Measurements without Hardware Exchange

Characterize Plastic Surfaces More Easily with Atomic Force Microscopy

Atomic force microscopy can be used to determine various properties of polymer surfaces. However, until now it was still necessary to change the hardware on the probe for different measurement methods. A special sensor technology eliminates the need to replace the head. The example of an investigation of a polymer thin film shows how this enables the precise characterization of polymers.

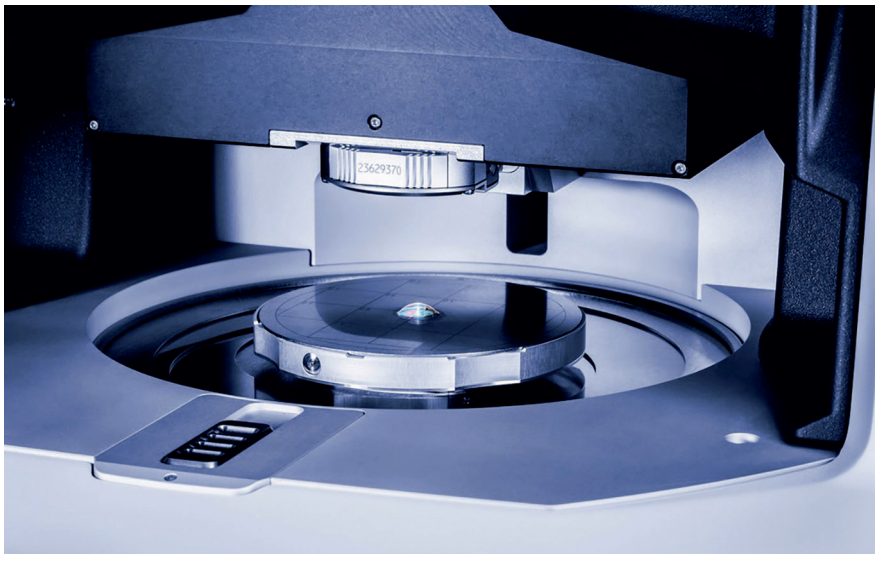
Atomic Force Microscopy (AFM) has been used for a long time to characterize mechanical, electrical, magnetic and other surface properties of plastics. When using this microscopy measurement method for characterization, it is often critical that all measurements are performed at the same location on the sample surface. In this case, different surface properties can be correlated accordingly and brought into a quantitative relationship.

Until now, however, AFM measurements with different modes at exactly the same location were difficult to perform, since this usually required a hardware change on the AFM measuring instrument. In this case, the AFM head must be removed and, after appropriate modification, reinstalled. This is not only time-consuming, but also carries the risk of damaging the AFM head. With the AFM-z sensor technology, Anton Paar GmbH has now developed a possibility that allows the use of all available AFM modes in the measuring instrument without hardware change. This allows switching between modes without lifting the AFM head. The characterization of a polymer thin film made from a mixture of polymethyl methacrylate (PMMA) and styrene-butadiene-styrene (SBS) shows how this works in practice.

In Anton Paar's Tosca series AFM, the z-sensor is integrated in a compact and lightweight "actuator body" without any cables, which ensures safe and easy handling (**Fig. 1**). All measurements for the different modes can be performed with only one actuator body. This allows various properties of the sample to be measured reliably and accurately on the nanoscale without hardware modification and associated repositioning of the cantilever. The following modes are available:

- Contact Mode,
- Tapping mode,
- Force Distance Curve (FDC),
- Contact Resonance Amplitude Imaging (CRAI),
- Electrostatic Force Microscopy (EFM),
- Magnetic Force Microscopy (MFM),
- Kelvin Probe Force Microscopy (KPFM),
- Conductive AFM (C-AFM).

In the aforementioned characterization, the polymer thin film was measured on a 25 µm x 25 µm area with a resolution of 400 x 400 pixels and a scan rate of 0.5 line/s. The force-distance curves, CRAI measurement, EFM and KPFM were performed at the exact same position. This makes it possible to learn more about the sample within one measurement procedure. Each measurement step determines further qualitative and quantitative sample properties, up to the complete characterization of the sample within the selected AFM resolution.



With the Tosca series, all AFM measurements can be carried out with only one actuator body and thus without hardware exchange © Anton Paar

CRAI Measurement Reveals Height Differences

First, the mechanical properties of the polymer thin film were investigated using the CRAI mode. This measurement mode is derived from contact mode. This means that the cantilever is in constant contact with the sample in order to record the surface height. At the same time, it oscillates with a certain frequency around its contact resonance frequency. This near-resonance operation exploits the fact that the contact

Fig. 1. Insertion of the actuator body with cantilever into the AFM: the z-sensor is integrated in the compact and lightweight actuator body without any cables © Anton Paar

resonance frequency and amplitude depend on the elastic modulus of the sample, so simultaneously recorded amplitude and phase channels reflect the difference in stiffness (**Fig. 2**).

The height image from the CRAI investigation of the PMMA-SBS blend shows structures or islands within a matrix representing the two different polymers in the blend. The structures are higher than the matrix, as can be seen from the height profile (**Fig. 3**). The contrast in amplitude and phase reflects differences in the surface mechanical properties. This reveals the information that the topography image does not show: the higher domains (islands) also include some of the other polymer, so they are not purely one polymer. This observation is a distinct advantage of the CRAI mode, as it enables a more accurate characterization of the nanoscale mechanical properties (**Fig. 4**).

The FDC measurement was used in the next step to quantitatively determine the elastic modulus of two distinct domains. FDC is a single point measurement of nanomechanical properties. The AFM measures the force between the probe and the sample as a function of the distance the probe moves (**Fig. 5**). For quantitative results, a calibration of the cantilever is required (determination of the spring constant, cantilever sensitivity, tip geometry). After the cantilever calibration and the subsequent measurement, using a proper contact mechanics model (**Fig. 6**), the quantitative information on Young's modulus, applied force, adhesion force, snap-in force and indentation depth can be easily obtained. The values determined are similar to the literature values for PMMA or SBS, but do not correspond exactly to these . This is due to the fact that, as seen from the CRAI analysis, the stiffer structures also contain the other, less stiff polymer. It can be concluded that the matrix is predominantly SBS and the structures consist predominantly of PMMA.

Two Pass Technique for the Determination of Contact Potential Difference

In the next measurement section, the electrical properties of the sample were investigated using the KPFM. KPFM measures an electrostatic force field between the tip and the sample and provides quantitative data by measuring the contact potential difference between the tip and the sample. The KPFM is implemented as a so-called two-pass measurement (**Fig. 7**). In the first pass, the height information is acquired by a tapping mode scan. This is then used as input for the second pass (lift pass). In this case, the cantilever is lifted and the rescans the surface line at a constant height above the sample surface. »

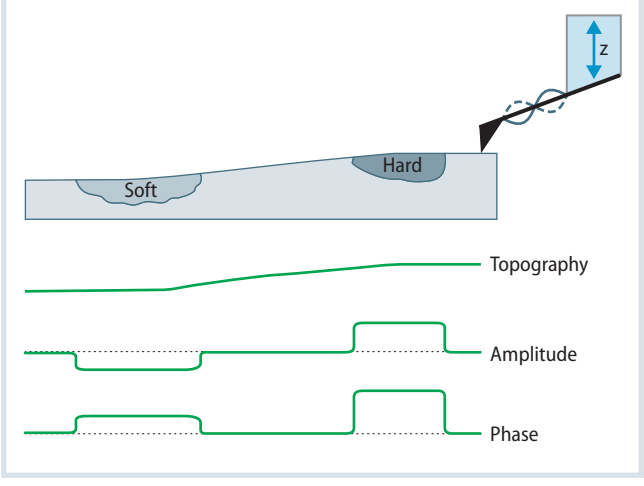


Fig. 2. Schematic representation of the CRAI measuring principle: differences in the stiffness of the specimen and a height image are generated © Anton Paar

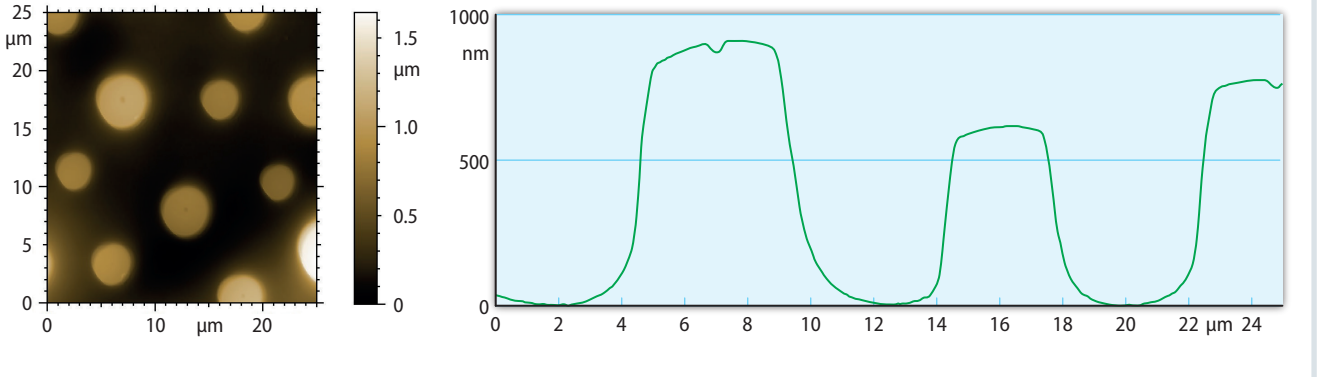


Fig. 3. The height image from the CRAI investigation reveals height differences in the polymer thin film. The determined islands are higher than the matrix Source: Anton Paar; graphic: © Hanser

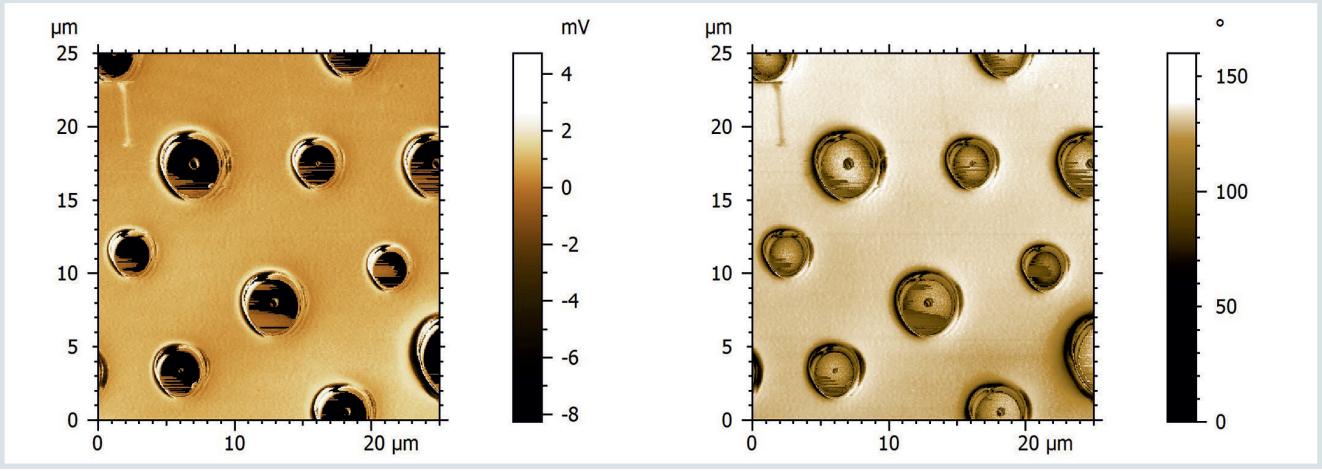


Fig. 4. The CRAI measurement shows a contrast in the amplitude (left) and the phase (right). This indicates that the higher structures consist of not only of one but of both polymers © Anton Paar

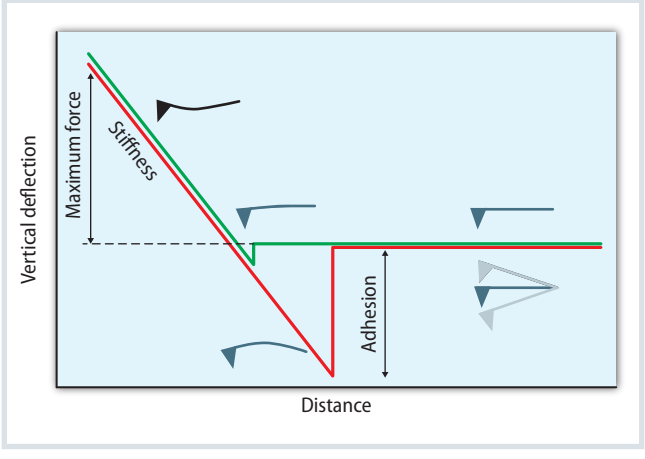


Fig. 5. Schematic representation of the force-distance curve (FDC): the force between the probe and the sample is measured as a function of the distance the probe moves Source: Anton Paar; graphic: © Hanser

The oscillation of the cantilever in the lift pass is not mechanically, but electrically driven, by applying an external AC voltage between tip and sample. The feedback electronics adjust the bias voltage until the oscillation amplitude is nullified. As the result, the contact potential difference between tip and sample, or the surface potential, is obtained. This contact potential difference depends on the difference of the work function between tip and sample. The work function (Φ) is defined as the minimum energy required to remove an electron from a solid and is therefore material specific. Therefore, it can be used to characterize the material composition and relate it to the topography.

Differences in Contact Potential Show Differences in Material Composition

The KPFM results show different electrochemical properties of the matrix and the structures. By correlating the extracted height and KPFM potential profile, it was concluded that the maximum contact potential difference between the matrix and the structures is about 250 mV. Furthermore, a nearly constant and uniform contact potential difference for the matrix is observed. However, this is not the case for the structures. A rather strong variation of the surface potential of the structures can be observed. The question arises whether the difference in contact potential can be unambiguously assigned to the material composition.

To answer the question of the exact polymer distribution and the composition of the structures, a superposition of 3D-CRAI and KPFM measurements is performed. This is only possible if both mea-

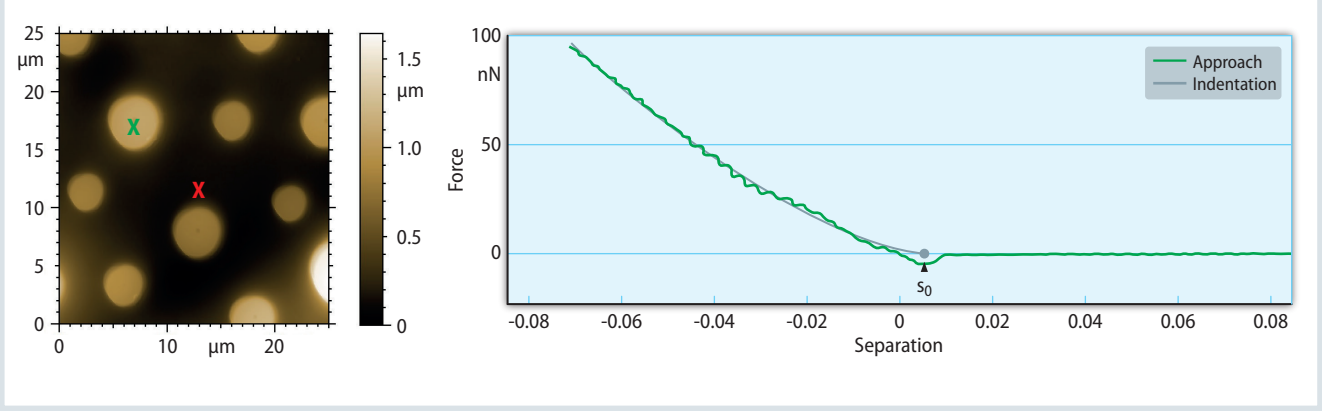


Fig. 6. Measurement of the force-distance curve (FDC) © Anton Paar

surements are performed at exactly the same position. The superposition of the two results provides important additional information. The contact potential difference clearly depends on the composition of the individual structures. The structures where one polymer predominates show the highest potential difference. In contrast, structures consisting evenly of both polymers show a smaller potential difference (**Fig. 8**).

By analyzing the KPFM results, the quantitative material properties can be determined using the work function. A structure in which a polymer predominates was chosen for the analysis. From the measured maximum contact potential difference, where the composition is dominated by a single polymer, a work function of 4.1 ±0.1 eV was determined for the matrix and 4.3 ±0.1 eV for the structures.

Combination of Measurement Methods Enables Accurate Characterization

The results show that an accurate characterization of different surface properties of polymers is possible by combining the different measurement methods. CRAI and FDC measurements were first used to investigate the mechanical properties of the polymer thin film. Amplitude and phase images of the CRAI mode show important information about locations with differences in mechanical properties i.e. stiffness between the different regions of this polymer blend. FDC measurements provide quantitative information about these differences in the form of the Young's modulus of elasticity.

KPFM shows different electrochemical properties of the matrix and the structures The analysis of mechanical and electrical properties at exactly the same location on the surface allows the superposition of the CRAI and KPFM results, which provides important insights into the polymer distribution. In addition, the work function allows a quantitative analysis of the material properties.

The investigations illustrate the measurement capabilities of the AFM Tosca series. Due to the AFM technology of z-sensor integration, Tosca series enables a faster and more extensive characterization of the polymer thin film. This allows different material properties to be determined sequentially at exactly the same position using different modes. ■

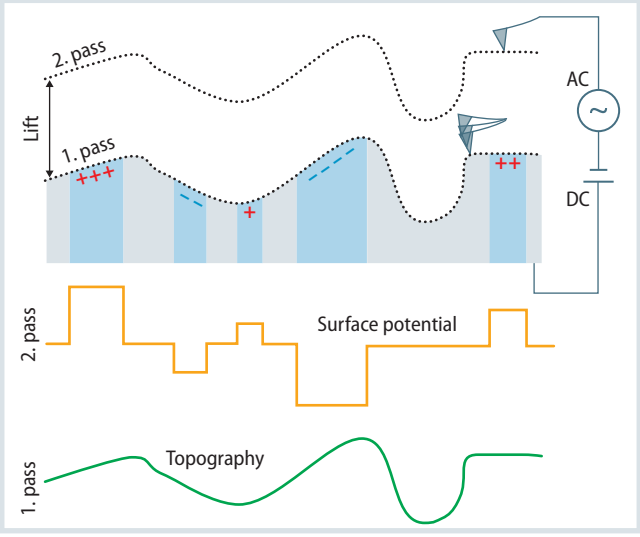


Fig. 7. In the KPFM, the height information is determined by tapping mode scan in the first pass. The second pass (lift) with the cantilever lifted takes place at a constant height above the sample

© Anton Paar

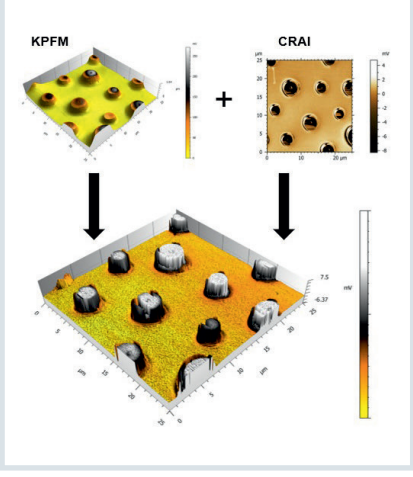


Fig. 8. Superposition of 3D CRAI amplitude and contact potential difference (CPD) shows the higher potential difference for structures which are mainly composed of one polymer

© Anton Paar

The Authors

Dr. Dr. Jelena Fischer has been working as a product manager for Anton Paar GmbH in Graz, Austria, since 2012.

Dirk Meister has been working as a product specialist for Mechanical Surface Characterization for Anton Paar Germany GmbH since 2019; dirk.meister@anton-paar.com

Michael Schäffler has held various positions at Anton Paar Germany GmbH since 2002, currently as Market Development Manager.

Service

Digital Version

↘ A PDF file of the article can be found at ***www.kunststoffe-international.com/archive***

German Version

↘ Read the German version of the article in our magazine ***Kunststoffe*** or at ***www.kunststoffe.de***