Polymer Bulletin 40, 549–554 (1998)

Polymer Bulletin

Apparent contrast reversal in tapping mode atomic force microscope images on films of polystyrene-*b*-polyisoprene-*b*-polystyrene

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Received: 30 December 1997/Revised version: 14 January 1998/Accepted: 15 January 1998.

Summary

Thin films of phase separated polystyrene-*b*-polyisoprene-*b*-polystyrene block copolymers were studied by tapping mode atomic force microscopy. The relative contrast in height and phase mode images of the phase separated regions was found to be very sensitive to changes in the operating conditions of the microscope. Contrast variations and reversals were observed for height and phase mode images as a function of the set-point amplitude ratio and drive frequency. No unique height or phase contrast was observed for the the tri-block copolymer system examined in this study.

Introduction

Atomic force microscopy (AFM) has proven to be a flexible and useful technique for the examination of a wide variety of surfaces from the micron to the Ångström scale (1–3). However, AFM is subject to a number of artifacts that can lead to erroneous conclusions about the nature of the system. For example, in contact mode AFM, topographical images can be affected by tip shape (4), humidity (5), sample deformation and modification (6), sample stiffness (7), and feedback loop interference. Additionally, lateral force microscopy images can be convoluted with topological features that can cause a twisting motion of the cantilever, and hence a modulation in the lateral force signal.

The method of tapping mode atomic force microscopy (TMAFM) was introduced to minimize sample damage during scanning. High pressures and lateral forces exerted on the surface by the tip can cause irreversible damage to the surface during scanning with the contact mode AFM. Since the tip of the TMAFM is in intimate contact with the sample for only a few microseconds, there are no lateral forces exerted on the sample. Due to delicate morphologies in phase separated block copolymer systems, the use of TMAFM for structural and material property elucidation is increasing. However to our knowledge, no systematic studies have addressed the influence of the scanning parameters on image contrast in phase separated block copolymer systems.

The TFM experiment (8) and phase imaging (9) have been described elsewhere in detail. Briefly however, a small microfabricated cantilever with an integrated tip is caused to vibrate by a small excitation piezo, usually at or near the cantilever's natural resonance frequency. The tip is then positioned very closely to the sample surface. The sample is mounted on a piezo electric tube used to control the sample's position in the X, Y, and Z directions. As the tip approaches the surface, forces act to modulate the cantilever's phase angle with respect to the excitation piezo, the amplitude, the resonance frequency, and the effective spring constant. Normally, a voltage is applied to the sample piezo by a feedback loop such that the amplitude of the oscillation of the cantilever remains constant. The voltage applied to the piezo in order to maintain a constant amplitude can then be used to generate a topological image. Additionally, the phase angle with respect to the excitation piezo phase can be recorded to produce a phase image.

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The images obtained from TMAFM could be difficult to interpret due to the complex behavior of the driven non-linear oscillator (10). This was evidenced by Magonov and co-workers who studied the behavior of polydiethylsiloxane patches on a silicon wafer substrate with TMAFM (11). They found that as the interaction of the tip and sample increased, the height contrast remained relatively constant, while phase images were observed to undergo contrast variations. In a study by Bar *et al*., reversals in phase contrast were noted as a function of set-point ratio and free amplitude of vibration of the cantilever on phase separated polymer blends (12). These phenomena were explained in terms of modulations in the phase signal caused by stiffness and changes in contact area under different imaging conditions.

The phase separation characteristics of the tri-block copolymers similar to those investigated in this study have been examined by a number of methods such as AFM (13), SAXS (14), and TEM (15). It has been shown previously that the polystyrene (PS) phase separates into cylinders contained within an amorphous polyisoprene (PI) matrix for the mole percentage of PS used in this study. Since PS and PI have very different material properties, contrast in material property sensitive could potentially be observed. If height and phase images are convoluted with material properties, it is imperative that these effects be understood in order to properly interpret image contrast.

Experimental Section

A PS-PI-PS copolymer (17% mol PS) obtained from Aldrich was used without further purification. A 30% weight solution of the copolymer was dissolved in toluene; a drop of the solution was placed on a piece of freshly cleaved mica. The solvent was allowed to evaporate and the films were examined immediately. It was found that the morphology of the films became rougher with time on the micron scale. Since we concerned ourselves with the nanoscale morphology, it was more convenient to examine these freshly prepared samples.

AFM experiments were performed on a Multimode Nanoscope III (Digital Instruments, Santa Barbara, USA) instrument equipped with phase detection electronics. The single tip used to obtain the results presented in this report was purchased from NanoSensors and had a fundamental resonance frequency of 259.477 kHz. An amplitude of oscillation at free vibration was set to a typical value of 5 V of photodiode voltage corresponding to approximately 150 nm of actual cantilever oscillation. The relative phase shift and apparent feature height were investigated as a function of the actual operating amplitude of the cantilever and the driving frequency. Height and phase images were recorded at 1Hz and 512 samples per line for a 1µm scan size. The relative contrast of this phase separated system was investigated by systematically varying the set-point ratio A_r and the driving frequency, ω. The operating setpoint ratio $A_r = A/A_0$ is inversely proportional to the amount of damping the cantilever experiences. A denotes the actual operating amplitude set by the operator and A_0, the amplitude at free vibration. A series of images was taken at various A_r values at several frequencies near the resonant frequency of the cantilever at free vibration.

Image analysis was performed with Image SXM, a modified version of the freeware program NIH Image available from ftp://zippy.nih.gov/pub/nih-image. Images were thresholded such that the bright phase separated regions were white and the dark regions were black. An average height and phase was then calculated for the two areas. The difference between these values is reported here as the apparent contrast.

Results

On-resonance imaging

In Figure 1, height and phase images are presented as a function of A_r. At setpoints close to free vibration the PS features appear to be below the PI matrix in the height mode image. Between A_r=0.99 and A_r=0.95, the phase contrast of the PS cylinders reversed from bright to dark. The phase contrast remained relatively constant until approximately A_r=0.5 when the contrast reversed. When A_r=0.4, the phase contrast increased again, and became bright at approximately A_r=0.3. The polystyrene features appeared progressively lower than the isoprene matrix in the height image until A_r=0.7, when the contrast began to increase, reversed at A_r=0.6 until approximately A_r=0.15. As the setpoint was further lowered, damage occurred to the surface due to the large forces exerted on the surface by the tip.

Image analysis was performed on these series of images to determine the apparent height and phase contrast of the PS phase relative to the PI phase. The relative height and phase contrast between the two phases was calculated. The results obtained from the series of pictures in Figure 1 are presented in graphical format in Figure 2.

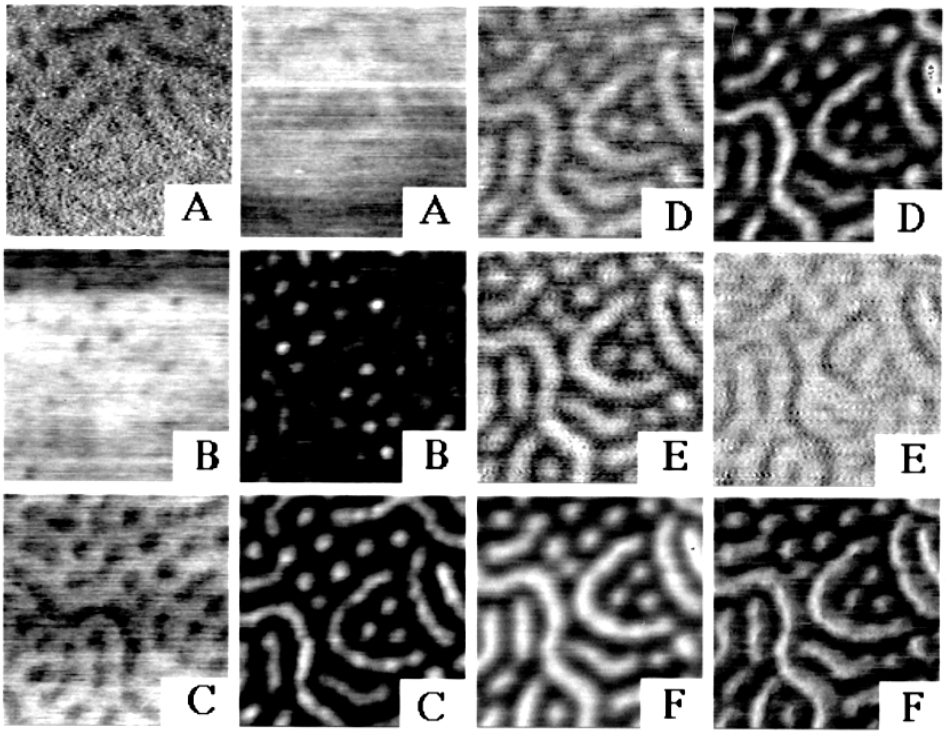

Figure 1: Height (left) and phase (right) images of film cast PS-PI-PS, $\omega=\omega_0$. This is a representative series of images taken at various set-point ratio values. The polystyrene cylinders are visible both parallel and perpendicular to the surface. Each image is 350 nm by 350 nm. The height z-scale is 8 nm and the phase z-scale is 10°. The corresponding set-point ratios are A) A_r=0.99, B) A_r=0.95, C) A_r=0.70, D) A_r=0.50, E) A_r=0.40, F) A_r=0.20.

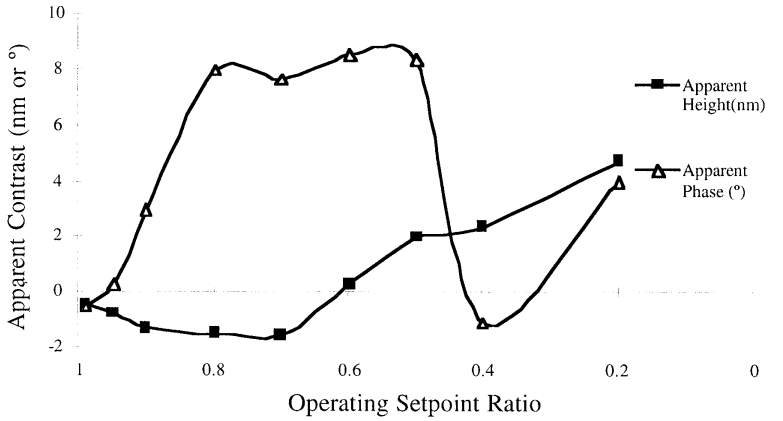

Figure 2: Apparent height and phase contrast as a function of A_r at $\omega = \omega_0$

Off-resonance imaging

When the cantilever was driven at a frequency above its natural resonance frequency, contrast reversals in phase and height were observed. As can be seen in Figure 3, the contrast of height and phase appeared such that the PS cylinders were below the PI matrix. The phase contrast reversed at A_r=0.8 and approached 0 at A_r=0.55, then increased until A_r=0.2 when the sample was damaged. The height contrast decreased from the first image at A_r=0.8, then reversed at A_r=0.6 and increased until to the final image taken at A_r=0.2.

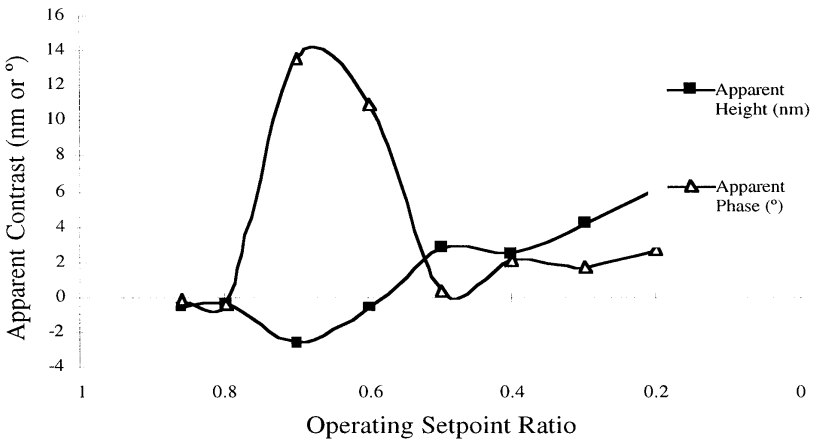

Figure 3: Apparent height and phase contrast as a function of A_r at $\omega = \omega_0$+300Hz

When the drive frequency was changed to below resonance frequency at ω=259.144 kHz, a different contrast profile was obtained. The polystyrene features appeared bright regardless of the operating setpoint, while the phase underwent an inversion and subsequent reinversion at high damping setpoints. These results are summarized in Figure 4.

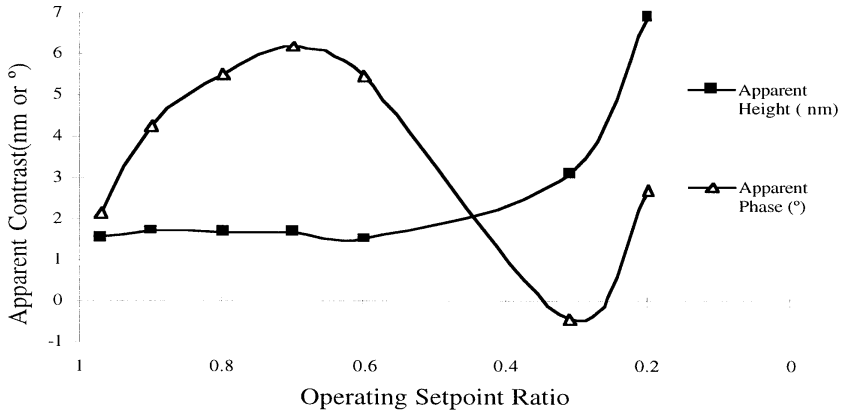

Figure 4**:** Apparent height and phase contrast as a function of A_r at $\omega = \omega_0$-300 Hz

Discussion

There are a growing number of experimental (16) and theoretical (17) studies that suggest that sample-tip interaction in TMAFM is a complex, hysteretic, and potentially chaotic process. It can be seen from the series of images and contrast profiles presented above that the height and phase contrast depends on a number of factors including actual surface morphology, operating setpoint, frequency of excitation as well as material properties such as adhesion and stiffness.

At very low interaction setpoints, a very small but measurable height contrast can be seen when the cantilever is driven at or above its resonance frequency. As has been discussed in the literature, the amplitude of the cantilever is altered due to a change in the effective spring constant. This effect is greater when the cantilever is driven at a frequency higher than its resonance frequency. For small interaction forces, contrast is most likely influenced by differences in adhesional force in the PS and PI regions. The adhesion would be expected to be much larger in the PI regions because PI is well above its glass transition temperature. This increase in attractive forces could cause a modulation in amplitude of the cantilever, causing an effective decrease in the amplitude of oscillation. The feedback loop of the AFM would thus lower the piezo in order to try to maintain a constant cantilever amplitude This would then result in a region of high contrast in the height image. Since the PS regions would have a lower adhesion, the cantilever's amplitude would increase; this could result in the feedback loop raising the piezo in order to decrease the effective amplitude of oscillation. In this case, a "low" topological feature would result.

Although there are variations in the contrast profiles at different drive frequencies, they all result in PS cylinders appearing above the PI matrix at low values of A_r. As the cantilever passes from the attractive into the repulsive regime, material properties such as stiffness and viscoelasticity result in modulations of the amplitude. Due to the fact that PS has a higher modulus than PI, the amplitude would be effectively lower in the PS regions. This could result in a contrast wherein the stiffer regions have an effectively higher topology.

When the TMAFM is operated in constant amplitude mode, the height profile results from a number of factors including actual surface morphology, sample deformation, and any modulations in the actual amplitude of the cantilever that are not detected by the feedback loop. In the case of polymer systems with nanometer scale morphology, these quantitites could have similar values and thus influence the image

obtained. When the system is heterogeneous with components of different compliances and adhesion, this could result in the observed changes and reversals in contrast in height mode images in the different regions.

In the case of the tri-block copolymeric system examined in this study, no unique contrast was produced by the TMAFM. Without prior knowledge of the surface morphology, it is not apparent how to assign material properties such as stiffness from phase data or even morphological results obtained from the atomic force microscope. Instead, an independent and absolute method such as TEM is required in order to correctly assign absolute heights to features or a beforehand knowledge of the morphology would be required in order to properly identitfy the phase seperated regions.

Acknowledgment

The Dutch Foundation for Chemical Research (SON/PPM) provided financial assistance for this project. Holger Schönherr is thanked for his helpful discussions. L.M. O'Connor is gratefully acknowledged for careful revision of the manuscript.

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