



# Studies of Polyvinyl Alcohol under Temperature and Humidity Control

## Application Note

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The atomic force microscope (AFM) is capable of imaging insulating materials with atomic resolution, thus making it an excellent tool for studying polymer surfaces. Atomic force microscopy can be used to measure many properties of polymers as well as surface structure, including friction, adhesion, and viscoelasticity. All of these measurements can be done without damaging preparative processes, such as metallic coating or placement in vacuums, which are common with many other analytical techniques. Additionally, AFM measurements can be performed at the molecular level.

Atomic force microscopy was first applied to a polymer surface in 1988 (1); it has subsequently become a standard research tool in the field. This application note will focus on the utility of AFM for investigating various temperature- and humidity-dependent properties of polymers.

It is well known that both the environment and the history of a polymer can drastically influence its morphology and its material properties (2). Typically, annealing

will drive polymer chains into ordered (crystalline) conformations, depending on interacting chemical functional groups, structure, and stereochemistry of the polymer (2). Not surprisingly, heating a polymer above its glass transition temperature ( $T_g$ ) gives the polymer chains the mobility to migrate into more energetically favorable orientations. For example, polyvinyl alcohol  $-(CH_2CHOH)_n-$  (PVOH) crystallizes upon heating. For a PVOH sample with only 1-2% water content, annealing at 90°C for up to 10 hours yields approximately 38% crystallinity, whereas heating PVOH to 200 °C for a few minutes produces approximately 60% crystallinity (3).

PVOH is somewhat special in that crystallization can occur in the atactic form. This is attributed to hydrogen atoms and hydroxyl groups ( $-OH$ ) having roughly similar sizes, which allows the close, regular packing of chains. Strong hydrogen bonding between  $-OH$  groups on neighboring chains also tends to hold the molecules in a regular structure despite the lack of stereoregularity (3).

For hydrophilic polymers such as PVOH, relative humidity (RH) exerts as strong an influence on the polymer's properties as temperature. When exposed to high humidity, some polymers can have water content of more than 25% (4). Absorption of water causes hydrophilic polymers to swell and elevates the mobility of individual polymer chains. The higher mobility allowed by the solvent greatly affects the polymer's properties. In particular, the glass transition temperature can be lowered, or "plasticized", by more than 60 °C with a solvent (4).

To demonstrate the capabilities of controlled-environment atomic force microscopy, two experiments using a PVOH film were conducted. The film was imaged in situ under precise temperature and humidity control using an Agilent atomic force microscope (AFM) with an environmental chamber and a temperature-controlled sample stage.



### Temperature

Figure 1 presents lateral force images of a PVOH sample acquired at (a) 22 °C and then at (b) 60 °C. Friction, or lateral force, images were used instead of topography since they often yield better contrast of different morphologies. This is primarily because softer, amorphous regions often produce more dissipative responses than the relatively stiffer, more crystalline regions (5). Humidity was kept constant during imaging, thus resulting in a  $T_g$  of approximately 25 °C. Subtle structural changes are especially evident in lateral force images; rounded structures have become longer and thinner, which is characteristic of nanocrystalline regions.

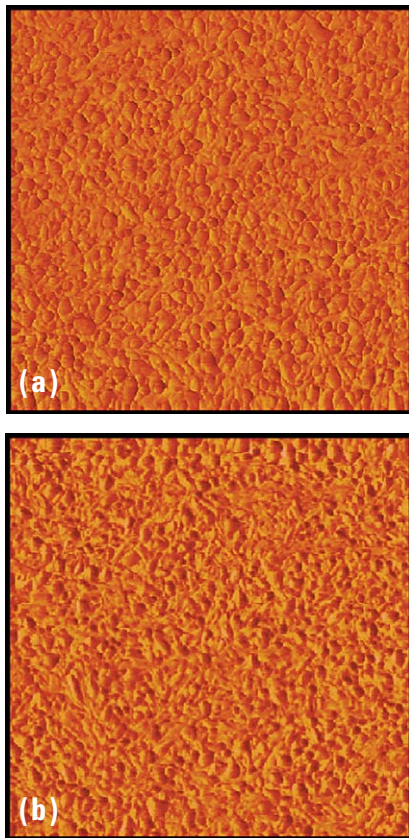


Figure 1. Lateral force images of polyvinyl alcohol acquired at (a) 22 °C and then at (b) 60 °C. Both images are 1.2  $\mu\text{m}$  x 1.2  $\mu\text{m}$ .

As expected, the polymer started to crystallize slightly when the temperature was elevated. In both images 1(a) and 1(b), the applied force was held constant and the tip-sample adhesive forces were determined to be constant, suggesting that the contact zone did not change appreciably during imaging.

### Humidity

Figure 2(a) shows topography and friction images of PVOH at 85% RH, where it has approximately 20% water content (4). After exposure to this moist air, the humidity was lowered to 10% RH and the sample was re-imaged. Figure 2(b) reveals large crystalline regions on the surface of the PVOH film at 10% RH.

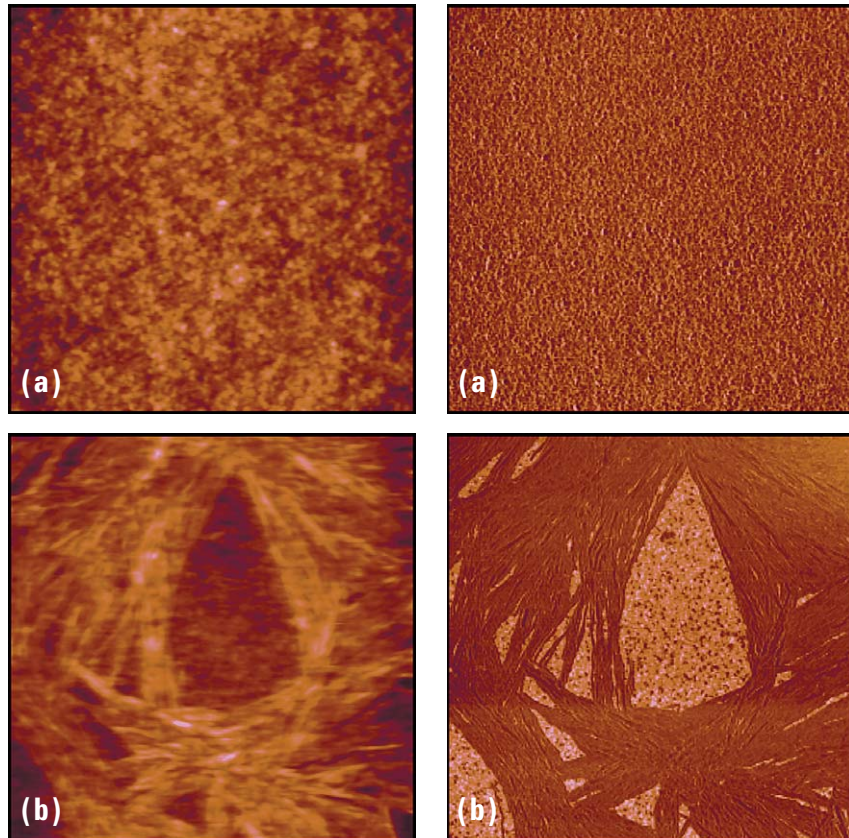


Figure 2. Topography (left) and lateral force (right) images of polyvinyl alcohol acquired at (a) 85% RH and then at (b) 10% RH. All images display the same area and are 5  $\mu\text{m}$  x 5  $\mu\text{m}$ .

Once again, surface crystallization occurred, but this time crystallization was attributable to extra mobility afforded by the solvent. The swollen film allowed reorganization of polymer chains and then, upon drying, locked a more highly ordered structure in place. The more crystalline film was less dissipative than the amorphous film.

### Conclusion

The *in situ* control of temperature, humidity, and other environmental parameters is essential when imaging polymers that are sensitive to their surroundings. *In situ* environmental control eliminates many experimental limitations, thus allowing more thorough investigations of polymer morphology and kinetics.

## References

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