Keysight Technologies
Atomic Force Microscopy of Heterogeneous Materials in Different Environments

Application Note
Visualization of individual components of heterogeneous samples and their distribution in complex materials is the subject of compositional imaging that allows establishing the correlation between materials morphology and their technological properties. In Atomic Force Microscopy (AFM) compositional imaging is based on recognition of the shapes and dimensions of the components or of their dissimilar mechanical or electric properties. Such studies are the important part of AFM applications to polymers. It is routinely used for visualization of microphase separation of block copolymers and polymer blends and for identification of constituents of composite materials.

In this application note AFM compositional imaging will be demonstrated by studies of ultrathin layers of several polymer blends. The samples were formed by mixing atactic polystyrene (PS) with equal amounts of low density polyethylene (LDPE), poly(vinyl acetate) (PVAC) and poly(butadiene) (PBD) in common solvents. A blend of PVAC with poly(vinylidene difluoride) - PVDF was also examined. Ultrathin layers of these blends with thickness in the 20-50 nm range were prepared by spin-casting the dilute polymer solutions on Si, Au and glass substrates. PS/LDPE, PS/PVAC and PS/PBD blends are immiscible compositions that undergo micro-phase separation with segregation of individual components. The polymer films were examined with Keysight 9500 scanning probe microscope in amplitude modulation (AM) and Quick Sense (QS) modes at different levels of tip-sample forces. In QS mode the probe oscillates with amplitudes in the 30-200 nm range at frequency of 1-2 kHz. In this mode a fast detection of probe deflection facilitates harvesting of force curves and topography tracking at set-point force. High-speed processing of force curves in QS mode enables on-line extraction of quantitative mechanical properties with nm spatial resolution. Hence, this mode enhances AFM compositional mapping.

In addition to imaging in air, studies of several polymer blends were performed in methanol vapor, which are available exclusively with Keysight 9500 microscope. Such AFM applications facilitate monitoring of surface modification, dewetting, swelling, and other important surface processes. So far, a large potential of environmental AFM studies of research and industrial samples has not been properly revealed. This application area can provide novel and unexpected information regarding materials’ behavior. Below it will be shown how selective swelling of the components of complex materials helps recognizing them in AFM images.
Examination of PS/LDPE Blend

In this blend LDPE is a semicrystalline polymer, in which crystalline lamellae coexist with amorphous polymer. Extended macromolecules of LDPE are characterized by long side chains. This molecular geometry imposes constrains on polymer crystallization and leads to high amorphous content in the material. PS, which was used in the blend is an amorphous polymer and does not have any structure. The different nature of the components of PS/LDPE blend helps assigning its film morphology. The height and phase images of this blend are shown in Figures 1a-1c. The film morphology is characterized by the domains embedded into a matrix. The latter have two circular holes of the \( \mu \text{m} \) size in the right part of the imaged area. The holes with slightly elevated rims are the consequence of dewetting process that has exposed the Si substrate to air. Among the domains, there are circular ones, which are slightly higher than the matrix. Other domains are the higher aggregates with a less perfect shape. In the phase image in Figure 1b the brightest are the substrate spots. They differ from the matrix and from the darker inclusions, whose contrast does not depend on the shape and height.

Figures 1a-d. AFM images of ultrathin film of PS/LDPE blend, which were obtained in AM mode.
The assignment of the film matrix to PS and the embedded inclusions to LDPE is supported by the phase images in Figures 1b-c, in which lamellar structures with the width dimensions of 20-30 nm are noticed inside of the circular domains. The lamellar structures were also seen in the images (not shown here) of the higher aggregates. In the given example the phase contrast correlates with elastic modulus of the locations: Si - 100 GPa, PS - 3 GPa, LDPE - 0.4 GPa. However, this is not the strict correlation as the phase changes are generally related to energy dissipation in the probe-sample contact and not to specific sample properties. The use of the elastic modulus contrast and values, which are obtained in QS mode, is better suited for compositional imaging of heterogeneous materials.

The QS height, adhesion and elasticity images of one of the locations of PS/LDPE blend are presented in Figures 2a-i. The height images show circular LDPE domains with lamellar structures are surrounded by PS matrix. These domains are about 5 nm higher than the matrix at 2 nN force. As the imaging force has been increased to 10 nN, the domains became depressed about 8 nm compared to the matrix. The stronger deformation of LDPE is also reflected by its lower modulus in the elasticity maps and by increase of adhesion force. The contrast of elasticity images correctly reflects the variations of local elastic modulus. However, reliable quantitative data could not be extracted from studies of ultrathin polymer films on hard Si substrate, where the sample deformation is strongly influenced by the substrate.

Figures 2a-i. AFM images of PS/LDPE blend in QS mode at forces of 2 nN (a-c), 4 nN (d-f) and 10 nN (g-i).
**Imaging in Methanol Vapor**

AFM is the only microscopic technique, which can be applied in different environments (air, vacuum, liquids). For imaging in methanol vapor, a couple milliliters of this solvent were injected into the microscope chamber. As boiling temperature of methanol is around 65°C its vapor saturates the microscope chamber in a few minutes. AFM studies of several polymer blends were performed in methanol vapor. First sample was an ultrathin film of PVDF/PVAC blend on Au substrate.

![AFM images of PVAC/PVDF blend on Au substrate in AM mode in air (a, b, d) and in methanol vapor (c). The image in (d) was obtained after methanol vapor has evaporated from the microscope chamber. The cross-section profiles along the white dashed line in (b-d) are shown on right.](image)

Morphology of PVDF/PVAC film is characterized by circular crystalline domains of PVDF (2D spherulites), which are embedded into PVAC layer (30 nm in height) that partially covers Au substrate, Figures 3a-b. When air in the microscope chamber was replaced with methanol vapor we have observed two related phenomena on PVDF/PVAC film. A detailed analysis of the area surrounding one of the crystalline circles (Figures 3b-d) shows that in methanol vapor PVAC layer shrinks, most likely, due to dewetting of Au substrate. This is noticed by an opening to the substrate in top left part of Figures 3c-d. In methanol vapor, PVAC material had formed thicker rim (~150 nm in height) around the PVDF spherulite. This change has preserved after methanol evaporation. Other observation is related to changes of the crystalline domain. In air, it is characterized by densely-packed branches, which are spread out of a nucleation center. In methanol vapor, the spherulite is coated by a condensate, which disappears together with vapor after the microscope chamber was opened to air, Figures 3c-d. A comparison of height profiles, which are taken along a white dashed line in Figures 3b-d, shows that the top condensate was ~20 nm in thickness.
Imaging of PS/PVAC Blend in Air and Methanol Vapors

In immiscible PS/PVAC blend both components are amorphous, and their elastic moduli are not very different. In this case visualization and recognition of the constituents can be assisted by their selective swelling in appropriate atmosphere. PVAC has charged groups, and it easily swells in methanol vapor. This is obvious from a comparison of AFM images in Figures 4a-f, which were obtained in AM mode. Morphology of this blend is typical for immiscible binary blend with one of components being segregated in the circular domains embedded into a matrix made of second component. In methanol vapor the domains have drastically expanded and their height became 3 times larger than in the images recorded in air. The domains have also softened, and this explains phase changes (Figure 4f).

Figures 4a-f. AFM images of PS/PVAC film on glass in AM mode, which were obtained in air (a–c) and in methanol vapor (d–f). (a) and (d) - 3D representations of surface morphology in air and in methanol atmosphere.
A monitoring of the morphology changes of PS/PVAC film on transition from air to methanol atmosphere was also performed with QS mode, Figures 5a-i. These measurements were conducted using Si probe with spring constant of 2 N/m and force of 2 nN. In air the domains and matrix were differentiated mostly in the adhesion image, Figure 5b. After introduction of several milliliters of methanol to the microscope chamber the alcohol fast evaporated and spread to the top of the chamber where the sample is located. The effect of methanol has been noticed as the probe was scanning in the downward direction in images in Figures 5d-f. The changes are evident at the low part of the adhesion and elasticity images. The domains have become stickier and softer. As scanning has proceeded from bottom to top in the images in Figures 5g-I, the transformations were continued in all three patterns. The domains became depressed (Figure 5g), and the probe practically has reached the glass substrate, which was used for this film. The adhesion contrast has saturated, and the elastic modulus of the domain became smaller. The described changes reflect swelling of PVAC domains and the probe penetration into soft swelled polymer. This structure transformation is completely reversible. After the chamber was opened and methanol has evaporated, the film has restored its initial morphology. Similar structural changes of PS/PVAC blend, which are caused by swelling in methanol vapor, have been described previously [1]. The enhancement of molecular mobility in swollen PVAC domains has changed their dielectric response in AFM-based electric measurements.

Figures 5a-i. AFM images of PS/PVAC blend on glass in QS mode in air (a-c) and in methanol vapor (d-i).
The described morphology of PS/PVAC blend and its changes in methanol environment were observed for the polymer layer formed on glass substrate. In case of Si substrate morphology of the blend film is quite different. Typical AFM image of such sample (Figure 6a) shows smooth surface layer with a number of circular depressions. Earlier studies of this sample with AFM-based electric modes allowed a tentative assignment of top layer to PS, and the depressions to PVAC. A dominance of PS in top layer implies that PVAC has spread underneath on the substrate. This suggestion was verified by examination of this sample in methanol vapor, Figures 6b-d.

A comparison of AFM images obtained in air before (Figure 6a) and after the sample immersion in methanol vapor (Figure 6b) shows that their overall morphology is similar with only few variations. The sample morphology in methanol vapor is quite different (Figures 6 c-d). A material, which appears inside the former depressions and on several top surface locations, can be assigned to swollen PVAC domains. The phase contrast shows that the brightest are the central depressions, which are only slightly enriched in material as seen in the height image, Figure 6d. Most likely, in these locations the probe taps through a soft material and interacts with the substrate. These data are in favor of the above suggestion that PVAC is constrained in this material, and it shows up in the circular depressions in swollen state.
Unexpected Behavior of PS/PBD blend in Methanol Vapor

In immiscible PS/PBD blend both components are amorphous materials but the elastic moduli of the components is quite different. The ultrathin film of PS/PBD exhibits surface morphology common to other two blends. Both AM and QS modes were used for imaging of this sample, Figures 7a-f. The film surface is characterized by sub-micron size domains, which are elevated over the matrix, as seen from height images, which were recorded in both modes. The phase contrast of the domains is darker than that of the matrix in the image obtained at low force (Figure 7b) and is brighter at higher force (Figure 7c). In QS mode the domains exhibit higher adhesion than the matrix (Figure 5e) and the map of elasticity (Figure 7f) shows their lower modulus at the operational force of 20 nN. The latter allows assigning the domains to PBD material and the matrix to PS.

Figures 7a-f. AFM images of ultrathin film of PS/PBD blend, which were obtained in AM (a-c) and QS (d-f) modes. The images in QS mode were obtained after the sample was temporarily subjected to methanol vapor.
In expanding AFM environmental studies the examination of PS/PBD blend was performed with QS mode in methanol vapor. After first cycle, in which the chamber has filled with methanol vapor and then brought back to air atmosphere, we have noticed small round domains in between PBD domains. Most likely, they are formed of surface material, which was soluble in methanol. After methanol being evaporated this material was left in a form of small domains.

A sequence of QS images, which were recorded during second methanol cycle, is presented in Figures 8a-i. This imaging was conducted at smaller force of 10 nN to prevent a possible damage of softening locations. First images (Figures 8a-c) were recorded after the injection of methanol into the microscopes chamber. The scanning was performed in the downwards direction, and the only changes were observed in the adhesion image (Figure 8b). This is expected as initially only top surface layer interacts with methanol vapor. The following images (Figures 8d-f), which were also collected during scanning in the downwards direction, have started to show the changes in the adhesion and elasticity images. This process has saturated, and the final morphology of PS/PBD blend in methanol vapor is shown in Figures 8g-i. They reflect the structural changes induced by swelling, and this transformation was reversible as the initial morphology has restored completely after air filled the microscope chamber again.
The analysis of QS images of swollen PS/PBD sample has revealed a number of interesting results. The height of the circular domains has increased 30–40%. This fact further supports the assignment of these structures to PBD, which was suggested due to their lower modulus in Figure 7f. Quite unexpected is the finding that these domains of PBD in swollen state exhibit higher elastic modulus (Figure 8i). This phenomenon requires further investigations.

Conclusions

Compositional imaging of heterogeneous samples is important application of AFM, which is demonstrated in studies of binary polymer blends with Keysight 9500 scanning probe microscope. Individual components of polymer blends are typically discerned by their specific shapes and dimensions as well as by differences of their mechanical or electric properties. These capabilities were illustrated on several samples. It was shown that the unique ability of Keysight 9500 microscope to study samples in different chemical vapors allows using selective swelling of the blend components for their recognition.

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References

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