Polymer 40 (1999) 5973–5976

polymer

Polymer Communication

Non-destructive imaging of delicate polymer surfaces using scanning force microscopy tips modified with hydrophobic self-assembled monolayers

B.D. Beake, G.J. Leggett*

Department of Chemistry, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester M60 1QD, UK

Received 10 November 1998; received in revised form 16 February 1999; accepted 18 February 1999

Abstract

Contact mode imaging of plasma-treated poly(ethylene terephthalate) films using bare silicon nitride tips yields poor image resolution because of tip-induced disruption of the surface structure. Deposition of a hydrophobic self-assembled monolayer onto the tip enables the minimisation of the interfacial free energy of the tip-sample contact, with such good effect that images are obtained in contact mode with comparable resolution to that observed in tapping mode. Control of tip chemistry therefore presents an important strategy for the imaging of delicate polymer structures by scanning force microscopy. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Scanning force microscopy; Friction; Polymers

1. Introduction

Scanning force microscopy (SFM) has facilitated significant insights into the structures of polymer surfaces. Recent technological advances have made available a plethora of local probe techniques capable of revealing not only topographical structure but interfacial properties. A characteristic of many polymer surfaces is their delicacy, and recent studies have also highlighted their susceptibility to tip-induced wear during scanning in contact mode. While tapping mode and related techniques offer one solution, there are valuable local probe techniques that are available through the application of contact mode that are unavailable in tapping mode. Recent studies in this laboratory have indicated that tip-sample adhesion plays a significant role in wear during contact-mode imaging of polymer systems [1]; consequently, control of the interfacial energy of the tip-sample contact should provide a route for control of wear and may facilitate the extension of contact-mode techniques to delicate materials. Here we demonstrate that the adsorption of a self-assembled monolayer (SAM) of methyl-terminated alkanethiols onto the tip of a scanning force microscope minimises the interfacial energy of the tip-sample contact with such good effect that resolution comparable with that observed during tapping mode is achieved.

There has recently been considerable interest in the modelling of phenomena such as boundary lubrication [2–4] using model organic surfaces such as Langmuir–Blodgett films [5,6] and SAMs [7–9]. There has also been interest in the deposition of SAMs onto SFM tips for the investigation of surface adhesion, friction and wear [10–15], known as chemical force microscopy (CFM). We have previously used CFM to study the frictional characteristics of plasma-treated polyester films [16]. A characteristic of the contact-mode images of plasma-treated polymers is their poor resolution, attributed to disruption of the surface by the action of the tip during scanning. While we have shown previously that tapping mode imaging enables the acquisition of well-resolved images of these delicate materials [17], the present study attempts to minimise tip-induced disruption by depositing a hydrophobic SAM onto the tip. Our hypothesis was that provided an adequately low interfacial energy could be maintained for the tip-sample contact, adhesive interactions between the tip and the plasma-treated polymer should be minimised and, consequently, tip-induced disruption of the surface should be reduced. The present study indicates that adhesive interactions do indeed play a significant role in the reduction of image resolution in contact mode and their minimisation,

* Corresponding author. Tel: + 44-161-200-4479; fax: + 44-161-236-7677.

E-mail address: graham.leggett@umist.ac.uk (G.J. Leggett)

PII: S0032-3861(99)00170-6

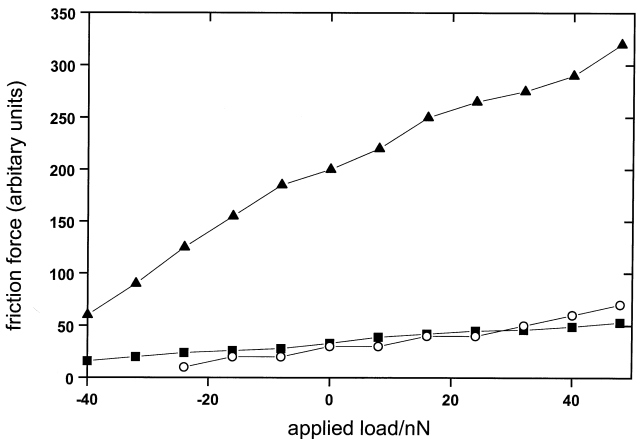

Fig. 1. Variation in friction force with applied load for different tip-sample combinations. Unmodified silicon nitride tip: MUA surface (triangles); unmodified silicon nitride tip: DDT surface (open circles); DDT tip: DDT surface (squares).

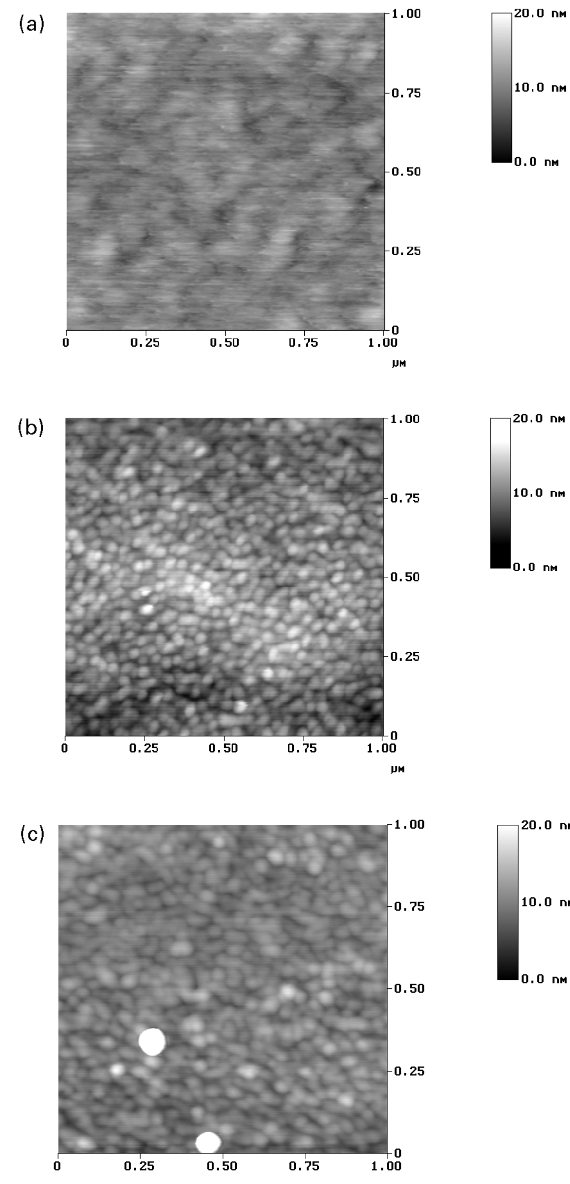

Fig. 2. (a) Contact mode image of plasma treated Melinex 'O' with unmodified tip. The image size is 1 μm × 1 μm and the *z*-scale covers height variations in the range 0–20 nm in all three images. (b) Contact mode image of plasma treated Melinex 'O' with DDT tip. (c) Tapping mode image of plasma treated Melinex 'O'.

through the deposition of a methyl-terminated SAM onto the tip, enables remarkably good resolution to be achieved.

2. Experimental

Melinex 'O' (ICI, Wilton, UK) was a biaxially orientated PET film used as received. Argon plasma treatments were carried out in an inductively-coupled radio frequency (13.56 MHz) at 0.1 mbar pressure and 10 W power. Topographic SFM images were obtained in ambient conditions with a Nanoscope IIIa MultiMode scanning probe microscope (Digital Instruments, UK). Contact mode imaging was performed using silicon nitride Nanoprobe cantilevers (nominal normal force constants 0.06 and 0.12 Nm^{-1}, Digital Instruments). Friction force imaging was performed simultaneously with the topographical imaging. The Scope Mode of the microscope was used to provide friction loops and thus obtain the (relative) friction-load plots shown in Fig. 1. Several friction-load traces were acquired for each tip-sample combination at different regions of the surface. The reproducibility was found to be excellent. The applied load was less than 10 nN for the contact mode images in constant force mode shown in Fig. 2(a) and (b). The tapping mode image Fig. 2(c) was acquired using a silicon cantilever with a resonant frequency of 300 kHz. The ratio of the amplitude of set-point oscillation to the free oscillation (ca. 90 nm) was 0.6.

Glass microscope slides and "Nanoprobe" SFM tips were modified with alkanethiol SAMs of either mercaptoundecanoic acid (MUA, synthesised in the authors' laboratory) or dodecanethiol (DDT, Fluka). 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 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. Once cool, the cantilevers and slides were immersed in 1 mM solutions of DDT or MUA in degassed ethanol for at least 18 h for the self-assembly process. The SAMs were kept in the alkanethiol solutions until use.

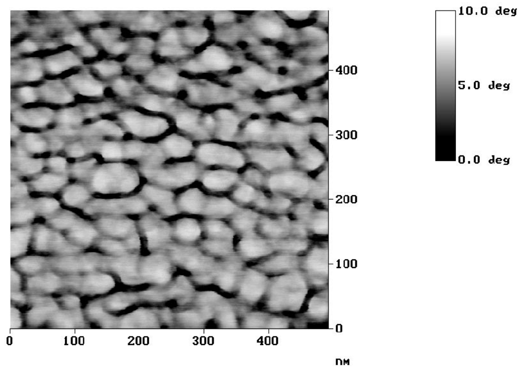

Fig. 3. Phase image of a sample of plasma-treated Melinex ‘O’. The image size is 493 × 493 nm.

3. Results and discussion

Fig. 1 shows illustrative friction-load plots between uncoated or DDT-functionalised silicon nitride tips and gold surfaces functionalised with MUA or DDT monolayers. The measured force is greatly affected by modification of the surface chemistry between the tip and sample, with virtually frictionless sliding being observed when either the sample or the tip and sample is coated with a DDT SAM. These findings are in agreement with those of other workers who have studied frictional interactions between SFM tips and SAMs. The bare silicon nitride tip is polar [18], having a thin layer of oxide at the surface, resulting in a significant interfacial free energy at the tip-surface interface. Introduction of the DDT SAM by coating either the tip or the surface reduced the interfacial free energy of the tip-sample contact and reduced the magnitude of the frictional interaction.

When a plasma-treated sample of PET is imaged in contact mode using uncoated silicon nitride tips, poor image resolution results. Fig. 2(a) shows a contact mode image of a specimen that has been subjected to argon plasma treatment for 20 minutes at a power of 10 W and a pressure of 0.1 mbar. Little structural detail is evident and commonly, streaking was observed that was attributed to movement of material by the tip. This image was recorded under ambient conditions; however, a significant improvement in resolution did not appear to be possible under liquid and, moreover, there was the possibility that interactions between the liquid phase and low molecular weight material at the surface produced during plasma treatment could lead to alteration of the surface structure.

Clearly conventional contact mode imaging of plasma treated surfaces leads to unsatisfactory results. This is probably the consequence of disruption of the surface structure by the tip during imaging. Wear caused by asperities arises from both ploughing and shearing deformation; adhesion between SFM tips and polymer surfaces contributes to the measured friction force and may therefore contribute to tip-induced deformation of the sample. Previous studies in this laboratory have demonstrated that tip-sample adhesion contributes significantly to the development of ridged morphologies during tip-induced wear; the results of Fig. 1 indicate that control of the tip chemistry may provide a means by which the adhesive contribution to the tip-sample interaction can be minimised and the shearing contribution reduced. This should lead to a reduction in tip-induced wear and, in the case of delicate materials, an increase in resolution.

This hypothesis was tested for plasma-treated PET films. Using a tip that had been coated with a monolayer of DDT, it was possible to obtain contact mode images of the treated surface that exhibited no signs whatever of tip-induced disruption. Fig. 2(b) shows a representative image. There is a wealth of structural information present that is absent from Fig. 2(a). It is clear that reduction of the interfacial free energy of the tip-sample contact has significantly reduced the disruption induced by scanning. In contrast to the featureless topography resulting from imaging with the bare tip, the DDT-coated tip reveals a surface that is composed of globular features of relatively uniform dimensions (diameters 30–60 nm). These globular features are densely but uniformly distributed at the surface.

Such is the quality of images recorded with the DDT-coated tips that they are indistinguishable from data recorded in tapping mode. Fig. 2(c) shows a tapping mode image of an identical specimen to that imaged with the DDT coated tip. The morphology is clearly very similar to that observed in contact mode with the methyl-coated tip, indicative of the magnitude of the improvement in image resolution that is possible in contact mode if the interfacial free energy of the tip-sample junction is minimised. This is an important result because it means that many local probe techniques based upon contact mode imaging may be extended to delicate polymer surfaces and employed to yield high resolution data given adequate control of the tip chemistry.

In an earlier study, we reported the formation of oriented, ridged structures at PET surfaces over periods of several hours of plasma treatment, which were attributed to the exposure of crystalline material at the surface by preferential etching of amorphous regions [17]. Because of the much shorter treatment period used in the present study, it is unlikely that the globular features observed in Fig. 2 are also due to the direct exposure of crystallites by plasma etching. However, phase imaging (performed simultaneously with tapping mode imaging) revealed a distinct phase structure (see Fig. 3). Because phase imaging reduces the influence of the sample topography on image contrast, the globular features appear to be enlarged. However, on close inspection, a direct correspondence is found between features in the phase and tapping mode images. We speculate that the globular features arise from a segregation at the surface of material that is distinct from the bulk, either in its crystal content (as a result of plasma-induced surface melting phenomena) [19], or its chemical composition [20].

Deposition of a monolayer of MUA onto the tip does not lead to any improvement in the image resolution over that offered by the bare silicon nitride tips. This confirms that the interfacial free energy of the tip-sample contact is an important parameter in governing the degree of wear induced during imaging, and excludes the explanation that DDT acts as a boundary lubricant: both MUA and DDT have long alkyl chains which would be expected to have comparable effectiveness as boundary lubricants.

4. Conclusions

Plasma-treatment of poly(ethylene terephthalate) at low powers over periods of tens of minutes leads to the evolution of a fine morphology composed of globular features some 30–60 nm in diameter. These details cannot be resolved in contact mode SFM using bare silicon nitride tips. However, they become clearly evident when imaged using tips that have been modified by the deposition of a SAM of alkanethiol molecules with methyl terminal groups. The resulting resolution is comparable to that achieved in Tapping Mode. Careful control of the interfacial energy of the tip-sample contact thus appears to be capable of minimising tip-induced wear, extending the utility of contact mode techniques to include fragile materials that would otherwise be difficult to image non-destructively.

Acknowledgements

The authors are grateful to the EPSRC (grant GR/K88071) and the Royal Society for financial support. GJL thanks the Nuffield Foundation for a Science Research Fellowship.

References

[1] Ling JSG, Leggett GJ, Murray AJ. Polymer 1998;39:5913.
[2] Xiao X, Hu J, Charych DH, Salmeron M. Langmuir 1996;12:235.
[3] Mate CM. IBM J Res Develop 1995;39:617.
[4] Bhushan B, Kulkarni AV, Koinkar VN, Boehm M, Odoni L, Martelet C, Belin M. Langmuir 1995;11:3189.
[5] Overney R, Meyer E. MRS Bull 1993;18:26.
[6] Meyer E, Overney R, Brodbeck D, Howald L, Lüthi R, Frommer J, Güntherodt HJ. Phys Rev Lett 1992;69:1777.
[7] Kim HI, Koini T, Lee TR, Perry SS. Tribology Lett 1998;4:137.
[8] Rühe J, Novotny VJ, Kanazawa KK, Clarke T, Street GB. Langmuir 1993;9:2383.
[9] Tsukruk VV, Bliznyuk VN. Langmuir 1998;14:446.
[10] Frisbie CD, Rozsnyai LF, Noy A, Wrighton MS, Lieber CM. Science 1994;265:2071.
[11] Noy A, Frisbie CD, Rozsnyai LF, Wrighton MS, Lieber CM. J Am Chem Soc 1995;117:7943.
[12] Green JBD, McDermott MT, Porter MD, Siperko LM. J Phys Chem 1995;99:10960.
[13] McDermott MT, Green JBD, Porter MD. Langmuir 1997;13:2504.
[14] van der Vegte EW, Hadziioannou G. Langmuir 1997;13:4357.
[15] Alley RL, Komvopoulos K, Howe RT. J Appl Phys 1994;76:5731.
[16] Beake BD, Ling JSG, Leggett GJ. J Mater Chem 1998;8:2845.
[17] Beake BD, Ling JSG, Leggett GJ. J Mater Chem 1998;8:1735.
[18] Williams JM, Han T, Beebe Jr TP. Langmuir 1996;12:1291.
[19] Collaud-Coen M, Dietler G, Kasas S, Groning P. Appl Surf Sci 1996;103:27.
[20] Greenwood OD, Hopkins J, Badyal JPS. Macromolecules 1997;30:1091.