

MAPPING CHEMICAL HETEROGENEITY OF POLYMERIC MATERIALS WITH CHEMICAL FORCE MICROSCOPY

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Introduction

The ability to probe chemical heterogeneity with nanometer scale resolution is essential to developing a molecular-level understanding of a variety of phenomena occurring at surfaces and interphases of polymeric materials, including adhesion, corrosion protection by organic coatings, and photodegradation. However, current analytical techniques lack the sensitivity and/or spatial resolution to fully understand these phenomena. For example, the degradation (thermal, photo, and hydrolytic) of polymers and polymeric materials has been observed to occur non-uniformly in which nanometer pits are formed locally, which deepen and enlarge with exposure. The chemical nature of the locations in a polymer film at which the degradation initiates is not exactly known.

The use chemically-functionalized probe in an AFM (chemical force microscopy (CFM))¹⁻³ has been shown as an excellent technique to discern hydrophilic and hydrophobic regions in a surface at the nanoscale spatial resolution. Much of current research using functionalized AFM tips has been performed in solvents using prefabricated, well-defined patterned SAM samples. However, for polar polymeric materials and biomaterials, solvent is not a desirable medium. Our research has shown that the chemical contrast of images obtained by hydroxylated or chemically-modified AFM tips can be greatly enhanced by increasing the relative humidity of the tip-sample environment.⁴ This study describes the use of this approach to map chemical heterogeneity in polymeric materials using both unmodified hydroxylated and chemically-modified AFM tips.

Experimental Conditions

Relative humidity (RH) of the tip-sample environment was controlled using a humidity generator and NIST-patented environmental chamber, shown in Fig. 1a and 1b, respectively. The humidity generator was designed based on the principle of dry air/moisture-saturated air mixture. The RH of the air pumped into the humidity chamber could be controlled and maintained to within 3 % of the preset values of between 0 % and 90 %. The environmental chamber is comprised of two major parts: the main chamber within which the AFM scanning head assembly is placed, and an integrated sample platform and spring-loaded base plate that allows samples to be loaded and unloaded. The chamber encloses the AFM scanner, tip assembly, optical lever detection system, sample, and the side-mounted optical microscope. It also contains one inlet and one outlet to allow air of desired RH to enter the chamber. The humidity in the chamber is measured by a humidity sensor placed at the outlet.

Results and Discussion

In order to better understand the effects of the tip-sample environmental RH on the chemical contrast enhancement for polymeric materials, such effect for less complex, well-define materials was investigated; one example is displayed in Figure 2. This is a hydrophilic (COOH terminated) self-assembled monolayer (SAM) laid out in a solid field adjacent to an area patterned with μm -scale lines. Subsequent deposition of a hydrophobic (CH_3 terminated) SAM from solution fills in the un-printed portions of the patterned area and forms another solid field opposite the first. Next, a gradient of UV/Ozone exposure is applied to the specimen along the direction perpendicular to the pattern lines. UV/Ozone exposure converts the CH_3 terminated SAM into oxygen-containing hydrophilic species, with the amount of conversion depending upon the exposure time.

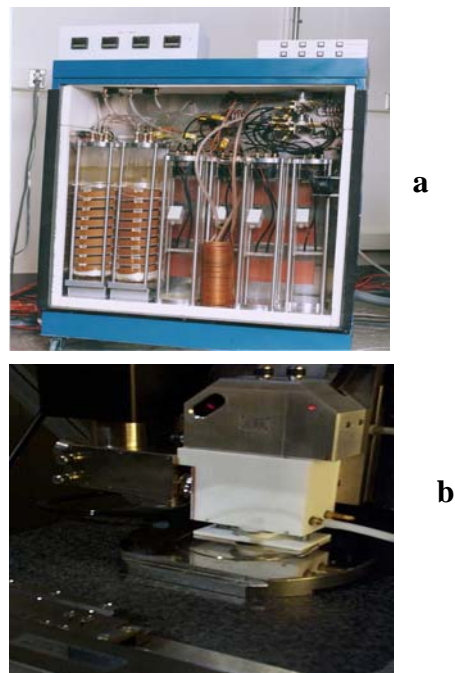


Figure 1. Humidity generator (a) and AFM environmental chamber (b) for studies of chemical heterogeneity.

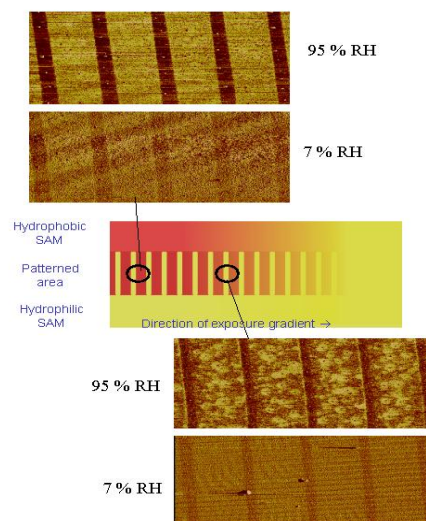


Figure 2. Effect of relative humidity on AFM phase image contrast for different hydrophilic/hydrophobic gradients obtained using an unmodified silicon tip (stripe: hydrophilic; matrix: hydrophobic).

The phase images shown in Figure 2 were obtained by tapping mode AFM and using an unmodified Si tip. Since at ambient conditions, Si substrate is normally covered with a layer of hydroxylated- SiO_2 (approximately 5-6 OH groups per 100 nm^2), Si tip is considered as a OH-terminated AFM probe. As shown in Figure 2, at low RH, essentially no contrast was observed even when the hydrophilic-hydrophobic gradient is greatest (top images). At high humidity, a distinction between the hydrophilic and hydrophobic is still observed even when the hydrophilic-hydrophobic gradient is low (bottom image).

(A) -CH₃ terminated tip (B) -COOH terminated tip

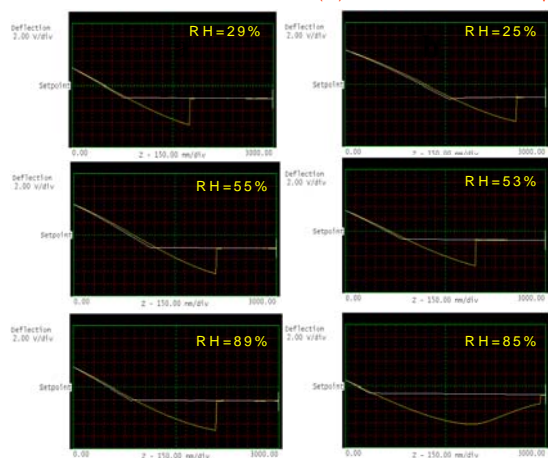


Figure 3. Force-displacement curves for (A) -CH₃ terminated tip on Si substrate (B) -COOH terminated tip on Si substrate. Deflection is 2.00 v/div for all plots.

Extensive AFM results (not shown) obtained using COOH and OH-terminated AFM tips in the friction mode showed similar RH effect. However, very little contrast enhancement was observed for the CH₃ -terminated tip. Similar effects are observed for tip-sample interactions, as shown in Figure 3, which shows force-displacement curves obtained using hydrophilic and hydrophobic AFM tips scanned on a solvent-cleaned, unmodified Si substrate at different RHs. For hydrophobic tips, RH affects the interactions very little. However, at elevated RH (>65%), the tip-sample interactions of the hydrophilic tips increase with increasing RH. These results seem to explain the reason for RH to enhance chemical contrast between the polar and nonpolar regions in a material. We hypothesize that only the hydrophilic regions (water adsorbing sites) on a sample or a tip adsorb polar water molecules through hydrogen bonding, while the hydrophobic regions, which contain very weak dispersion forces, do not adsorb water. The result is an increase in the level of hydrogen bonding interactions between the hydrophilic tip and hydrophilic surface with increasing RH – an effect that would not occur between non-polar tips and non-polar specimen domains or between the non-polar tip and polar samples. It should be noted that the functional groups of hydrophilic surfaces, such as NH₂, OH, and COOH, are highly hydrogen-bonded and tend to associate weakly with other chemical species except strong electron donors such as water. For SiO₂ surface, two thirds of the SiOH groups are hydrogen-bonded, and water preferentially reacts at these sites⁵. Once water is adsorbed the site then has a free active hydrogen for adsorption through hydrogen bonding. This water-induced increase of the hydrogen bonding sites explains the interaction increase with increasing RH for silicon substrate. The results of Figure 2 and 3 clearly show that the distinction between the hydrophilic and hydrophobic domains in a thin organic film can be distinguished by the functionalized tips and that the AFM hydrophilic-hydrophobic contrast is enhanced by increasing RH.

The applications of RH-enhancement technique for mapping hydrophilic and hydrophobic domains in polymeric samples are demonstrated in Figures 4 and 5. These images were obtained by tapping mode AFM and using unmodified hydroxylated Si tips. Figure 4 shows the effect of RH on chemical contrast of a 50/50 mass fraction blend sample of polystyrene (PS) and poly(acrylic acid) (PAA) spin coated on a silicon substrate. The thickness of this film was approximately 200 nm. In this figure, micrographs on the left represent topography data, and right-hand micrographs represent phase data, which is related to mechanical properties and adhesion. Micrographs of the blend specimen were obtained at ambient conditions, 86 %RH, <1% RH, and back at 86% RH respectively (the last images were used to test the reversibility of the contrast). The results show that the hydrophilic PAA regions (bright particles in the phase images) can

only be detected at elevated RH, and the chemical contrast enhancement is reversible.

Figure 5 shows the effect of RH on chemical contrast of a cryogenically-cleaved, commercial block co-polymers of PS and poly(ethylene oxide) (PEO). As seen in this figure, the phase images provide good contrast between the hydrophilic and hydrophobic domains. The dark (softer) domains are believed to be PEO and bright regions are PS materials. Figure 5 clearly shows that exposure to high humidities has resulted in a substantial increase of the dark domain areas, suggesting that a marked surface rearrangement has occurred on these hydrophilic/hydrophobic copolymer samples. In general, the effect of RH in polymeric materials is more complex than that for ultra thin SAMs since water not only adsorbs onto the hydrophilic polymer surface, but also diffuses into the bulk material resulting in swelling. The swelling reduces the polymer stiffness, which directly affects contrast in the phase image.

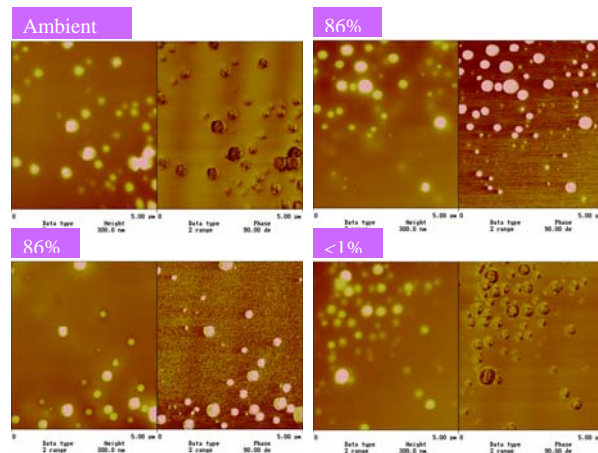


Figure 4. Effect of humidity on phase contrast of 50/50 Polystyrene/Poly(acrylic acid) blend using OH-terminated Si tip. Scale size is 5 μm × 5 μm; color scale in height image is 300 nm and phase image is 90 °.

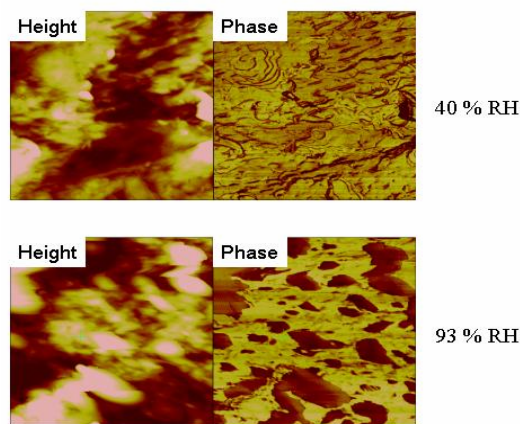


Figure 5: Effect of relative humidity on AFM phase image contrast of fractured commercial PS-PEO block copolymer samples using OH-terminated silicon tip. Scale size is 3 μm × 3 μm; color scale in height image is 150 nm and phase image is 90 °.

Conclusions

The effects of relative humidity on AFM image contrast of chemically-heterogeneous, patterned SAM and polymeric samples were investigated. The results show that RH is a useful tool that can enhance the chemical sensitivity of AFM, making it more effective for nanoscale characterization of surface chemical heterogeneity in both model and complex polymer materials. Work is continuing to better understand the contrast enhancement mechanism for heterogeneous polymers imaged in humid environment.

Acknowledgements

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