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Application of lateral force imaging to enhance topographic features of polypropylene film and photo-cured polymers

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Abstract

It is well known that topographic features can give rise to edge effects when making lateral force measurements in contact mode atomic force microscopy (AFM). Using a ‘smooth’ polypropylene film, which was also imaged by non-contact mode AFM, we showed that the edge effect can be used to reveal topographic features clearly through an enhancement of their outlines. Using photo-cured polymers we demonstrated that lateral force imaging is especially useful in revealing topographic features on surfaces which have large height differences.

Keywords: AFM; Lateral force imaging; Edge effect; Polypropylene; Photo-cured polymers

1. Introduction

In contact mode atomic force microscopy (AFM), a soft cantilever is used to sense the interaction between the sharp tip attached to the cantilever and sample surface [1]. The torsional movement of the cantilever, indicative of the lateral force, occurring in the course of scanning the tip across a surface is usually used to measure friction forces on a surface arising from differences in material composition, adhesion and other properties [2–5]. Lateral force imaging is also used to distinguish phase separation on polymer surfaces as this usually results in varying friction force [6]. The relationship between averaged lateral force and scanning direction has been used to evaluate the regularity of molecular chain folding on polyethylene single crystals as a function of molecular weight (M_w) [7].

The torsional movement of the cantilever occurs when the tip scans across abrupt changes in the height of topographic features. In this paper, we use this edge effect to enhance topographic features on two types of samples: ‘smooth’ polypropylene (PP) films and ‘rough’ photo-cured polymers.

The PP film has been used to investigate surface modification by UV/ozone treatment to increase surface energy [8], which also results in changes of topographic features [9]. Because the film is flat and predominantly characterized by a nanometer-scale fiber-like network structure, we present the results of both contact and non-contact mode AFM as a demonstration of the usefulness and accuracy of lateral force imaging in revealing surface structures.

Photo-curing of polymer from liquid monomer is a promising technology to fabricate free form polymer products [10,11]. Structures of the wall side

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surfaces of photo-cured polymers may influence the mechanical strength and may have important implications for the plating process. Topographic measurements showed large height differences on the wall side surface. Lateral force imaging seems to be especially useful in revealing different structures on such ‘rough’ wall side surfaces.

2. Experimental

Both modes, contact and non-contact AFM, of a commercial AFM (Explorer, TopoMetrix) were used in this study. A soft silicon nitride cantilever with a nominal spring constant of 0.03 N/m was used in contact mode AFM. The cantilever was 0.6 μm thick, 18 μm wide and 200 μm long with an attached tip whose apex radius was about 20 nm. The deflection and torsion of the cantilever, which are used, respectively, to obtain topographic and lateral force images, are measured with a four-segment-photodetector using a laser light irradiating the backside of the free end of the cantilever. The torsional movement of the cantilever during scanning can be used to construct the lateral force image simultaneously with the topographic image. Repulsive forces of 1–5 nN were used in contact mode AFM imaging. The direct output of the photodetector corresponding to the torsional movement of the cantilever, in units of nA, is the photo-induced current which was directly used to construct the lateral force image. A stiff silicon cantilever with a spring constant of ∼28 N/m which was 130 μm long, 29 μm wide and 3.7 μm thick was used in non-contact AFM. The tip apex radius was about 20 nm. The resonance of this cantilever was ∼280 kHz. Non-contact AFM is operated by controlling the reduction of the oscillation amplitude of the cantilever when the tip scans close to but without contacting the surface.

Thermally extruded, biaxially oriented isotactic PP film [8] produced from a homopolymer resin ($M_w = 1.9 \times 10^5$, polydispersity = 6.0) and photo-cured samples of du Pont DP3110 (DP) and Ciba-Geigy SL5195 (SL) liquid monomers were used in this study. The DP3110 (SL5195) contains 40–60% acrylate oligomer (cycloaliphatic epoxy resin), 20–40% diacrylate monomer (aliphatic glycidyl ether), 10–30% triacrylate monomer (polyols), 1–5% photoinitiator (modified acrylate ester), and < 1% stabilizers (acrylate ester and photo-curing agent). The two photo-cured polymer samples, DP and SL, were prepared by curing the liquid monomer with a UV laser. An elevator was immersed in the liquid monomer to support the cured polymer. By lowering the level of the elevator approximately 100 μm per step, cured polymer samples were fabricated layer by layer. Wall side surfaces were examined in this study.

The AFM measurements were performed in air atmosphere at room temperature. AFM images consisted of 500 lines with 500 points per line. Scan rates for smaller and larger scan areas were 25 and 100 μm/s, respectively.

3. Results and discussion

3.1. PP film

Fig. 1a and b show, respectively, the topographic and lateral force images obtained from a PP film using contact mode AFM. While the topographic image is not clear enough to show the surface structure, the lateral force image shows a clear picture of the surface structure. From the lateral force image we can see three different structures on the PP film surface. The fiber-like network structure is shown on the left hand side of the image. On the fiber surface there are some veins which run parallel to the machine-draw (MD) direction. On the right hand side of the image is a part of a stripe which runs exactly parallel to the MD direction. We selected the scan site on the sample surface where the three types of structures were included. Measurements on many other locations showed that the PP film is dominated by the fiber-like network structure. This structure is the result of the two direction stretching, i.e., MD stretching followed by transverse-draw (TD) stretching. The veins are believed to be a residual effect of the MD stretching. The stripe may be pressed into the film by tiny protrusions on the rollers during film conversion [12].

Fig. 1c shows a non-contact AFM image obtained on a different location of the same polymer. A vein, which is about 30 nm high, runs almost parallel to the MD direction. On the right hand side of the vein,

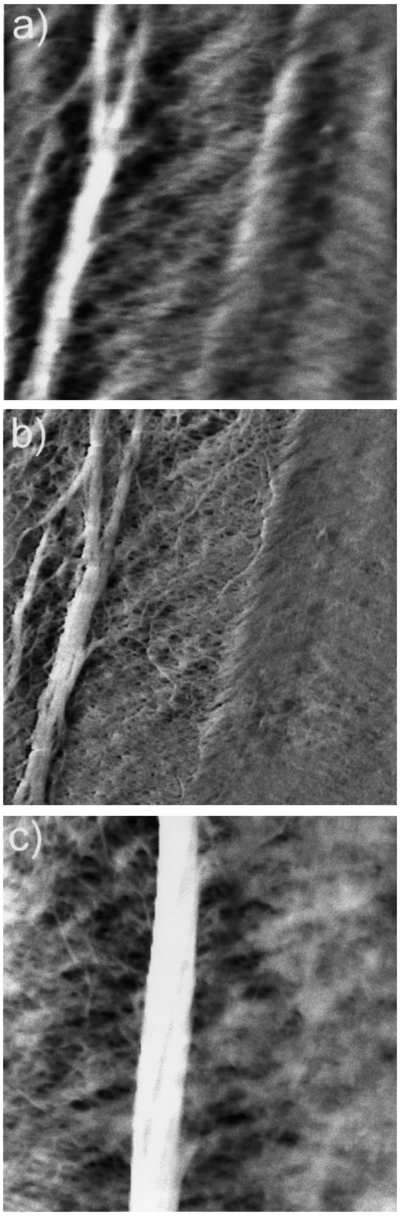

Fig. 1. Contact mode AFM topographic (a) and lateral force (b) images obtained in an area of 4.5 μm^2 on the PP film. A non-contact mode AFM topographic image obtained on another location is shown in (c). Gray-scale ranges for (a) and (c) are 25 and 44 nm, respectively. Gray-scale range for (b) is 2 nA, the direct output of the photodiode corresponding to the torsional movement of the cantilever.

a part of a stripe is shown and the area close to the vein shows a faint fiber structures. On the left hand side of the vein, there is a fiber-like network structure. The surface structures are similar to what were observed in the lateral force image in Fig. 1b.

By comparing Fig. 1b and c, we can see that, in some parts of the images, the lateral force image shows a clearer image of the surface structures than the topographic image. This occurs because the lateral force at the edges of the topographic features are enhanced. The surface structures are clearly expressed with an emphasis on the outline of the topographic features, not on their absolute height. The experimental fact that the lateral force image shows similar surface structures as the non-contact AFM leads us to conclude that the lateral force imaging can be used to reveal surface structures because of the enhancement of the edge effect. This lateral force imaging can be especially important in the case of imaging surfaces with large height ranges.

3.2. Photo-cured polymers

Seeing the usefulness of the lateral force image in providing local topographic information about the PP film surface as shown above, we applied lateral force imaging to polymer samples which have a relatively large range of heights. Fig. 2a and b shows the lateral force images for the wall side surfaces of DP and SL samples, respectively. The lateral force image in Fig. 2a shows clearly that the surface of DP consists of two different structures: one is amorphous in appearance as seen at the lower part of the image and the other is glassy in appearance as seen on the remainder of the image. The glassy-like portion seems to be broken into pieces, while the amorphous-like portion exhibits a surface with much smaller features. By magnifying the two different structures, we found that the amorphous-like surface has a nanometer-scale structure while the glassy-like surface has locally flat surface features.

We can see from Fig. 2b that the surface of SL also consists of two types of structures which are separated abruptly. On the left hand side of the image in Fig. 2b, there are two surfaces with an appearance of dried mud, which are separated by white bands which correspond to abrupt height changes. In fact, they are, as can be seen below, the steps of the stacked layers. Also shown in Fig. 2b is a very different structure on the right hand side, on which there are faint white lines which are thought to be caused by local topographic features.

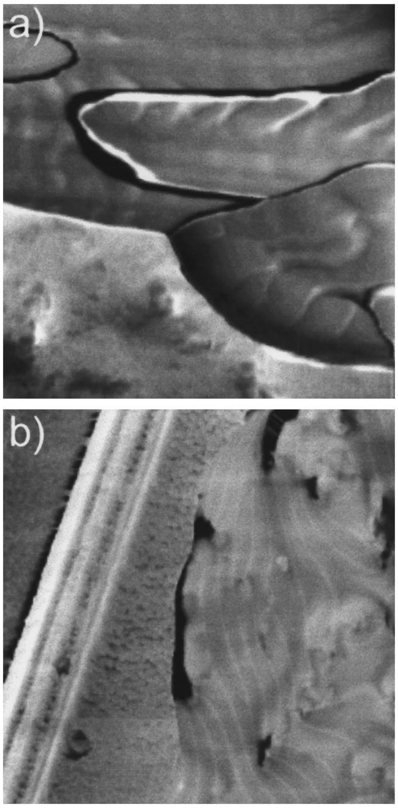

Fig. 2. Lateral force images obtained on wall side surfaces of the photo-cured (a) DP in an area of 4.5 μm^2 and (b) SL in an area of 20 μm^2, respectively. Gray-scale ranges for (a) and (b) are 7 and 8 nA, respectively.

The topographic images of the DP and SL samples under gray scale show nothing but the white and black which correspond to the highest and lowest part of the surface. The range of the heights for the surface features is too large, ~1 and ~9 μm, respectively, for subtle changes to be seen. In order to see if the topographic images provide information on surface structure, we present them in Fig. 3 in 'shading' mode where the height information is converted to its shadow angle obtained when theoretically shining a light from the left hand side. It is obvious from the lateral force and shaded topographic images shown in Figs. 2 and 3 that these two types of images are complementary, i.e., lateral force images reveal the local features over the whole area while shaded topographic images provide information on height differences between different plates.

Fig. 3a shows that the different structures seen in Fig. 2a correspond to different plates. In Fig. 3b, we can see that there is a liquid-like shaped material on the flat, dried-mud-like terrace. Shown in Fig. 3c is a cross-sectional profile across the surface as indicated by an arrow in Fig. 3b. There are several layers stacked up to make a height difference of ~3 μm and separation of ~4 μm between the two terraces.

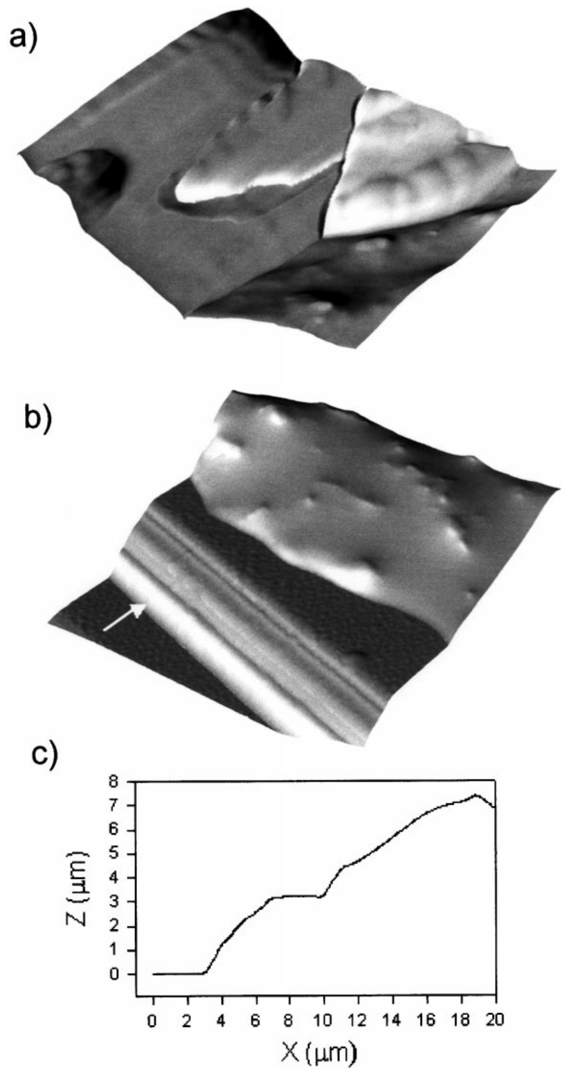

Fig. 3. Perspective images for (a) DP and (b) SL of 'shaded' topographic images obtained simultaneously with those lateral force images shown in Fig. 2a and b, respectively. Height ranges for (a) and (b) are ~1 and ~9 μm, respectively. Shown in (c) is a cross-sectional profile obtained from (b) as indicated by the insert arrow.

Lateral force imaging showed that the wall side surface of photo-cured samples consists of very different regions which usually have large height differences among them. These very different structures, however, were not observed on the top surface of the cured polymer samples which was seen to have a flat surface. Because the samples were prepared by curing layers of the liquid monomer, it is likely that the edges of each layer would not be completely aligned. Another possibility is that there may be some liquid adhering to the wall side surface when the sample was lifted up from the liquid. These different regions observed on the wall side surface may affect the mechanical properties of the cured piece and its susceptibility to chemical etching. Interfaces between the layers can be an indication of the quality of the photo-curing process. The results we obtained using AFM with lateral force imaging provide an insight into the wall side structure and may have an important impact on the plating procedures used on these materials.

4. Conclusions

Using a polypropylene film, we demonstrated the use of lateral force imaging as a method which can result in substantial improvement in the definition of images of soft surfaces. The contrast in the lateral force image was significantly clearer than that of the topographic image alone. This contrast is attributed to an edge enhancement effect of the torsional movement of the cantilever occurring during scanning of the tip across the PP film surface. Lateral force imaging provided insight in evaluating the surface structures on the wall side of photo-cured polymers where the height range was very large (e.g., ~ 9 μm in an area of 20 μm^2). Our preliminary results indicated that there are at least two very different structures on the wall side surfaces which may result from the photo-curing process and may have effect on the mechanical properties of the materials.

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