Application Note

Soft IC: Soft Intermittent Contact AFM mode

Introduction

Atomic Force Microscope (AFM) has become a versatile instrument to characterize a wide variety of properties of surfaces at the nanoscale beyond topography. Electric and magnetic properties can be mapped with different measurement modes like Magnetic Force Microscopy (MFM), Electric Force Microscopy (EFM), High Definition Kelvin Force Microscopy (HD-KFM) and (Soft) ResiScope. Heat exchange rate and local phase transitions can be mapped with Scanning Thermal Microscopy (SThM mode) where the tip can be used alternatively as a nano-thermometer or nano-heater. Another important physical property that becomes relevant to develop new material is the Young Modulus which provides information about how it deforms under an applied load or stress. This is of great interest in polymer science: the increasing interest on additive manufacturing (3D printers) technology has stimulated the search for polymers with improved flexural strength, (visco)elastic response or temperature deformation that could improve the standard ones like polypropylene (PP), polylactic acid (PLA) or acrylonitrile butadiene styrene (ABS). There is also an increasing interest on developing new materials for flexible packaging films with recyclability properties to preserve the environment. All these new developments require a deep knowledge of the material properties at the nanoscale.

In this application note we will show different examples of the brand-new mode developed by CSI called Soft IC that in combination with the software module Soft Mechanic allows to map stiffness(Young Modulus) and adhesion at standard scanning speed (upto 5 lines/seconds).

CONTACT MODE, FORCE SPECTROSCOPY AND RESONANT MODE

In AFM a micro cantilever with a sharp tip on its free-end is placed in close contact with a surface. The interaction force between the atoms of the tip apex and the surface atoms below affects to the deflection of the cantilever and typically shows a Lennard-Jones type dependence with the separation distance. If the net interaction force is attractive (negative) the cantilever will bend downwards while if it is repulsive (positive) the cantilever will bend upwards. Thus, an image of the surface with nanometric resolution can be obtained by scanning the tip in continuous contact with the surface while keeping the interaction force (cantilever deflection) constant. This last condition is achieved by means of an electronic feedback operating on the vertical displacement of the scanner that allows moving the cantilever line-by-line over the sample. This is operation mode is usually referred as “Contact mode” and it was historically the first to be implemented. One of the main advantages of this mode is its easy theoretical modeling: the quasi-static force that the tip applies onto the surface can be measured by means of the Hooke’s law:

$$F=k(z-z_0) \qquad (1)$$

Where F is the interaction force, k is the spring constant of the cantilever, z is the vertical deflection of the cantilever and z0 is the deflection value that corresponds with the rest position of the cantilever. However, it has the inconvenience that friction forces raised due to the movement of the tip respect to the sample due to the continuous contact may damage either the surface or the tip.

In addition to the capability to obtain an image, contact mode has been also implemented with the force spectroscopy mode. This mode allows to position the tip on an specific location of the surface and perform an approach-retract cycle like the example shown in Fig. 1.

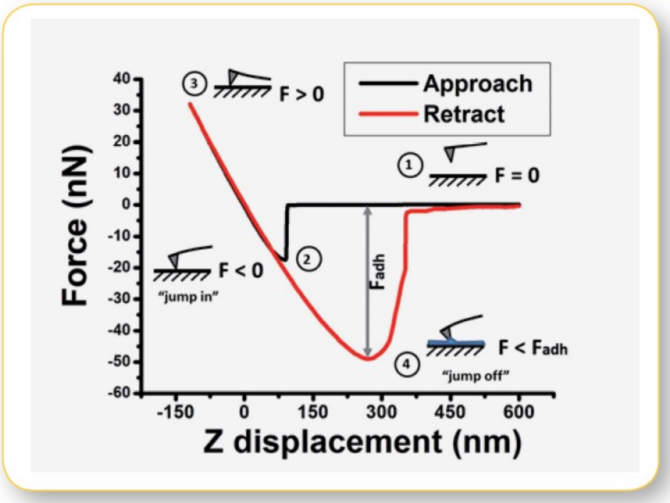

Figure 1: Typical Force spectroscopy curve.

Fig. 1 depicts a typical force spectroscopy curve (or F-z curve) obtained in contact mode, and its relevant features.
The horizontal axe represents the vertical movement of the scanner that holds the sample, while the vertical axe represents the deflection (or force, according to eq.(1)) of the cantilever.
The curve begins at the right side of the graph, representing full sample/piezo retraction (point 1); then the scanner starts to expand reducing the separation distance until a maximum cantilever deflection is reached (left side of the graph-point 3).
Then the piezo retracts again. Typically the vertical movement of the scanner is referred as “Approach” (black line) and the retraction (red line) as “Retract”.
As the sample (or Z scanner) begins to extend, the deflection remains constant (point 1 indicated by “Zero force level” in Fig. 1) which serves as a reference indicating that the interaction force acting on the cantilever is null. The attractive force gradient increases as the separation distance is decreased; the point at which it becomes greater than the cantilever spring constant is where the cantilever comes into contact with the surface (point 2). This point, usually referred as “jump-in”(point 2 in Fig. 1), is characterized by a sharp decrease of deflection. After this point there is mechanical contact, i.e., the tip is engaged with the sample surface.

As the scanner extends further (moving to the left on the graph), the cantilever deflection increases linearly in response to the repulsive force between the tip and sample.
After reaching the maximum deflection (or force) when the scanner fully expands (point 3 in Fig. 1), the scanner retracts and the cantilever deflection decreases linearly, retracing the curve. Depending on the magnitude of the adhesion between tip and surface, the deflection may decrease from few to hundred nanometers beyond the “jump-in” point until the tip breaks free from the surface. This point is usually referred as the “jump-off” point (point 4 in Fig. 1), is characterized by a sharp increase in deflection. After the jump-off point, the cantilever deflection is again constant.
By using different models for contact mechanics, the region of the F-z curve where the tip and sample are engaged can be used to calculate the Young Modulus. Depending on the type of sample and environmental conditions models like Hertz, DMT or JKR must be used. In addition to this, tip-sample adhesion can be extracted for the curve and be used as a magnitude to characterize the sample.
The main advantage of force spectroscopy curves (like imaging in contact mode) is that conversion from cantilever deflection to force is straightforward by means of eq (1) and also to set the maximum force applied to the sample.
However, the main drawback of using force spectroscopy curves for mapping mechanical properties (Young Modulus or tip-sample adhesion) with high lateral resolution is the intrinsic slowness: an standard image of 512 x 512 points with an approach-retract cycle of 1 s would require 3 days.
To avoid the inconvenient of friction forces, dynamic or resonant modes can be used instead. The cantilever is mechanically driven at its natural resonance frequency and the oscillation amplitude is used to control the interaction force(instead of the quasi-static deflection). As the tip is being scanned over the surface, it is also oscillating vertically with typical amplitudes that can range from few to tens of nanometers. The effect of the interaction force is to increase (decrease) the oscillation amplitude as the averaged tip-sample separation is increased (decreased). This mode has been extensively used over the past decades as it allowed obtaining high resolution while preserving the tip or sample.
However, in resonant mode is not easy to calculate the applied force from the amplitude/phase of the oscillation.
Moreover, as these are averaged quantities over several oscillation periods, the analytical models can only provide an averaged force that may be significantly different from the instantaneous maximum force (that typically occurs at the bottom part of the tip oscillation). There have been also many attempts to develop theoretical models that can be used to extract intrinsic properties of the surface like Young modulus, however they imply restrictions that cannot be fulfilled in many experimental situations.

SOFT IC MODE

Concept Scientific Instruments has developed an alternative measurement mode called Soft Intermittent Contact mode (or Soft IC) that combines the advantages of contact mode and force spectroscopy but presentencing from their inconvenient like friction forces or intrinsic slowness. Soft IC mode works as follows (Fig. 2) : The tip is separated some safe distance (referred as «lift height») from the surface and moved fastly to the next measurement point (determined by the number of pixels of the image), when it reaches the position the tip is stopped and it performs a force spectroscopy curve as described in the previous section.

The maximum force applied is set by the user by a setpoint value in a similar manner as in contact mode. Another advantage of Soft IC respect to contact mode is to avoid the instabilities due to changes in the adhesion force during the scan as it happens frequently in contact mode. By setting a lift height higher than the adhesion force, tip can be totally disengaged from the surface. This also has the advantage that even softer cantilevers (typically they experience very high adhesion forces) can be used routinely with this mode.
In addition, stiffness and adhesion can be obtained directly from every measured point. The stiffness (i.e., the ratio of the applied force and the deformation of the sample) can be used in combination with Soft Mechanic software module to calculate the Young´s Modulus

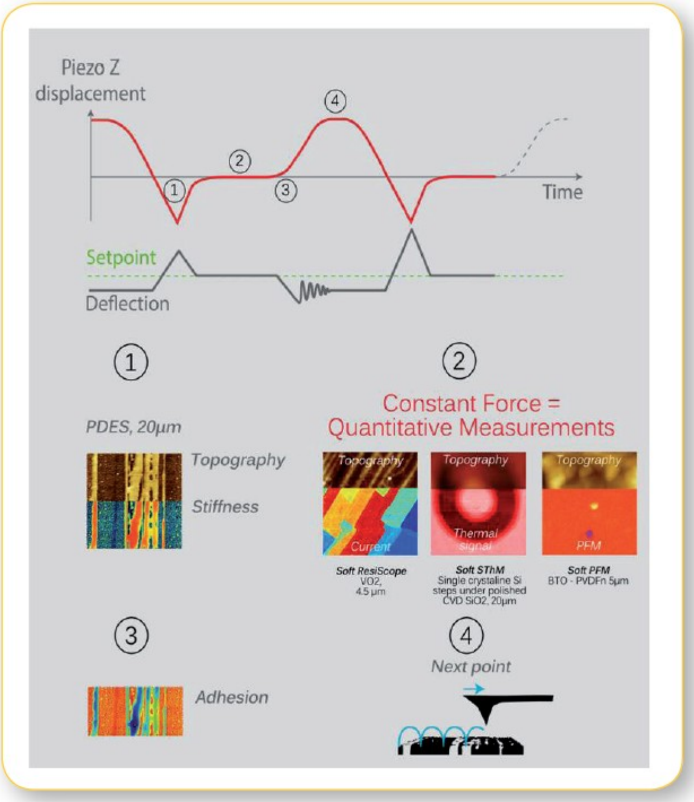

Figure 2: **1. Topography & Stiffness**
2. Constant Force = Quantitative Measurements
Soft IC is compatible with Soft ResiScope, Soft SThM, Soft PFM, Soft CAFM…
3. Adhesion
4. Next point

SOFT IC ON POLYMER MATERIALS

An example of the application of Soft IC mode on a polymer sample is shown in Fig. 3. A sample of poly(dimehtylsiloxane) (or PDMS) covered with a TEM grid was irradiated with ultraviolet (UV) light, thus creating areas with different mechanical properties. The area inside the squares defined by the TEM grid becomes stiffer due to cross-linking induced by UV light. Stiffness and adhesion are shown respectively in Figs. 3(a) and 3(b) with FORT cantilever (AppNano, k = 1.7 nN, applied force of 80 nN). As it can be seen in Figure 3a, PDMS areas (green areas) have a smaller stiffness than cross-linked PDMS (blue squares). On the contrary, adhesion does not show much difference among them. In both cross-sections it can be noticed how the histogram of values in the image shows two well defined peaks for the stiffness, but only one for the adhesion.

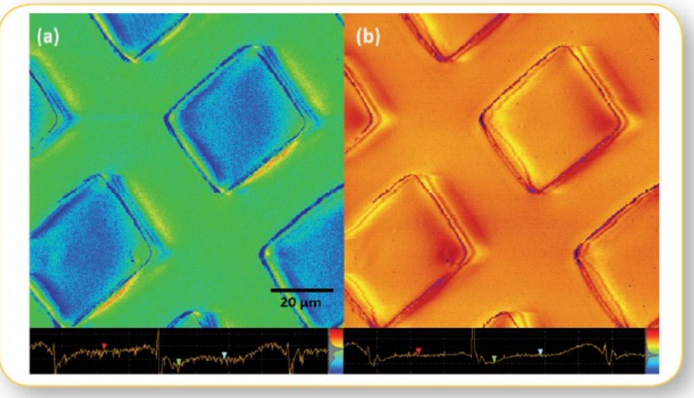

Figure 3: Soft IC mode on PDMS irradiated to UV. (a) stiffness and (b) adhesion maps with corresponding cross-sections and histograms.

The concept of stiffness is explained in Figure 4 where two force spectroscopy curves on both regions are depicted. For a given value of the applied force (deflection set point used during the image) the stiffness is the force/deformation ratio (i.e., the slope around the set point value). A higher stiffness implies less deformation for the same applied force.

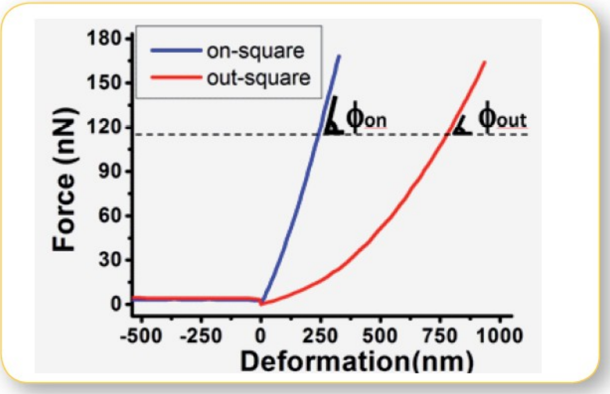

Figure 4: Force vs deformation curves on the PDMS sample of Fig. 3. The stiffness magnitude is the ratio between the applied force and the deformation of the surface. A stiffer material (blue curve-inside square) has higher slope.

Soft IC is the suitable measurement mode to identify compounds in polymer blends with the information provided with the stiffness and adhesion channels. An example of this utility on a blend of PS/PMMA is shown in Fig. 5 with an ACT probe (k = 37N/m, AppNano , $F_{setpoint}$ = 12nN). The topography image (Fig. 5(a)) does not show much details as the surface has been previously polished showing a roughness of less than 12 nm except for two trenches of 10 nm deep on both sides of the image (dark brown stripes) and a smaller one around the middle. The adhesion (Fig. 5(b)) and stiffness (Fig. 5(c)) shows two well differentiated phases that can be matched with PS and PMMA. In the case of the stiffness, red areas (higher stiffness values) would correspond with PS, while blue areas with PMMA. In the adhesion image, orange areas (higher adhesion values) would correspond with PMMA and yellow areas with PS. More interestingly it can be seen that in the trenches visible in the topography (dark brown areas) the stiffness values are the same in both trenches, however the adhesion values change from one trench to another, and are different to the values of PS and PMMA on the flat areas. This reflects the fact that the adhesion can also be more sensitive to the contact area that is significantly higher in the deep trenches than in the flat parts. It is also interesting to notice in the stiffness image some tilted lines of PMMA on the PS areas which are presumably small parts dragged during the preparation of the surface.

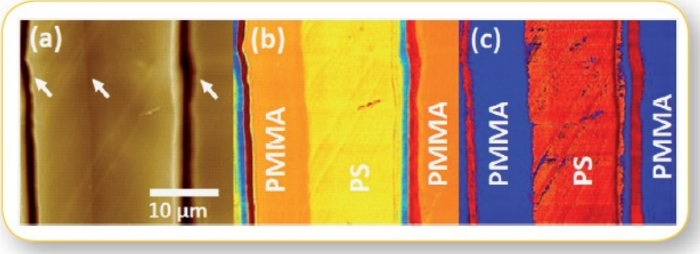

Figure 5: Soft IC on PS/PMMA mixture.(a) topography, (b) adhesion and (c) stiffness.

Soft IC mode can be used also to characterize not only polymer blends but several phase states within the same polymer.
In Figure 6 it is shown topography (Fig. 6a), stiffness (Fig. 6b) and adhesion (Fig. 6c) of a PDES film spin coated on a silicon substrate. A similar cantilever than previous example was used with an applied force of 17.8 nN. The morphology of this sample is expected to have stiffer lamellar domains surrounded by amorphous softer phases. In topography it can be appreciated the presence of two phases differentiated by two well defined heights (brown areas and yellow areas) with an average height of 8.9 nm. Additionally it can be seen in the layer covering the center of the image some horizontal lines that can represent horizontal crystalline lamellae as described in similar substrates in the literature. On the sides of the image there can be seen also circular droplets with similar height, so that in principle two different phases could be expected.
However, the information obtained with the stiffness (Fig. 6(b)) and adhesion maps; it seems that there are three different types of phases with increasing stiffness value (blue, yellow and red respectively). In the adhesion map the same 3 phases are defined by decreasing adhesion values (yellow, dark blue and blue). Thus it seems that the central domain would correspond to a well ordered crystalline lamella, the small droplets to a semi-crystalline phase and the surrounding matrix (blue regions in the stiffness image) to amorphous phase.

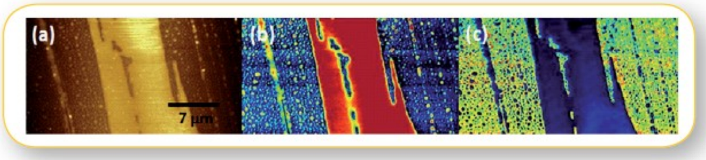

Figure 6: Soft IC on PDES sample. (a) topography, (b) stiffness and (c) adhesion.

HIGH RESOLUTION IMAGING WITH SOFT IC

Soft IC allows to obtain high resolution imaging as friction forces do not play a role during the imaging and maximum force can be controlled more accurately than in resonant mode. In Figures 7 (a) and (b) are shown to examples on circular chains of DNA and block copolymer PS/PMMA blend respectively with an ACT cantilever (k = 28.9 N/m, AppNano). Figure 7(a) corresponds with the topography (image size 1.5 µm) obtained with an applied force of 2.9 nN. At this force the dna chains show the expected circular geometry (diameter around 50 nm) with a lateral resolution of 8-10 nm which allows to resolve the inner part of the chain. In Figure 7(b) it is shown the topography (image size 5 µm) obtained with Soft IC of the lamellar structure of PS/PMMA block copolymer sample. On the bottom part of the image the applied force was 1 nN and then increased to 5 nN, 10 nN and 20 nN respectively. For 1 nN the contrast is not high enough to see clearly both phases. On the contrary, for 15 nN and 20 nN, the force was too high and some deformation is induced.

The best conditions are achieved for 5nN which is the force applied on the bottom part of the image and the phases of the PS and PMMA blocks are resolved with an spacing of 38.6nm. models has to be chosen.

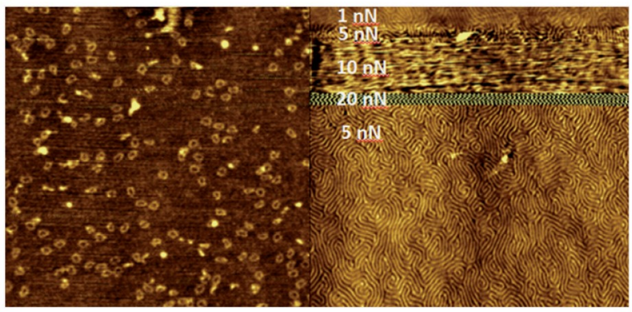

Figure 7: High resolution imaging with Soft IC on (right) 50nm dna rings and (left) PS/PMMA block copolymer with 38.6nm spacing.

SOFT MECA SOFTWARE MODULE ELASTICITY MODULUS MAPS

Although Soft IC has been proved to be the best suitable choice to characterize materials with different mechanical properties, stiffness itself is not an intrinsic property of the material. This makes that the quantitative values obtained may become meaningless when it comes to compare different samples or using different type of cantilevers. Soft IC in combination with Soft Mechanic software module allows to apply different types of models to the approach/retract cycle of the tip against the surface to calculate the Young modulus. This model can be applied to the data obtained with different measurement modes like Soft IC, force spectroscopy or FlexGrid.
The most frequently used contact mechanics models used in atomic force microscopy are the Hertz, JKR and DMT.
Hertz model relates the applied force and the induced deformation as follows:

$$F = 4/3 E^{*} R^{1/2} d^{3/2} \qquad (2)$$

Where F is the applied force (i.e., the cantilever deflection in Soft IC), E* is the reduced Young modulus, R the tip radius and d the surface deformation. However, the assumptions made (purely elastic sample, infinite thickness, no preferential direction and no adhesion) on this model cannot be applied to many of the experimental situations. Hertz model is widely used to measure elasticity of cells in liquid media where the adhesion is negligible.
The JKR model is known to be appropriate for cases of compliant bodies in contact with large effective radii and short range adhesion forces. Compared with the JKR model, the DMT model incorporates the long range adhesion interaction outside the contact area. Thus, the DMT model is widely used to describe the contact behavior of stiff bodies that have small radii and long range adhesion forces. Thus, depending on the nature of the interaction between tip and surface, one of those

An example of the combination of Soft IC and Soft Mechanic software is shown in Fig. 8 on the same PDMS sample of Fig. 3. Fig. 8(a) shows a 3D representation of the sample with an overlay of calculated Young Modulus (APPNano FORT-tip, k = 1.7N/m, $F_{setpoint}$ = 117nN). Blue and green areas have an average E of 50.1MPa and 2.7MPa respectively. In Fig. 2(b) it is shown a comparison of calculated E values with a nanoindentor (Nanomechanics Inc.) and values obtained with Soft Mechanic for different indentation values showing a good agreement between them for indentation values higher than 100nm.

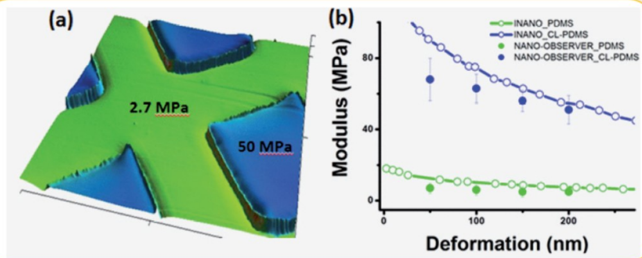

Figure 8: (a) Young´s modulus image obtained with Soft IC and Soft mechanic of sample of Fig. 3. (b) Comparison of the Young modulus values obtained with Sof IC and Soft mechanic and a nanoindentor on PDMS sample of Fig. 3.

Another example is shown on Fig. 9 on a harder substrate consisting on a PS film of 30 nm spin coated on a silicon substrate. In this case a Flex Grid matrix of force spectroscopy curves was made on the surface with an ACT tip (AppNano, k = 25.5nN) applying a maximum force of 1.4µN. After that a load/unload curve was made with a nanoindentor (Nanomechanichs inc). Fig. 9(a) shows a comparison of the values obtained with the AFM (green dots) and the nanoindentor (brown curve). The values are quite similar for the PS film, however the nanoindentor is capable of penetrate into the silicon substrate while the AFM cantilever is not hard enough. Fig. 9(b) shows the topography after the indentation tests of the same area: it can be clearly noticed that the AFM tip is only capable of penetrating the PS film (about 30nm).

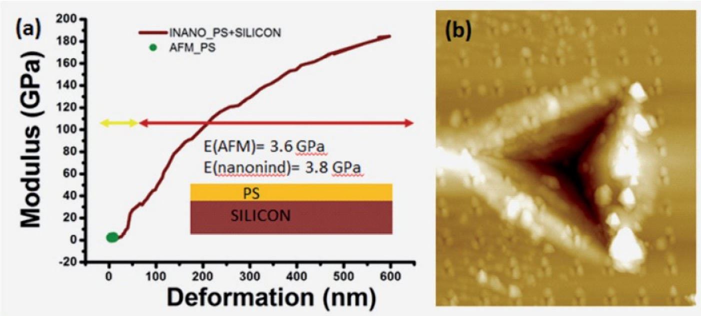

Figure 9: (a) (b) Comparison of the Young´s modulus values obtained with Sof IC and Soft mechanic and a nanoindentor on PS sample. (b) topography image showing the indentations matrix made with the AFM and the indentation made with the nanoindentor.

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