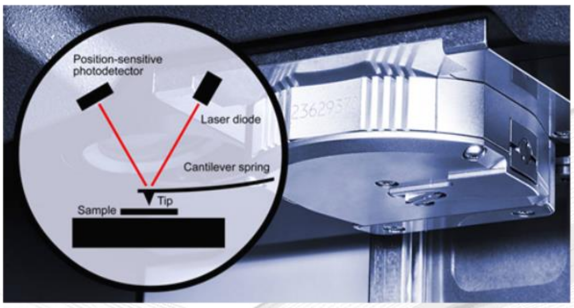
Full Atomic Force Microscopy Investigation of a Polymer Thin Film with Tosca series AFMs

Relevant for: Polymer thin film, AFM, EFM, KPFM, CRAI, force distance curves

Due to its unique design, Tosca AFM offers the exceptional possibility to investigate mechanical, electrical and magnetic sample properties on the same location with a single hardware set-up. In this report we describe the investigation of a polymer thin film sample by force distance curve, contact resonance amplitude imaging (CRAI) and Kelvin probe force microscopy (KPFM) with a single hardware set-up.

1 Introduction

For some AFMs in the field it is necessary to operate with the entire AFM head (to take it out and put it back in) which is not only heavy and impractical, but also risky as the user operates with the entire AFM head, which is the “heart” of the instrument.



Patented z-sensor integration

Tosca series AFMs have the z-sensor integrated in the very small and light “actuator body” without any wires or connectors, so the handling is safe and straightforward.

The Tosca actuator body includes:

- Z-piezo
- Z-sensor (capacitive)
- Tapping actuation
- Signal preconditioning
- Built-in calibration is automatically loaded[1]

Small and compact actuator body with no wires or connectors

Inserting the actuator body with the cantilever

[1] Except some features in some regions for IP reasons

In addition to easy and safe handling (the actuator body fits onto the palm of your hand), one of the most prominent advantages of this patented design is the possibility to perform all measurements for all modes with one and the same actuator body. This opens up the flexibility to measure various properties of the sample without any hardware handling - with one and the same cantilever (if applicable): Contact, Tapping, Force distance curve, Contact resonance amplitude imaging (CRAI), Electrostatic force microscopy (EFM), Magnetic force microscopy (MFM), Kelvin probe force microscopy (KPFM), Conductive AFM (C-AFM, 3 gains) – on the same location with one actuator body.

2 Investigation

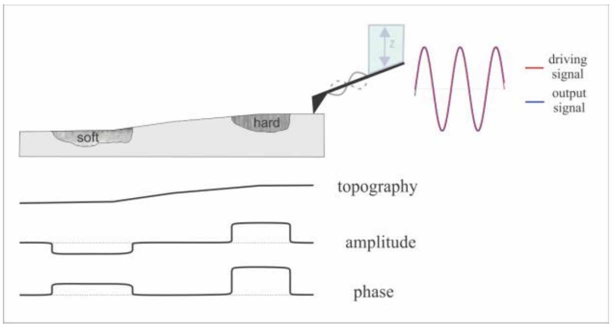
To demonstrate this capability, an AFM investigation of a PMMA/SBS polymer blend was performed on a 25 x 25 µm area with a resolution of 400 x 400 pixels and a scan rate of 0.5 line/seconds. Force distance curve, contact resonance amplitude imaging (CRAI). Electrostatic force microscopy (EFM) and Kelvin probe force microscopy (KPFM)[2] were employed at the same position with a single hardware set-up and the same cantilever – without any hardware changes in between the measurements.

3 Mechanical investigations

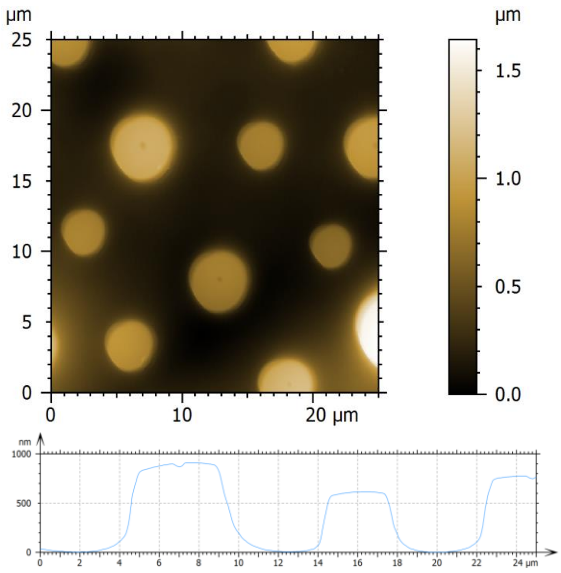
3.1 Contact Resonance Amplitude Imaging (CRAI)

First, mechanical properties of the sample were investigated by means of the Contact Resonance Amplitude Imaging (CRAI) mode. Contact resonance amplitude imaging is derived from contact mode. The cantilever is in constant contact with the sample to record the surface height. Meanwhile, it oscillates at a certain frequency around its contact resonance. Near-resonance operation exploits the fact that the CR frequency and amplitude depend on the sample's elastic modulus, so simultaneously recorded amplitude and phase channels reflect the difference in stiffness.[3]

[2] In this report, KPFM results without EFM investigation are discussed
[3] Scanning Probe Microscopy in Industrial Applications, Wiley 2014, Edited by Dalia G. Yablon

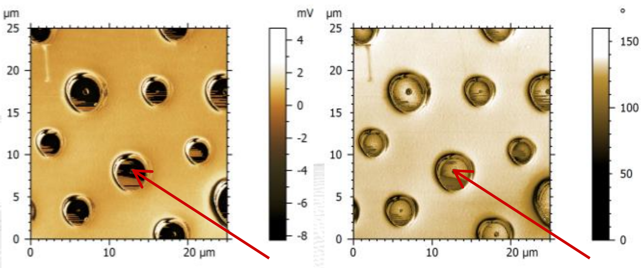


CRAI measurement principle schematic



Height image (top) and height profile (bottom)

The height image from the CRAI investigation of the polymer blend sample shows domains or islands within a matrix, which are two different polymers. The structures (or islands) are higher that the matrix, as can be seen from the height profile.



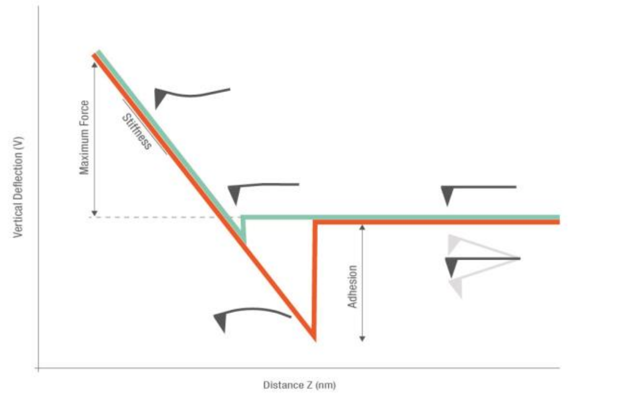
Amplitude (left), Phase image (right)

The contrast in amplitude and phase reflects differences in surface mechanical properties. What the amplitude and phase reveal is something that the height image does not show: also the higher domains/islands include some of the other polymer, so they are not purely one polymer. This observation is a distinct advantage of the CRAI mode as a dynamic contact AFM technique, which enable more accurate characterization of nanoscale mechanical properties[3].

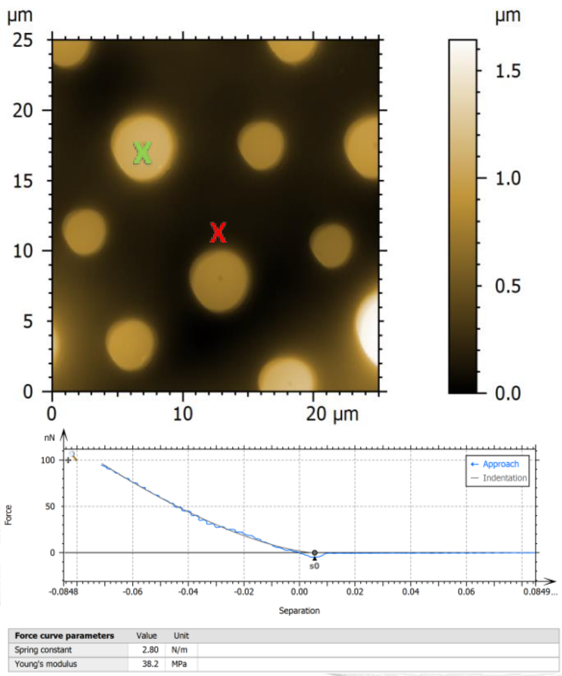
3.2 Force Distance Curve Investigation

Force distance curve mode was then used to quantitatively determine the Young's modulus of two distinct domains.

Force distance curve is a single point measurement of nano-mechanical properties. The AFM measures the force between the probe and the sample as a function of the distance the probe moves (which is Z in nm). For quantitative results, probe calibration is required (spring constant, cantilever sensitivity, tip geometry). After the calibration of the measured data and using a proper contact mechanics model one can easily get the quantitative information on Young's modulus, applied force, adhesion force, snap-in force and indentation depth.



Force distance curve schematics



Force distance curve measurement

FDC measurement results:		
	Matrix (red X)	Island (green X)
Young's modulus	38 MPa (30-50 MPa)	2.6 GPa (1.2-3.1 GPa)
Literature	SBS ~ 30 MPa	PMMA ~ 3.3 GPa

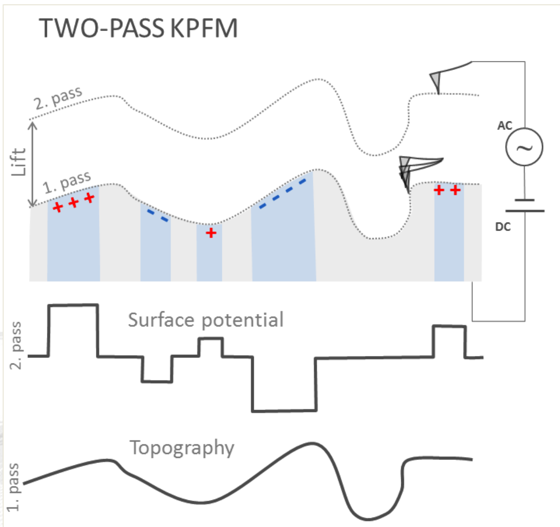
The values are similar to literature values for SBS and PMMA, but do not exactly correspond to those. This is due to the fact that, as we have seen from the CRAI analysis, the more stiff domains/structures contain the other polymer, which is less stiff. We can now conclude that the matrix is SBS (or predominantly SBS) and the structures/islands consist predominantly of PMMA.

4 Investigation of electric sample properties

Next, we were interested in the electrical properties of the sample and for this purpose we opted for the Kelvin probe Force microscopy investigation[2] of the same location on the sample surface without any change in the hardware set-up.

4.1 Kelvin Probe Force Microscopy (KPFM)

KPFM probes an electrostatic force field between tip and the sample and provides quantitative by measuring the contact potential difference between tip and sample.



KPFM schematics

Tosca AFM implements a so called two-pass KPFM.

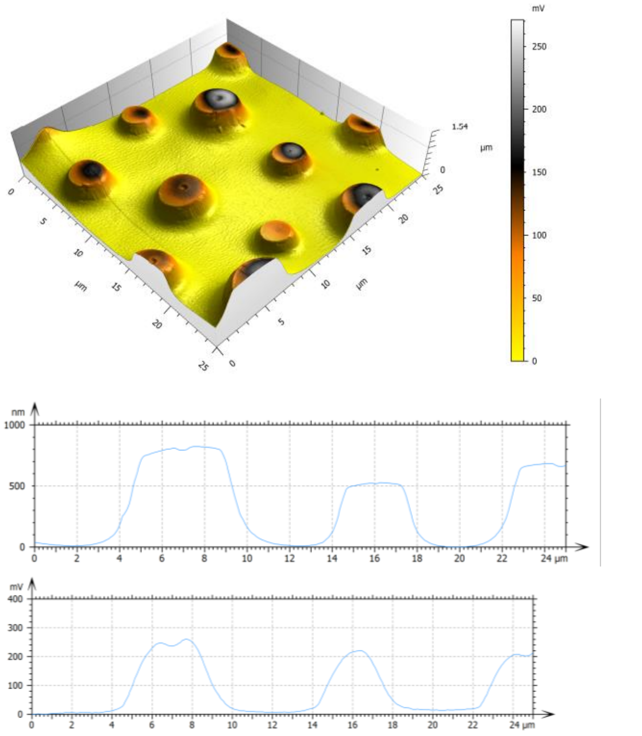
In the first pass, the height information is acquired by a tapping mode scan.

This height information is then used as input for the second pass -or lift pass, where the cantilever is lifted and rescans the surface line at a constant height above the sample surface.

The oscillation of the cantilever in lift pass of KPFM is not mechanically but electrically driven by applying an external AC voltage between the tip and the sample.

The feedback electronics adjust the bias voltage until the oscillation amplitude is nullified. As the result, we get the contact-potential difference between the tip and the sample, or the surface potential.

This contact-potential difference depends on the difference of the work function between tip and sample. The work function is defined as the minimum energy needed to remove an electron from a solid, and is material specific, so it can be used to identify the material composition and relate it to topography.



KPFM measurement results:
- Superposition of 3D topography and the contact potential difference or surface potential (top)
- Contact potential difference (CPD) distribution (middle)
- Contact potential profile (bottom)

KPFM results reveal different electrochemical properties of the matrix and the domains (structures).

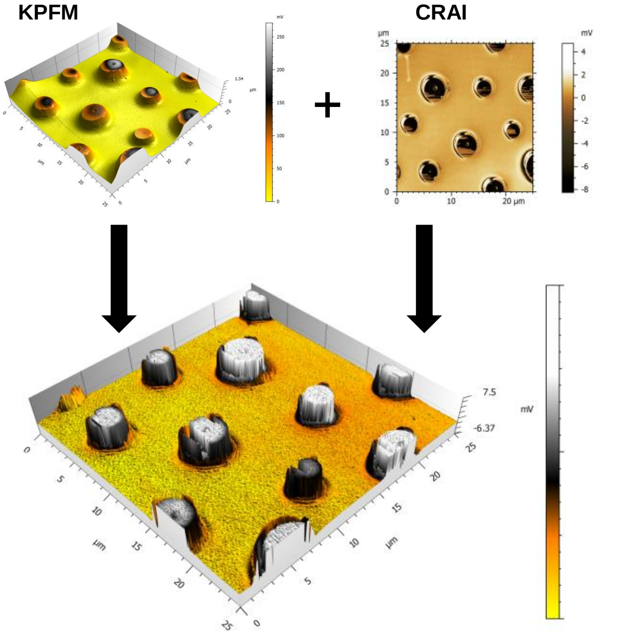
By correlating the extracted height and KPFM potential profile, we found that maximum contact potential difference between the matrix and the structures is about 250 mV.

Furthermore, nearly constant and uniform contact potential difference for the matrix can be observed. However, this is not the case for the structures (islands). We can observe quite strong variation in the surface potential of the structures.

The question is, can the difference in the contact potential be unambiguously assigned to the material composition (in this case, SBS and PMMA polymers)?

4.2 Correlating KPFM and CRAI investigations

To answer the question on the precise polymer distribution and the composition of islands (structures), we have made superposition of 3D CRAI and KPFM measurements, which is only possible if the two measurements were performed at exactly the same position:



Superposition of 3D CRAI amplitude and contact potential difference (CPD)

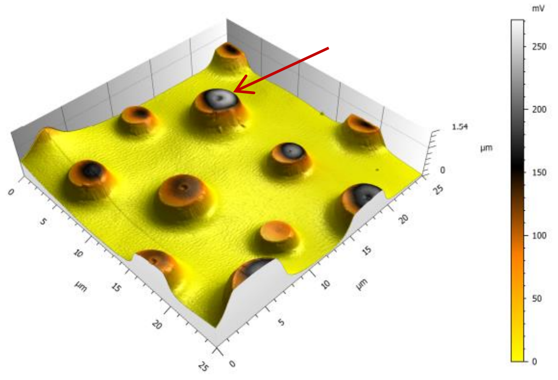
The superposition of the two results yields important information as added value.

As we now see, the contact potential difference clearly depends on the composition of the individual structures.

The structures where one polymer predominates show the highest potential difference, whereas the structures consisting of both polymers show lower potential difference.

4.3 Determination of the work function

By analyzing the KPFM results, we obtain the quantitative material properties by means of the work function. Work function (Φ) is the energy that is needed to remove an electron from the solid material. For the analysis, we have chosen this structure where one polymer predominates.



KPFM investigations: work function (Φ)

From the measured maximum contact potential difference, where the composition is most strongly dominated by a single polymer, we have obtained the following values of the work function:

For the Matrix: $\Phi = (4.1 \pm 0.1)\text{eV}$

and for the structures $\Phi = (4.3 \pm 0.1)\text{eV}$

The value of the work function of PMMA is in good agreement with the one reported in the literature, which is about $\Phi_{\text{PMMA}} \approx 4.3$ eV

5 Results, conclusions and Tosca operation

Mechanical Sample Properties

Contact resonance amplitude imaging and force distance curve were first used to investigate mechanical properties of the polymer blend sample.

Amplitude and phase images of CRAI mode revealed important information on locations with differences in mechanical properties i.e. stiffness between the different regions of the polymer blend. Force distance measurements then provided quantitative information of these differences in form of Young's modulus of elasticity.

Electric sample properties

Due to the unique Tosca design, analysis of different sample properties is possible on the same location with the same hardware set-up, without changing the cantilever for example. Kelvin probe force microscopy revealed the electrochemical properties of the matrix and the domains. The analysis of mechanical and electric properties on exactly the same location on the surface allows for superposition of the CRAI and KPFM results, that delivers important insight on the polymer distribution. Furthermore, work function allows for quantitative material properties analysis.

In summary, the possibility of the Tosca series to investigate different sample properties on the same sample location with the same actuator body and the same cantilever, if applicable), allows for applying the following modes for the analysis: Contact, Tapping, Force distance curve, Contact resonance amplitude imaging (CRAI), Electrostatic force microscopy (EFM), Magnetic force microscopy (MFM), Kelvin probe force microscopy (KPFM), Conductive AFM (C-AFM, 3 gains) – on the same location with one actuator body.

Tosca series AFMs are distinguished by unique, innovative operation, saving time for user training, speeding up the time-to-result and simplifying overall AFM handling. See the patented elements of the Tosca operation and what they can do for you here in the Tosca video.

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