicates that viscoelastic effects are important for these materials.

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