High-Resolution Mapping of Quantitative Elastic Modulus of Polymers

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Mechanical properties in Atomic Force Microscopy (AFM) are evaluated with the help of force curves, which are recorded at single or multiple locations of surface area. Here we report a progress in quantitative studies of elastic modulus of polymer materials with the Hybrid mode [1]. Although the mechanical properties can be derived from the deflection-versus-distance (D-v-Z) and amplitude-versus-distance curves obtained in the contact and amplitude modulation modes, the use of the deflection-versus-time (D-v-t) curves recorded in the Hybrid mode is most efficient for on-line mapping of elastic modulus. In this mode a sample vertically oscillates at 1-2 kHz that is well below the resonances of the probe and scanner. In each cycle the probe deflects in response to the tip-sample forces to a set-point deflection level and retracts back. The related D-v-t curve is characterized by the baseline, approach and retracting parts. The wells and slopes of the approach/retract traces reflect the sample adhesion and deformation. When the microscope's optical sensitivity and spring constant of the probe are known, a force-versus-deformation (F-v-h) dependence can be retrieved from the D-v-t curve or related D-v-Z curve. The F-v-h curve can be analyzed with solid state deformation models (Hertz, DMT, JKR) to get the elastic modulus and work of adhesion. Due to 1-2 kHz rate of the D-v-t curves, they can be collected as the maps of up to 1024×1024 points during scanning with 1 Hz rate. A fast AFM controller enables on-line analysis of the force curves and the derived modulus and adhesion maps can be viewed simultaneously with the height image. A correlation between the elastic modulus values of neat polymers obtained in the Hybrid mode and macroscopic studies, and the use the modulus maps for compositional imaging of heterogeneous polymers are the main questions. In addition, we will address the spatial resolution of the mapping.

The samples of polycarbonate (PC) and high-density polyethylene (HDPE) were prepared as blocks (thickness > 1 mm) by hot pressing. A film (thickness > 100 nm) of blend of PS with low-density polyethylene (LDPE) was made by spin-casting on a piece of Si wafer. The Hybrid mode studies were carried out with a scanning probe microscope Next (NT-MDT), which was placed in the electronically-controlled temperature, acoustic and vibrational enclosure. The low thermal drift (<0.2 nm/min) facilitates high-quality studies with scanning rate of 0.4 - 0.8 Hz, particularly, at the sub-micron scale. Si probes with spring constant near 30 N/m were applied. The probe spring constant probe and inverse optical sensitivity of the microscope were measured with thermal tune method. On-line analysis of D-v-t curves was made by fitting a retract part using DMT (Deruigin-Muller-Toporov) model. This elastic deformation model was used because a difference of the approach and retract parts of the cycle for studied polymers was small.

The experimental results are summarized as follows. During scanning of 1 micron area of PC block we changed the force level from 20 nN to 30 nN and to 60 nN. The height image of PC, which shows a sample flat topography, is not shown here. The deformation and modulus maps, which were recorded simultaneously with the height image, are given in Figure 1. As a sample deformation increased stepwise, the elastic modulus stays in the 3.0-3.5 GPa range. The data are in line with the macroscopic PC modulus [2]. The same consistency was observed in our studies of other polymers with elastic modulus from tens of MPa to 7GPa. Study of polymer blends is illustrated by the height image and modulus map with the profile of PS/LDPE blend (Figure 2).

The matrix and inclusions exhibit different modulus with quantitative values seen in the modulus profile. The modulus of the inclusions is below 0.5GPa - close to the macroscopic modulus of LDPE [2]. The matrix is characterized by the modulus of ~ 2.5GPa that matches the modulus of PS [2]. This assignment justifies the modulus mapping as the tool for compositional imaging of polymer blends and block copolymers. The spatial resolution of the modulus mapping was estimated in study of HDPE, which has a high lamellar content. In this case, the height image and modulus map with a profile (Figure 3) show the modulus changes on the 20 nm scale. This example of the mapping demonstrates its high resolution, which is comparable with the tip size. Similar resolution of the modulus mapping of block copolymers will be reported later.
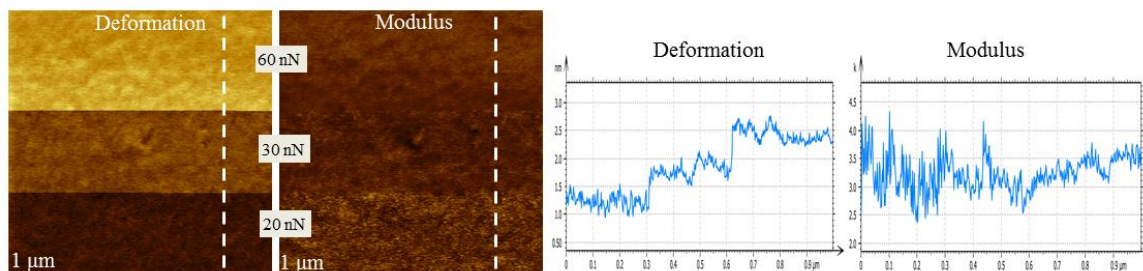

Figure 1. Deformation and modulus maps with the profiles along the white dashed lines for PC. During scanning the tip force has changed step-wise as shown in the maps.
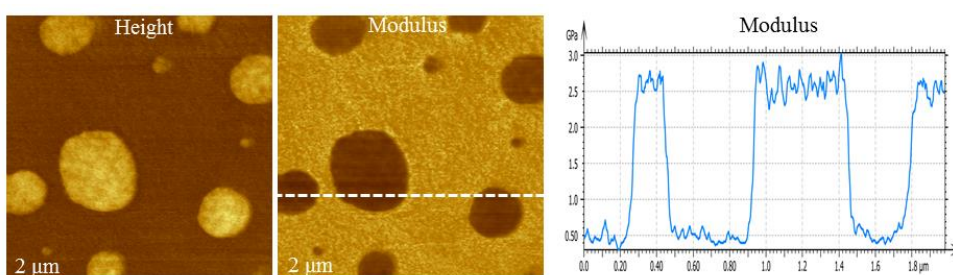

Figure 2. Height image and modulus map with a profile along the dashed white line for PS/LDPE.
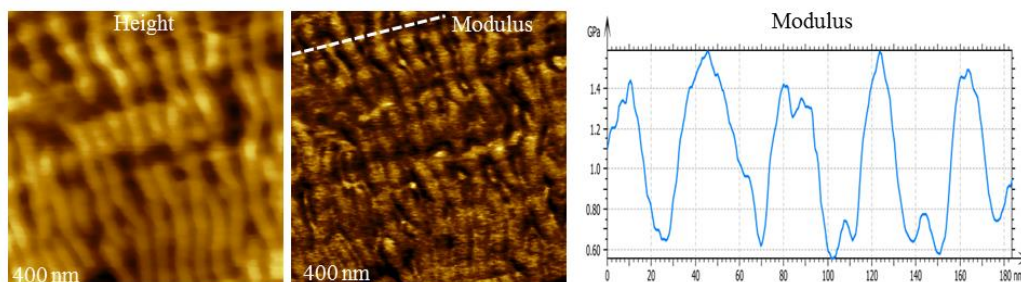

Fig. 3. Height image and modulus map with a profile along the dashed white line for HDPE.

References
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