# ATOMIC FORCE MICROSCOPY STUDIES OF PHASE ORDERING IN POLYMER BLENDS AND CLAY-FILLED SYSTEMS

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## Introduction

Many industrial applications require a control of the morphology of thin polymer films. The morphology of such films depends on many factors: method of formation (dipping, evaporation, spin casting), tendency of film components to phase separate or dewet, the crystallization of film components, presence of filler particles, etc.

In the present note, we explore the use of Atomic Force Microscopy (AFM) as a tool for probing changes in film morphology that accompany phase ordering processes (phase separation, crystallization). We also investigate how the presence of clay filler particles in polymethylmethacrylate films modifies the local "stiffness" and morphology.

## Experimental

All of the AFM measurements described below are carried out in air using a Dimension 3100 from Digital Instruments operating in a Tapping Mode™ [1]. Integrated silicon tips with a radius of curvature of about 10 nm and cantilevers (model TSEP) with a nominal spring constant 30 Nm$^{-1}$ are used in our measurements. In the Tapping Mode™, the cantilever oscillates vertically at a drive frequency close to its resonance frequency and contacts the sample surface briefly in each cycle of oscillation. As the tip approaches the surface, the vibrational characteristics of the cantilever oscillation (e.g. amplitude, resonance frequency and phase angle) change due to the tip–sample interaction. "Height" images are obtained by using a feedback loop that keeps the amplitude at a constant value $A_{sp}$ by vertically translating the sample with the piezoelectric scanner. The feedback loop is controlled by the set–point amplitude ratio $r_{sp} = A_{sp}/A_0$ where $A_0$ is the amplitude of free oscillation. The recorded "height" images are the vertical displacements of the piezoelectric scanner. Simultaneously, the phase of the cantilever oscillation relative to the signal exciting the piezoelectric driver can be measured. The corresponding recorded images represent the phase of the cantilever oscillation and are called "phase" images [2-4]. "Amplitude" images are obtained when the feedback loop is not connected. The amplitude can then vary and the resulting image reflects this variation.

As mentioned by Aime et al. [5-7], it is essential to understand changes of the amplitude and phase as function of the tip–surface distance by making approach and retraction curves. These curves allow us to understand the origin of the contrast in both the "height" and "phase" images.

Michel [4] has shown that the images of the surface of a triblock copolymer, PS–PI–PS, obtained in the repulsive interaction mode, exhibit a contrast that is due to change of the local mechanical properties. By varying the experimental parameters, the contrast of both "height" and "phase" images can be monitored and good contrast can be achieved. As an example, for a set–point amplitude ratio $r_{sp} = 0.95$ and a drive frequency (F) of 263.5 KHz, the contrast varies with the free amplitude $A_0$. For example, both "height" and "phase" images show similar contrast for $A_0 = 28.3$ nm [same localization of the black (PI, elastomer) and white (PS, glassy) areas; lateral resolution is also the same]. For $A_0 = 10.6$ nm, the contrast of the "height" images is weak while the contrast of the "phase" images is enhanced and the lateral resolution is significantly increased. Thus, the local mechanical properties are imaged with the best contrast using the "phase" mode with a small free amplitude $A_0$ in the case of this triblock copolymer material.

In the following work, different values of the free amplitude $A_0$ and set–point amplitude ratios $r_{sp}$ have been used, depending on the material and the type of measurement, topographical or mechanical.

## Results and Discussion

**Discrimination between amorphous and crystalline regions in a semi-crystalline polymer film.** The crystallization of a polymer film (or even bulk polymer materials) often occurs far from equilibrium and a wide range of film structures can be obtained by varying the conditions of crystallization. These variations in film morphology have a large impact on the film properties (e.g. barrier properties, mechanical strength, etc) that are important in applications.

A semicrystalline polymer such as polyamide 6 (PA 6) normally crystallizes in the form of spherulites. There are many outstanding questions about how these crystals grow. We focus on utilizing AFM to map out the morphology of the PA6 from the spherulitic scale to the lamellar one. **Figure 1a** shows the spherulitic morphology of an isothermally crystallized PA6 sample. The dark pearl-shaped region is characteristic of the "eye" of the spherulite. No fine structure can be distinguished in this image. However, using Phase Imaging (**figure 1b**), it is possible to reveal the fine morphological details of the PA 6 spherulite. The dark regions in the figure 1b are characteristic of the inter-lamellar amorphous regions within the spherulite. Moreover, individual lamellae (bright features in **figure 1b**) can be imaged. Their size was determined by analyzing the profile of phase image data across the lamellae. This method yields a value of the long period (L) that agrees well with X-rays experiments, $L \approx 10$ nm.
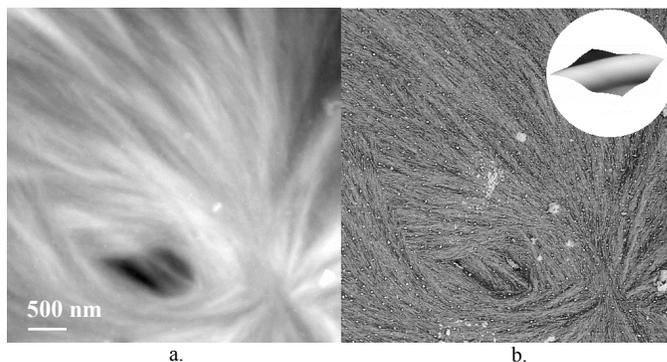


**Figure 1.** AFM image of the spherulitic morphology of an isothermal crystallized Polyamide 6 at $T_c = 152°C$. a) "Height" image, b) "Phase" image. F = 263.8 KHz, $A_0 = 18.6$ nm and $r_{sp} = 0.7$. Inset of figure 1b shows an individual lamella. Fine details are visible by Phase Imaging™.

**Interaction between phase separation and crystallization in thin polymer blends.** Polymer blends characteristically tend to phase separate due to the low entropy of mixing and blend separation has been shown to lead to a wide range of film morphologies in thin blend films. For thicker films it is usual for the components to enrich near the boundaries and for composition waves to form so that the local composition oscillates near the film boundary along the coordinate normal to the plane of the film [8-9]. In films thinner than the wavelength of these compositional oscillations it is possible for phase separation to occur within the plane of the film. AFM has been previously utilized to study the kinetics of phase separation in these "ultra-thin" films [10-11].

In the present case, we consider an added feature where both phase separation and crystallization simultaneously occur. The crystallization process rather than the film boundary is the source of the symmetry breaking perturbation that biases the films structure. **Figure 2a** shows a topographic image of a film of polyethyleneoxyde (PEO) and polymethylmethacrylate (PMMA) spun cast on an acid-cleaned silicon substrate. The film thickness is approximately 150 nm and clay particles (5% by mass of polymer blend) were added to nucleate crystal growth. We observe the growth of large-scale dendritic crystals at 30/70 relative PEO/PMMA composition (PEO crystallizes into a spherulitic form for a relative concentration less than 50/50).

A novel feature is revealed in our AFM images of the dendrites at higher magnification. Figure 2b shows that the dendrite has a "corrugated" form at a 1 µm scale. This morphology is representative of previous studies of phase separation in blend films using AFM [12-13]. We then prepared a PEO/PMMA blend film without the nucleating clay agent (but otherwise identical) and found a corrugated morphology as in **figure 2b**, but a large scales crystallization morphology was not observed. In this case, the polymer blend phase separates *within* the growing dendritic crystal. We investigate the evolution of the roughness of the film using AFM and found that the surface height features depend on the molecular mass of the PMMA. In a separate paper, the dynamics of the dendrite growth is examined by optical microscopy. Studies of the dendrite growth using AFM would provide many

further details in the dynamics of non-equilibrium crystal growth. We note that the slow rates of crystallization and high degrees of supercooling can be obtained in these materials, making these materials potentially important for fundamental studies of crystallization.
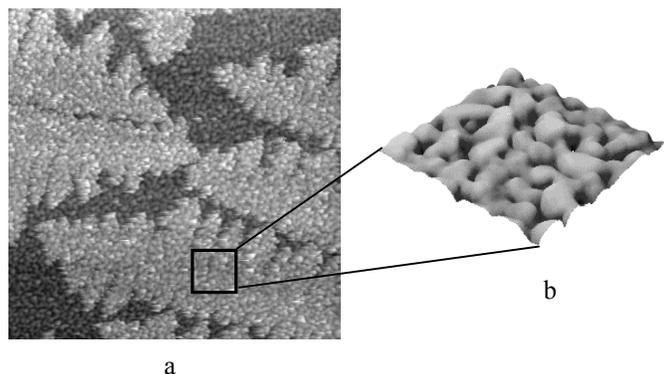


**Figure 2.** "Height" AFM image of the dendritic morphology for a clay filled PEO/PMMA blend. a) 20 μm x 20 μm, b) 3 μm x 3 μm. Phase separation is occuring within the PEO-rich dendrite.

**Heterogeneity in polymer properties arising from filler particles.** Polymer materials are usually mixed with other materials to change their properties (pigments, hard fillers that make the polymer more conductive thermally or electrically, fillers to enhance the hardness or toughness of the polymer material, etc). An important question is how this heterogeneity alters the *local* properties of the polymer material. We utilize AFM to examine the simple question of how the local stiffness of the film becomes modified with the inclusion of clay filler particles.

A common synthetic polymer PMMA is employed and we add the same filler as described in the previous section. The cast film is very smooth and the topographic AFM measurements show a film roughness scales of a few nanometers. AFM measurements are then performed in the "phase imaging" mode. We observe dark regions having dimensions of the clay particles (as measured by using TEM) and the particles are surrounded by PMMA regions that have a different relative stiffness (white regions in **figure 3**) than the polymer far away from the particles. Thus, we observe that the local stiffness of the film is perturbed by the presence of filler particles.
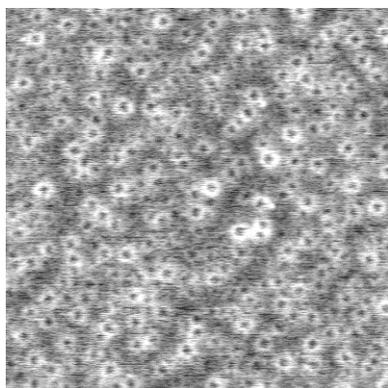


**Figure 3.** "Phase imaging" picture of a clay filled PMMA film (5 μm x 5 μm). TEM images of the clay particles show that they have an average size of about 100 nm.

A finite-element calculation for an elastic continuum containing hard and soft inclusions has been made to analyze and understand the AFM data. The calculations involve a similar deformation as employed in the AFM measurements and also reveal regions about the particles in which the local "stiffness" is changed. The large scale over which the stiffness changes occur in both the measurements and calculations is notable (comparable to the size of the filler particles).

**Conclusions**

AFM is an important tool for probing the fine structure of multiphase materials. This method should help us to obtain an improved understanding of phase ordering in polymer materials – both equilibrium and dynamical properties. Such studies are important more generally for developing a greater understanding of phase separation and crystallization in polymeric materials. Polymer systems are interesting for fundamental studies by AFM because of their large viscosity and because of the large time-scales normally found for phase ordering processes in these materials. We envision that AFM and related probe microscopes will become powerful tools for studying local property changes that occur in thin polymer materials.

**References**
(1)  Certain commercial materials and equipment are identified in this article in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessary the best available for this purpose.
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