

Morphology of thin films, prepared from a blend of amorphous (atactic) polystyrene (PS) and low density polyethylene (LDPE) on Si substrate, are characterized by a microphase separation of the components because these polymers are immiscible due to their chemical nature. Several other properties of these polymers are relevant to AFM studies. PS is an amorphous material and does not have any particular structure whereas LDPE being a semi-crystalline polymer is formed of crystalline lamellae, which are embedded in amorphous material. On heating PS exhibits a glass transition point at 100°C – temperature when the glassy polymer becomes rubbery. Near the temperature where LDPE melts. The polymers are also different in mechanical properties: at room temperature typical elastic modulus of PS is 3.0 GPa and LDPE is 0.2 GPa. AFM images of PS/LDPE morphology, which were recorded in AM-PI (aka tapping) mode, are shown in **Figure 1-4**.



Figure 1a-d. Height and phase images of PS/LDPE blend on Si substrate.



The large-scale AFM height images exhibit corrugated surface profiles with domains of regular (circular) and irregular shapes, **Figure 1a, 2a-b**. This morphology suggests a binary composition of the film material that is confirmed by phase image with two levels (bright and dark) of the contrast. Furthermore, the assignment of a dark contrast domains in phase images in **Figure 1b, c, d** to LDPE is facilitated by observations of fine nanostructures inside these domains. These are lamellae of crystalline LDPE. The same lamellae are well resolved in the phase image, which was recorded on a raised surface area in **Figure 2d**. One also sees small PS domains surrounded by lamellar network.



Figure 2a-d. Height and phase images of PS/LDPE blend on Si substrate in AM-PI mode.

The phase contrast can be assigned to differences of elastic modulus of the components and it becomes more pronounced at high force imaging, **Figure 3a-f**. At gentle imaging (set-point amplitude is close to free amplitude) the phase variations barely differentiate the sample composition, **Figure 3a-b**.



As set-point was reduced, LDPE lamella, which are embedded in amorphous polymer, and featureless PS blocks are seen in **Figure 3f.** The sample is also handy for proof of elastic modulus mapping in D-CNT (aka PeakForce[™]) mode.



Figure 3a-d. Height and phase images of PS/LDPE blend on Si substrate in AM-PI mode.

Low Force

High Force

High Force



The sample of PS/LDPE blend can be subjected to heating above 100°C and structural transitions of the components related to softening, melting and re-crystallization. These transformations can be observed directly during heating/cooling or afterwards when the sample is again at room temperature. The latter case is presented by AFM images in **Figure 4a-d**. The images demonstrate several changes caused by melting and re-crystallization of LDPE domains inside PS matrix. Melting of LDPE domains was accompanied by a partial polymer dewetting on Si substrate and the neat substrates became seen in the locations previous fully occupied by LDPE domains. These domains have recrystallized and two different crystalline morphology is observed in these domains. The large domains became the stacks of edge-on standing lamellae, which extend along the whole domain. The edge width, which represents the lamellae thickness, is ~15 nm. The smaller LDPE domains, such as one magnified in the insert of **Figure 4d**, are formed from the bundles of tiny lamellae.



Figure 4a-d. Height and phase images of PS/LDPE blend on Si substrate in AM-PI mode. The sample was heated to 100°C and cooled back to room temperature.