Characterization of Polyethylene with DriveAFM

Polyethylene

Polyethylene (PE) is a semicrystalline polymer and is one of the most widely produced plastics globally for use in consumer goods and packaging with wide-ranging applications. Shopping bags, milk bottles, storage containers, toys, wires, and cables all employ polyethylene. PE is also a key component of fuel tanks and storage tanks in automobiles. The attractiveness of polyethylene lies with the combination of its physical appearance, mechanical properties such as toughness and stiffness, easy processability into various structures including films, and low manufacturing cost.

Polyethylene is classified by its density and branching, with the various kinds of PE having different mechanical properties and processability. High density polyethylene (HDPE) is a linear structure of ethylene shown in Figure 1a which results in a much higher degree of crystallinity. Linear low-density polyethylene (LLDPE) has some branching off this main backbone, as shown in the schematic in Figure 1b, and has similar strength as HDPE but is much more flexible. Low density polyethylene (LDPE) has significant branching off its main chain as shown in Figure 1c which results in lower crystallinity and greater flexibility. The mechanical properties for these different PE's vary significnatly, for example, the modulus of LDPE ranges from 102-240MPa while the linearly and organized HDPE has an elastic modulus of 960-1000MPa.

Polymer crystallization of PE occurs through a complex mechanism involving both partial alignment of their molecular chains into ordered structures, as well as amorphous regions with less ordered structure. The ordered structures occur through chain folding and form regions called lamellae. Chain folding proceeds more easily among linear chains (such as HDPE) and it is restricted for branched chains (such as LDPE). In dilute solutions of linear PE chains, the multiple chain folding leads to a formation of crystalline lamellae with the lamellar thickness defined by the straight portion of the chain. When crystallization takes place in the melt, or in concentrated polymer solution, different lamellar structures can form. They can be reduced from 2D platelets to 1D fibrils and even nanoscale grains.

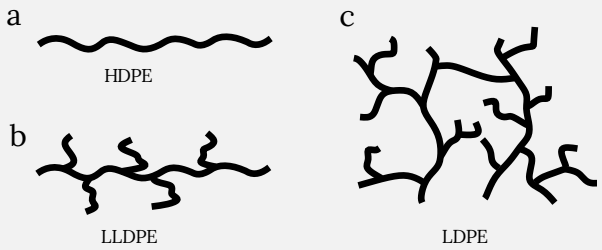

Figure 1.: Types of polyethylene: (a) high density polyethylene (HDPE) linear, no branching of molecular chains; (b) linear low density polyethylene (LLDPE), short branched chains; (c) low density polyethylene (LDPE) long branched chains.

Characterization of polymers

Polymers have nanoscale morphology that require high resolution methods to properly discern its structures. However, high resolution microscopy methods such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM) rely on impinging of electrons with the sample to generate contrast, an approach that does not always work well for polymer materials that do not have much chemical heterogeneity. Since AFM relies on a mechanical interaction between the tip and sample, it is ideal for imaging and characterization of polymers, as they

exhibit a large spectrum of mechanical properties such as adhesion and modulus, which then serve as a basis for contrast and differentiation in the AFM image.

The DriveAFM was used to characterize different grades and blends of this ubiquitous and important polymer. All images were collected using CleanDrive technique to deliver superior performance and data quality. CleanDrive actuates the cantilever photothermally providing cleaner and more reliable cantilever tunes over conventional piezo actuation. The cantilevers used in this study were commercially available soft dynamic mode cantilevers with nominal stiffness of 1-7 N/m.

HDPE

The surface of an HDPE sample is shown in the height images in Figures 2a and 2c; the

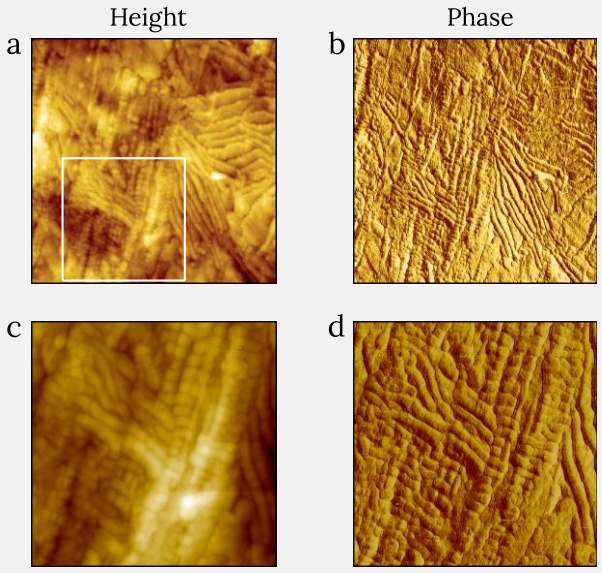

Figure 2.: Height (a) and phase (b) images of melt-crystallized HDPE sample measured with CleanDrive technique. Image size: 1.2 x 1.2 μm², height range: 34 nm, phase range 18°. White square in (a) shows the area where images (c) and (d) were recorded. Image size for (c) and (d) is 0.6 x 0.6 μm², height range: 42 nm, phase range 10°.

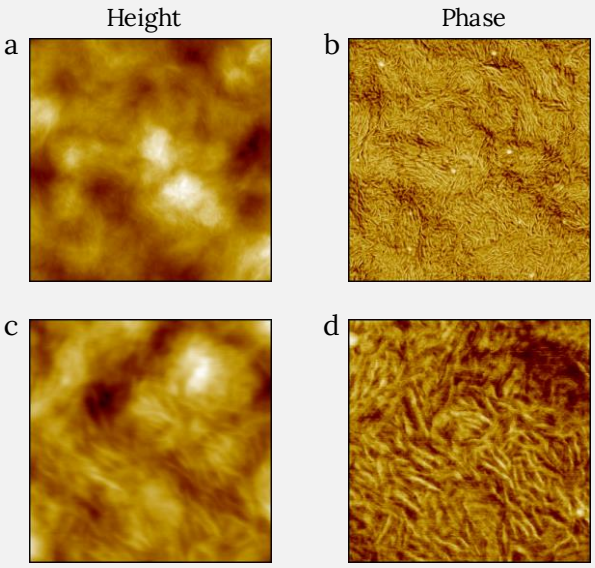

Figure 3.: Height (a) and phase (b) images of LDPE film measured with CleanDrive technique. The sample was prepared by spin-cast of its toluene solution on Si substrate. Image size: 2 x 2 μm², height range: 75 nm, phase range 55°. (c) and (d) images were recorded on the same sample with the image size 0.6 x 0.6 μm², height range: 33 nm, phase range 25°.

HDPE surface formed by melting the polymer between two glass slides followed by subsequent cooling These structures observed in the AFM images in Figure 2 are characterized by multiple sequences of lamellar blocks (width of ca. 25 nm) with some of them forming tightly packed ribbons as can be observed in the 1.2 μm image in Figure 2a.

LDPE

The surface structure of LDPE reveals a different morphology as seen in Figures 3a, and 3c. This film was prepared by spin-casting a hot solution of PE dissolved in toluene onto a silicon substrate. The surface of LDPE is made of multiple fibrils with different orientations, which are best resolved in the phase images (Figure 3b and 3d). At higher magnification (Figure 3c and 3d) one can distinguish thicker fibrils with width of ca. 15 nm and thin fibrils with width

below 10 nm. They are not tightly packed in contrast to lamellar blocks of HDPE.

LLDPE

LLDPE chains have less branching than LDPE, but their density and elastic modulus are quite similar to LDPE. The morphology of an LDPE film is shown in Figures 4a-d; this film was prepared in a manner similar to LDPE by spin-casting a hot toluene solution in which the PE was dissolved onto a silicon substrate. In contrast to the LDPE film, the surface fibrils of LLDPE alternate with wider structures, which are seen as raised features in height image (Figure 4a).

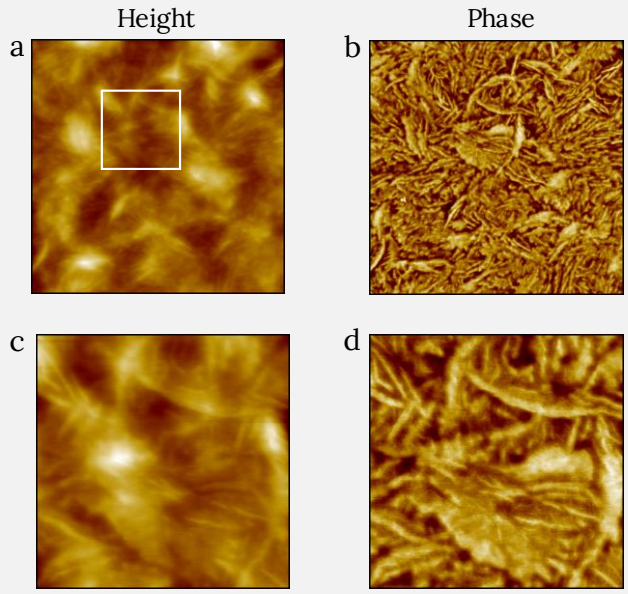

Figure 4.: Height and phase images of LLDPE film measured using CleanDrive technique. The sample was prepared by spin-cast of its toluene solution on Si substrate. Image size: 2 x 2 μm², height range: 76 nm, phase range 65°. White square in (a) shows the area where images (c) and (d) were recorded. Image size for (c) and (d) is 0.6 x 0.6 μm², height range: 32 nm, phase range 57°.

Heterogenous polymer blends

In addition to high-resolution visualization of surface structures, which was demonstrated with images of lamellar order in HDPE, LDPE and LLDPE samples,

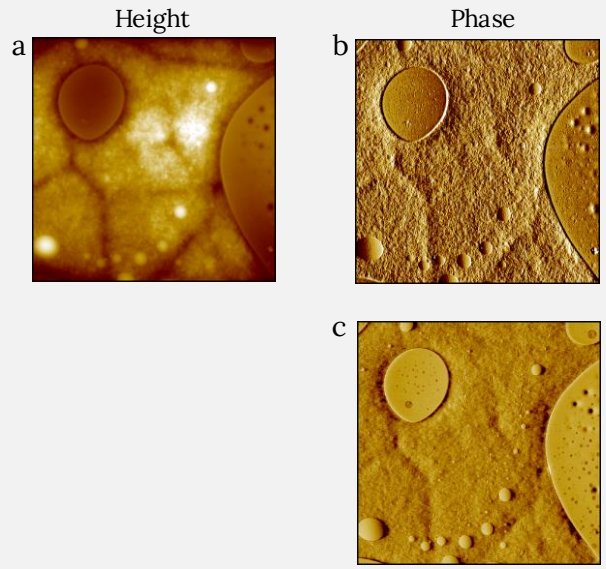

Figure 5.: Height (a) and phase (b,c) images of PS and LDPE blend film measured with CleanDrive technique. The sample was prepared by spin-cast of its toluene solution on Si substrate.
Two phase images were measured with different tip forces by varying the setpoint amplitude of cantilever oscillation. Lower setpoint corresponds to higher force (b: 65%, c: 50%). Higher force image shows higher phase contrast. Image size: 10 x 10 μm², height range: 120 nm, phase range 25° (b) and 90° (c).

AFM provides compositional imaging of heterogeneous polymer systems (blends, block copolymers, composites, filled rubbers) an important capability for industrial researchers working on the synthesis, design, and formulation of plastic materials as well as their applications. A film composed of a blend of LDPE with atactic polystyrene (PS) is analyzed with AFM to discern morphology and distribution of the two materials this blend.

A series of height and phase images of this PS/LDPE blend is shown in Figures 5a-c and Figures 6a-f. The elastic modulus of PS is ca. 3 GPa that is approximately 10 times higher than that of LDPE. Height image of PS/LDPE blend (Figure 5a) shows a relatively flat surface with several round-shaped domains embedded into a surrounding matrix. The different phase contrast between the two materials is easily

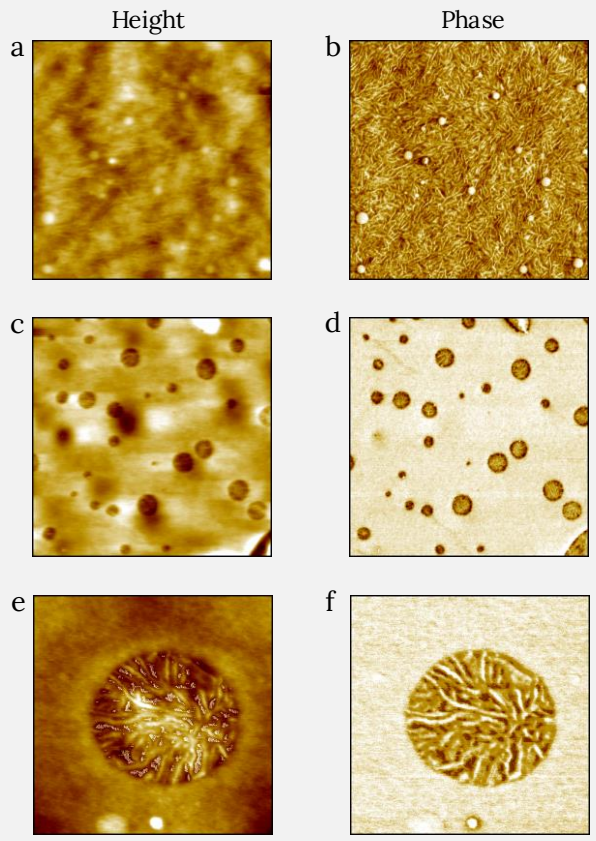

Figure 6.: Images of PS and LDPE blend film measured with CleanDrive. The sample was prepared by spin-cast of its toluene solution on Si substrate. (a) and (b) show the height and the phase image of the LDPE matrix (zoom between the round domains in Figure 5) with fibrils clearly visible in the phase image. Image size: 2 x 2 μm², height range: 30 nm, phase range 55°. (c) and (d) show the height and the phase of higher resolution images of the surface of one of the round PS domains from Figure 5. The flat area in the phase image shows microscopic dark inlusions of LDPE material with additional contrast. Image size: 2 x 2 μm², height range: 10 nm, phase range 50°. (e) and (f) show the height and the phase images of a zoom on one of the inclusions from (c) and (d), showing that the increased contrast orginates from a clearly resolved fibrillar structure. Image size: 0.6 x 0.6 μm², height range: 6 nm, phase range 110°

observed when setpoint amplitude was half of the amplitude of the probe free oscillation, as in Figure 5c. Higher resolution 2 x 2 μm² images were then collected on the blend's matrix (Figures 6a-b) and the round domain (Figures 6c-f). The matrix material (6a-b)

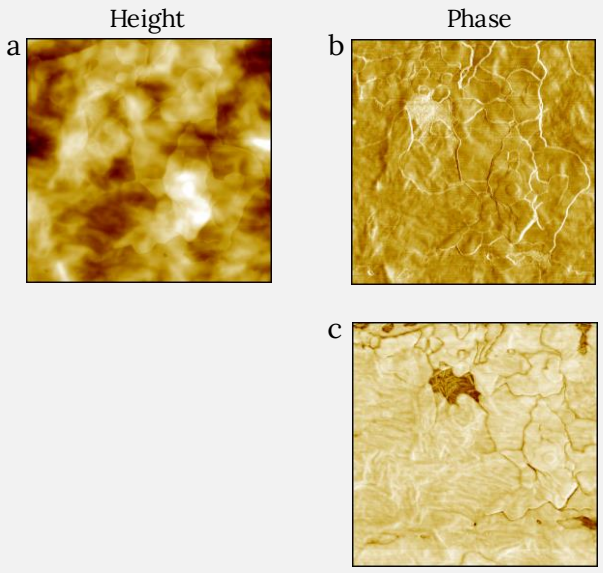

Figure 7.: Height (a) and phase (b) and (c) images of LDPE packaging film measured with CleanDrive. The phase images were recorded at low and raised tip-sample forces by varying the setpoint amplitude of cantilever oscillation. Lower setpoint corresponds to higher force.
A higher force image (c) demonstrates a missing platelet in the film coating – area with darker contrast. Usual LDPE fibrils are visible in this patch. Image size: 2 x 2 μm², height range: 50 nm, phase range 17° for (b) and 112° for (c).

reveals fibrillar structure that is indicative of lamellar morphology of LDPE. This LDPE matrix also includes bright circular domains with the diameters ranging from 20 nm to 110 nm, which represent individual PS droplets. The zoom in on the large of the circular domains from Figure 5 are shown in the images of Figures 6c-f and reveal a smooth morphology with bright yellow contrast, punctuated by smaller

dark round microstructured domains that range in diameter from 20 nm to 210 nm. A zoomed in 0.6 x 0.6 μm² image of one of these dark inclusions is shown in Figures 6e-f and shows a thin, fibrillate-like lamellar structure of LDPE. The widths of the fibrils are smaller than that observed in the LDPE matrix (Figure 6a-b).

LDPE Packaging

PE is widely used as packaging material and LDPE is especially popular for packaging of bread, frozen food, and for shopping bags. These packaging materials are typically marked on the bags with the recycling label accompanied by “#4” for LDPE. An LDPE commercial bag was thus analyzed with the DriveAFM. The height and phase images, which were recorded at low and high tip-sample forces, are shown in Figure 7a-c. The low-force imaging revealed that top surface is enriched in the platelet structures with their contours and edges are well distinguished in the phase image (Figure 7b). In this image there is a brighter patch that hints on a dissimilar material. Indeed, the phase image at the higher force (Figure 7c) shows much darker contrast and individual brighter fibrils. Most of the surface of this packaging film is coated with clay platelets that modifies surface adhesion toreduce sticking of the packaging film in the bags.

Conclusion

AFM is a powerful tool for high resolution imaging and characterization of polymer materials, where mechanical contrast is the key to discriminating key structures and morphology. Here, AFM is applied to the characterization of various grades of polyethylene as well as PE-containing blends, one of the most ubiquitous plastics in the consumer market. Lamellar structure of the polyethylene is clearly observed in the various images, providing insight into the overall packing and organization of PE. This study reveals the power and utility of AFM to evaluate the structure-property relationships of important materials such as polyethylene, which can be used to advance the understanding and formulation of such materials into end-use products.

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