Advancing AFM Applications

Gentle and high-resolution AFM profiling assumes the minimal tip-sample force interactions at every surface location during scanning in the contact or oscillatory modes. In case of heterogeneous samples, besides surface topography, the researchers are often interested in discerning dissimilar surface locations and getting maps of individual components. This is a subject of compositional imaging that can be realized in different AFM operational modes. In contact mode the differences of local friction (Lateral Force Microscopy) and stiffness (Force Modulation) are used for mapping samples with variations of mechanical properties. AFM applications were boosted with introduction of the resonant oscillatory mode, also known as tapping or amplitude modulation mode. Compositional imaging in this mode has benefited with implementation of phase imaging. Images of a film of polystyrene/low-density polyethylene (PS/LDPE) blend on Si substrate in **Figure 1** shows that phase contrast differentiates a matrix of PS, LDPE domains and spots of Si substrate opened due its partial dewetting by the polymers.
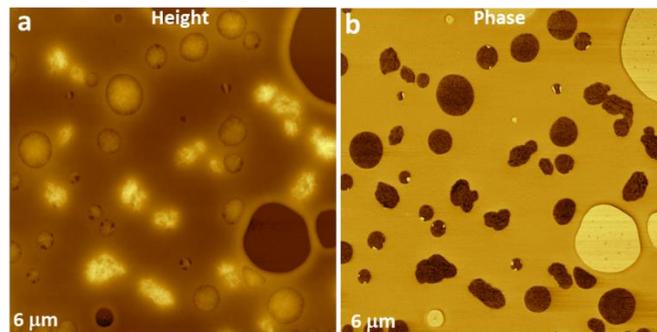

Figure 1. Height (a) and phase (b) images of PS/LDPE film on Si, which were obtained in AM mode.

For many samples the phase contrast is pronounced, particularly, as tip-sample forces are increased. As phase changes are related to the tip-sample dissipation, their assignment to exact mechanical or adhesive properties is not possible. Composition imaging, which is based on differences of local mechanical properties, became available in non-resonant oscillatory modes (Quick Sense in Keysight 9500 microscope). In this operation the tip intermittently contacts a sample at frequency smaller than the probe resonant frequency. A Z-servo is made by keeping the peak deflection constant while scanning. Concurrently, the deflection-vs-distances curves are measured and used for extraction of mechanical properties (stiffness, elastic modulus, work of adhesion, etc), which are shown in maps of PS/PB blend (PB – polybutadiene) together with surface topography, **Figure 2**.
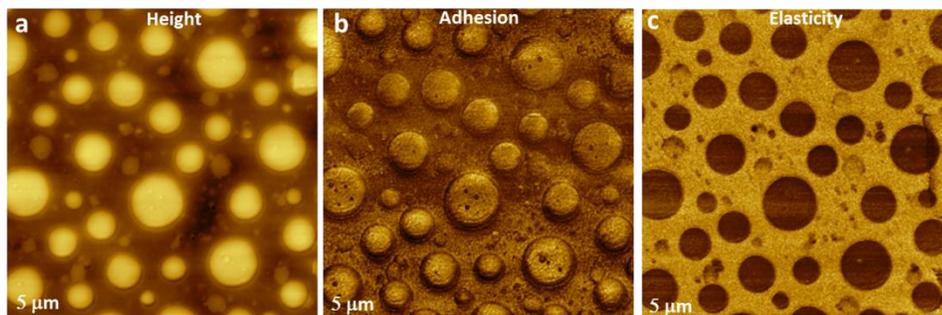

Figure 2. Images of a film of PS/PB blend, in which PS matric and PB domains differ by adhesion and elasticity.

The implementation of fast scanning in the Keysight 9500 microscope made most AFM modes time efficient as imaging in air can be performed with scanning rates up to 80 Hz and on areas up to 100 μm on side, **Figures 3-5**. Imaging of semi-fluorinated alkanes (300 nm scan) was performed at scanning rates up to 100 Hz, and large-scale morphology of polymer blend (75 μm scan) was recorded at 10 Hz rate. A regular AFM imaging at similar areas proceeds 30 - 80 times slower. Height profiles of self-assemblies of semi-fluorinated alkanes (**Figure 3a-c**) show that the pattern became distorted at 100 Hz rate.
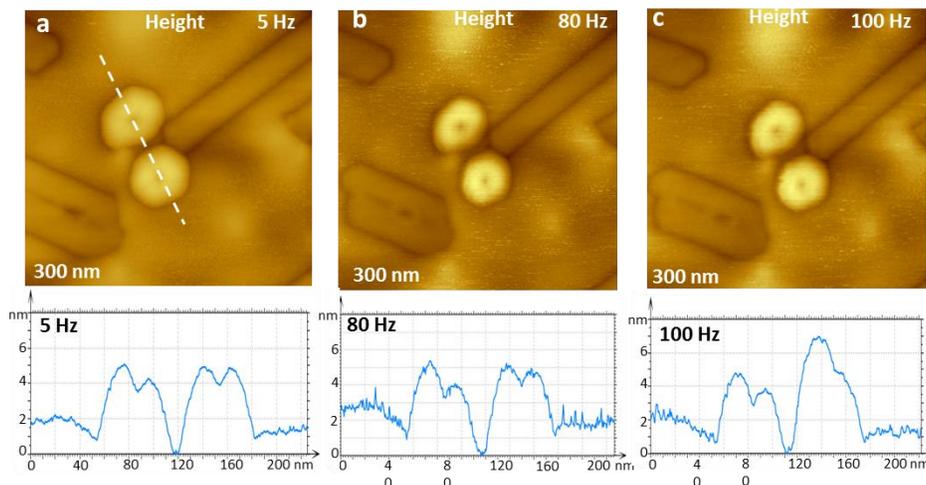

Figure 3. Images of self-assemblies of semi-fluorinated alkanes obtained at different scanning rates. Height profiles along a direction marked with a white-dashed line, which were recorded at different rates, are shown underneath.

Fast scanning of a large area (**Figure 4a**) was performed slower (10 Hz) but the recorded image (512×512 data points) distinctively reproduces the blend morphology. The small scale images (**Figures 4b-c**), which were recorded at 20 Hz rate, show several LDPE domains in PS matrix. The phase contrast differentiates not only the polymers but also lamellar structures (~20 nm wide) inside LDPE domains.
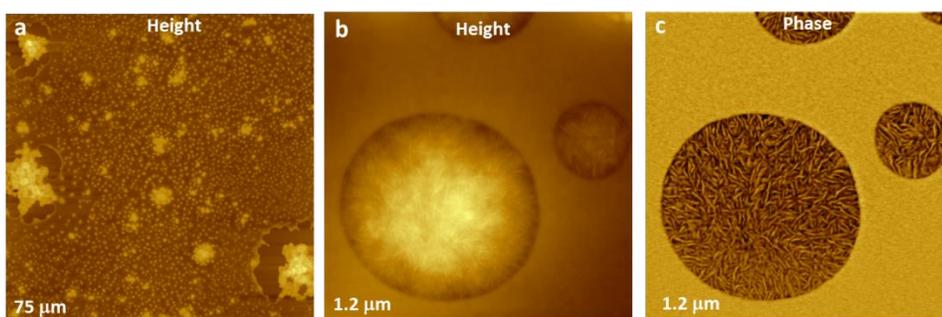

Figure 4. Height and phase images of PS/LDPE blend on Si, which were recorded at 10 Hz (**a**) and 20 Hz (**b-c**).

Fast imaging was demonstrated also on the surface of a nitrocellulose membrane with the peak-valley profiles ~ 500 nm, **Figure 5**. For a precise tracking of the corrugated surface, which was checked by a coincidence of the trace and retrace curves; scanning rate at 40 μm area was lowered to 10 Hz.
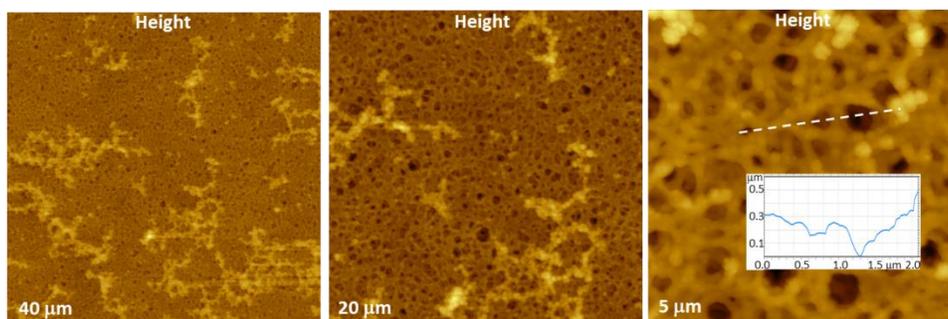
Figure 5. Height images of nitrocellulose membrane, which were recorded at 10 Hz (**a**) and 20 Hz (**b-c**). The topography profile along a direction indicated with a white-dashed line in (**c**) is shown in the insert.

It is worth noting that in the Keysight 9500 microscope fast scanning was realized with a new actuator, which is incorporated in the agile small nose cone and regular piezo-scanner, the advanced electronic control and use of a probe with the resonant frequency ~ 1.5 MHz. The studies were made with low set-point ratio of amplitudes - the low Q condition that facilitates the quick probe response.

AFM studies at different humidity and in organic vapors are routine with the Keysight 5500 and 9500 microscopes equipped with an environmental chamber. This allows monitoring of surface changes induced by hydration and swelling. Structure transformations, which were found in images of liquid crystalline cholesteric cyclosiloxane oligomer SilGreen as the microscope chamber was slowly filled with chloroform vapor, are shown in **Figures 6a-e**. A chloroform-induced morphology change has generated a new periodical pattern, whose pitch is related to wavelength of optical reflectivity. When the chamber was opened to air, the initial pitch was restored with some orientational changes, **Figure 6f**.
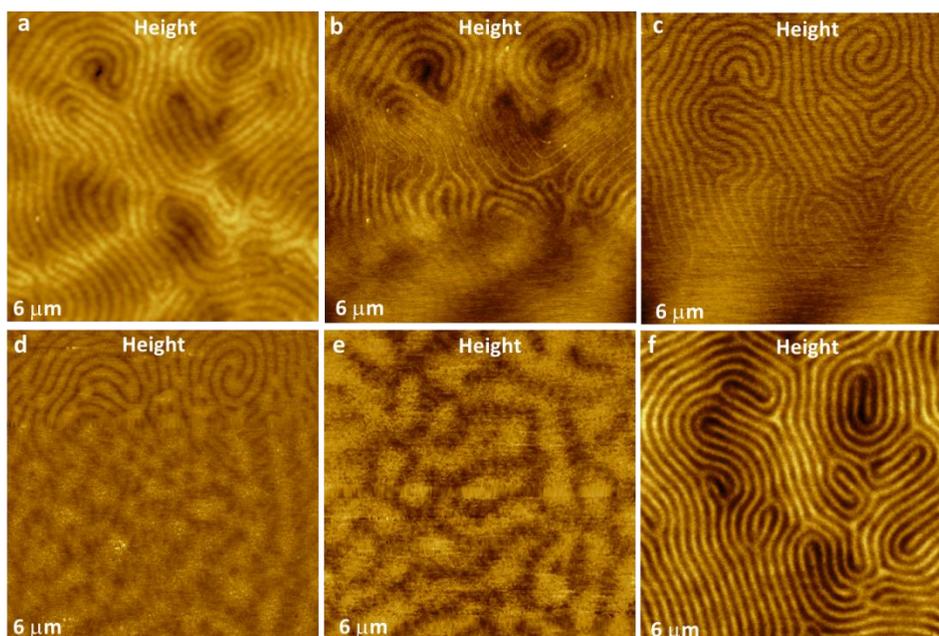

Figure 6. Height images of surface changes induced by chloroform injection into a microscope chamber (**a-e**). Height image of the modified surface after the chamber was opened to air (**f**).

In studies of brush macromolecules such as poly(methacrylate)-graph-poly(n-butyl acrylate) their high-resolution visualization requires a high-force imaging in oscillatory modes. Only their overall profile is observed in low-force images, **Figure 7a**. The situation is simplified by imaging in ethyl acetate vapor, **Figure 7b**. This agent, most likely, induces selective swelling of side chains that allows a tip penetration through their softened moiety to the macromolecule backbone. This effect helps distinguishing the polymer backbone conformations.
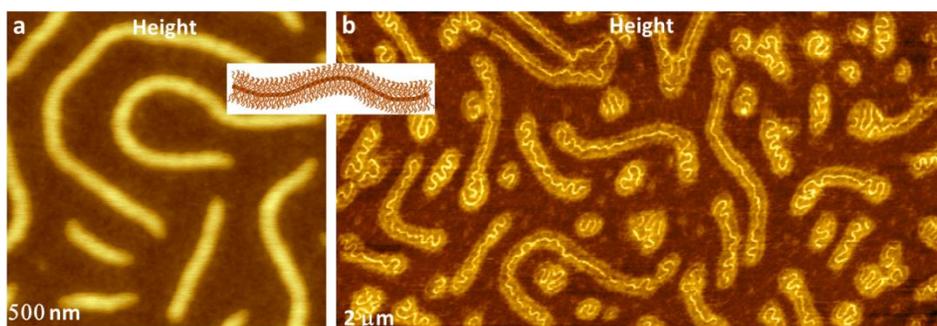

Figure 7. Height images of brush macromolecules in air (**a**) and in ethyl acetate vapor (**b**). A sketch of the brush macromolecule is shown in the insert.

Another example of selective swelling is induced by methanol vapor in binary polymer blend of PS and PVAC – poly(vinyl acetate). The blend morphology is characterized by the round-shaped raised domains of PVAC, which are spread in PS matrix. This assignment, which was suggested in AFM-based electric studies, is fully supported by the images in **Figure 8**. After methanol was introduced into the microscope chamber the domains have further raised due to their selective swelling, **Figures 8a-b, d-e**. A related softening of the domains has manifested by phase contrast in **Figure 8f**. In air, elastic moduli of the polymers are similar, and their phase contrast is alike.
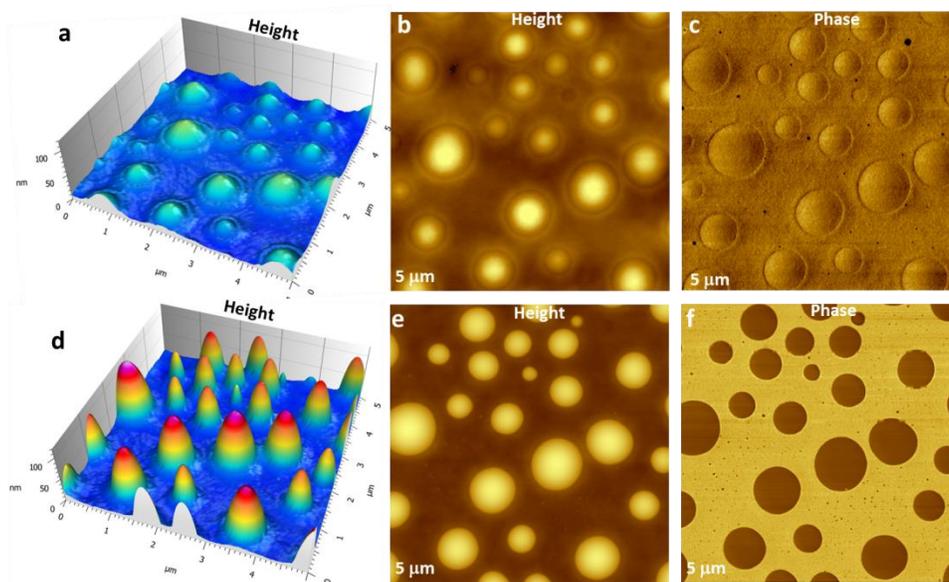

Figure 8. The height and phase images of PS/PVAC blend in air (a-c) and in methanol vapor (d-f).

The environmental studies can be performed in fast scanning regime, which allows monitoring of swelling dynamics of PS/PVAC blend, as shown in **Figure 9**. The rim structures, which are seen around the circular PVAC domains in air (**Figure 9a**), are the result of immiscible character of this blend. They have disappeared as the domains are gradually swollen in methanol, **Figure 9b-d**. The domain height has increased from 20 nm to 35 nanometers due to the swelling.
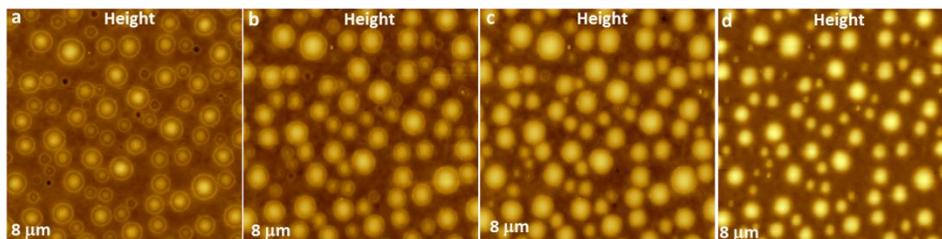

Figure 9. Height images of PS/PVAC blend, which were extracted from a sequence of 30-µm images recorded at 20 Hz rate during the sample swelling in methanol vapor.

AFM measurements are often performed at variable temperatures to monitor structural changes of materials at thermal transitions and related variations of local mechanical and electrical properties. The structural transformations of polymer blend of amorphous PS and semi-crystalline LDPE on heating are shown in **Figure 10**. In this blend, two types of LDPE domains are distinguished by their different elevations above PS matrix, **Figure 10a-b**. The lower circular domains have softened as seen by a darker phase contrast as sample temperature increased from 35°C to 80°C (**Figure 10c**). Melting of LDPE has started at 100°C and was completed at 120°C (**Figure 10d-e**). This is confirmed by a loss of lamellae inside the domains and by a leveling of the domains' phase contract that discerns them from PS matrix and substrate spots opened due to a partial polymer dewetting. As the sample was cooled to 35°C, LDPE has crystallized with a formation of lamellar structures, which are better resolved in large domains.
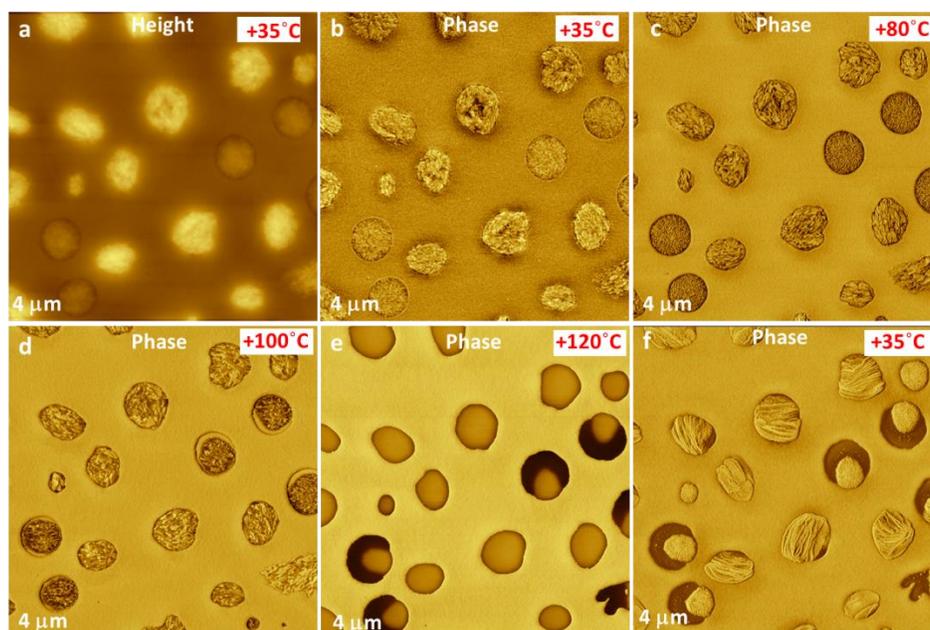

Figure 10. Height and phase images of PS/LDPE blend at different temperatures.

Fast scanning also enhances AFM studies at different temperatures. Because experiments at variable temperatures are often required imaging on areas from hundreds nm to a hundred μm, the studies are benefited from rapid monitoring of morphological transformations and nanoscale structures. A recording of images every degree of temperature at 5°C/min changes facilitates a comparison of AFM data with results of differential scanning calorimetry, which operates at similar heating/cooling rates. Structural changes, which were observed during cooling and heating of polydiethylsiloxane (PDES) adsorbates on Si substrate (**Figure 11**), will be used for demonstration. The phase contrast of this sample reveals two types of mesomorphic structures. The PDES domain in the top right quarter of the image was examined at different temperatures, and the related phase images are collected in **Figure 12**.
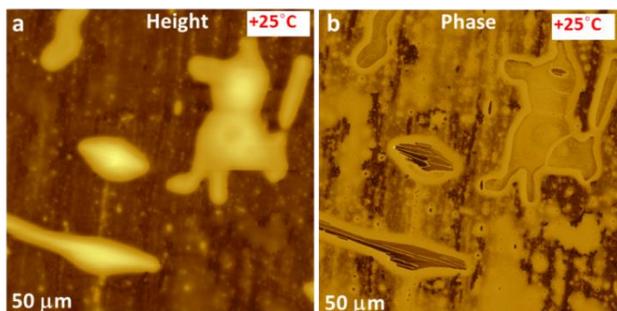

Figure 11. Height and phase images of PDES on Si at room temperature.

A smooth phase contrast at room temperature has abruptly changed at +7°C (α-type crystallization) faster than time of single scan line (~100 ms), **Figures 12a-b**. On cooling to -20°C PDES has completely broken into crystalline blocks, **Figure 12c**. On heating, the blocks inside the domain remained even when the sample's temperature increased to +15°C (**Figures 12d-e**). A complete conversion of PDES to isotropic state occurred at T = +45°C (**Figures 12f-h**), as confirmed by a featureless phase contrast. Fast monitoring of PDES temperature transitions demonstrated that it is a valuable addition to AFM modes.
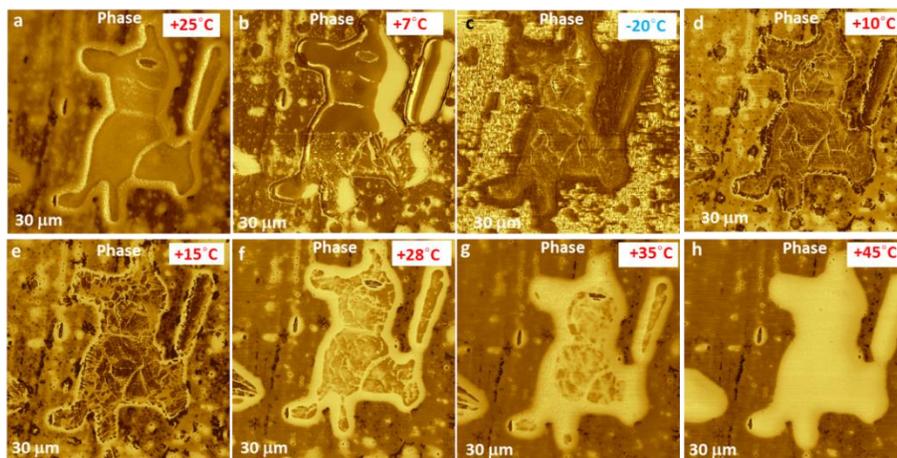

Figure 12. Phase images of PDES on Si taken from a series of images obtained at 10 Hz rate during 5 °C/min cooling and heating processes.

In summary, this document clearly illustrates the advanced nature of AFM applications made with Keysight 9500 microscope.