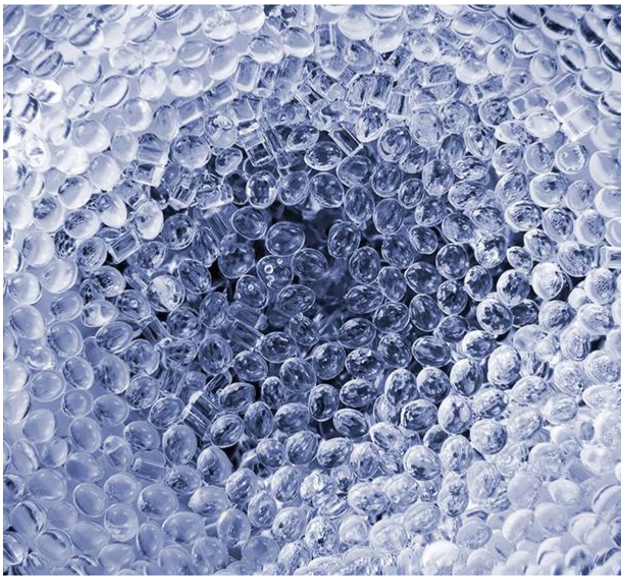
Surface Characterization of Polymer Thin Films using Atomic Force Microscopy

Relevant for: Polymer blends, AFM, Contact Resonance Amplitude Imaging

We have used dynamic Tosca AFM's Contact Resonance Amplitude Imaging mode to study surface distribution of polymers in PMMA/SBS polymer blends.



1 Introduction

Atomic force microscopy has been widely applied to acquire high resolution 3D surface topography at micro- and nanometer scale. As the AFM technology has evolved, different modes have been developed so that a wide array of data types can be collected in order to gain different information on the examined sample. Here we introduce a mechanical mode called Contact Resonance Amplitude Imaging.

Contact resonance techniques[1] are a class of dynamic contact AFM methods where a piezoelectric actuator is used for CR excitation. CR methods deliberately operate in the vicinity of a resonance. The high frequency of the dynamic excitation (kilohertz to megahertz) used in CR methods also allow for improved sensitivity to small changes in mechanical properties compared to quasi-static approaches, due to time averaging of the cantilever vibration response. Near-resonance operation exploits the fact that the CR frequency and amplitude depends on the sample's elastic modulus due to tip–sample interaction forces. In Contact Resonance Amplitude Imaging, qualitative modulus information can be obtained by monitoring the relatively large shifts in signal amplitude that occur near resonance. In the resulting "CR Amplitude Image" the signal intensity corresponds to the amplitude of the cantilever vibration at the excitation frequency. In turn, the variation in cantilever vibration amplitude throughout the sample depends on the relative elastic stiffness or modulus of various sample components.

Method	Contact Resonance
Mode	Amplitude Imaging
Excitation Frequency Relative to Resonance	On (near) resonance
Excitation Frequency Range (kHz)	100-2000
Excitation Orientation	Out of plane
Information Obtained	Qualitative Images

In this application report we compare Contact Resonance Amplitude Imaging with tapping mode. In CR Amplitude Imaging the cantilever deflection is kept constant, similar to contact mode, while a very small amplitude (typically sub-nm) is modulating the cantilever and the amplitude and phase of this modulation is detected. Changes in amplitude and phase correlate to surface mechanical properties like stiffness and dissipation.

[1] Scanning Probe Microscopy in Industrial Applications, edited by Dalia G. Yablon, John Wiley & Sons, 2014

2 Experimental

Poly(methyl methacrylate) (PMMA) and poly(styrene-butadiene-styrene) (SBS) polymer blend were spin coated on a silicon wafer. The thin film was then imaged by Tosca AFM using tapping mode and Contact Resonance Amplitude Imaging at ambient conditions. Tapping mode used Arrow NCR cantilever. CR Amplitude Imaging used Arrow FMR cantilever, applying the frequency of contact resonance at around 800 kHz.

3 Results and discussion

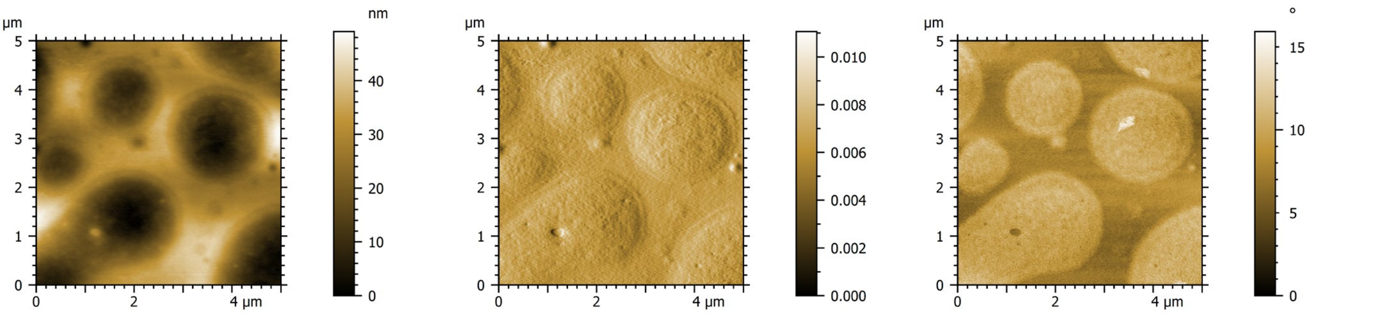


Figure 1. Height (left)), amplitude (middle) and phase (right) images acquired by tapping mode

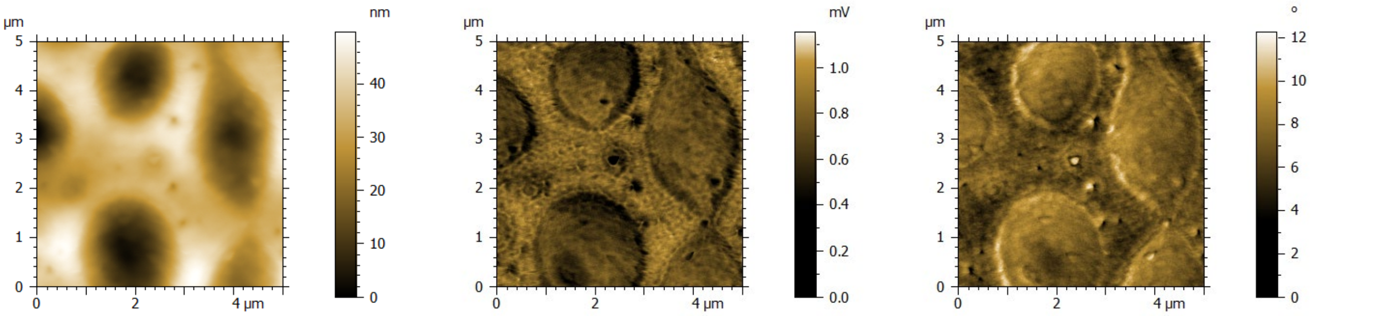


Figure 2. Height (left), amplitude (middle) and phase (right) images acquired by CR Amplitude Imaging

Figure 1 shows the surface topography (left) and the corresponding phase image (right) acquired by tapping mode. It is clearly observed that PMMA/SBS polymer blend displays a two phase separated surface structure. According to our previous studies ‘Polymer Surface Characterization by AFM’ and ‘Characterization of Surface Mechanical Properties of Polymer Coatings using AFM Force Distance Curves’ The brighter color in the phase image suggests the regions contain softer or more adhesive materials, SBS in this case. Therefore we can determine in the height image that the bright regions are PMMA regions and the dark regions are SBS regions.

Figure 2 shows the surface topography (left), amplitude (middle) and phase (right) images acquired by Contact Resonance Amplitude Imaging. Here a more detailed distribution of materials is disclosed. In amplitude image the PMMA regions (brighter) show a clear contrast to SBS regions (darker). However, it is noticed that both PMMA and SBS regions have shown granular structures with color contrast instead of a uniform color. It suggests that neither of the regions is homogeneous, that is, each region is rich in one polymer, but still contains some amount of the other. The same phenomenon can also be observed in the phase image with a reversed color contrast. This also explains why in our previous study of the same sample, ‘Characterization of Surface Mechanical Properties of Polymer Coatings using AFM Force Distance curves’, the measured modulus of each polymer phase deviated from the typical values for pure PMMA and SBS.

4 Summary

We have successfully used Contact Resonance Amplitude Imaging to study the surface structure of a PMMA/SBS polymer blend. Since CR Amplitude Imaging is derived from contact mode, the amplitude and phase is not influenced by tip/sample adhesion. Compared to tapping mode, CR Amplitude Imaging provides a better insight of surface distribution of the polymer components only due to their different mechanical properties such as stiffness.

5 References

1. *Scanning Probe Microscopy in Industrial Applications. edited by* Yablon, Dalia G., *Hoboken*: John Wiley & Sons, 2014.

2. Wu, Ming, *Characterization of Surface Mechanical Properties of Polymer Coatings using AFM Force Distance curves.* Graz : Anton Paar, 2018.

Contact Anton Paar GmbH

Measurements & Text: Dr. Ming Wu

Tel: +43 316 257-0

support-nsp@anton-paar.com | www.anton-paar.com