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INTRODUCTION

The interface/interphase between a polymer film and a substrate controls the adhesion and durability of a variety of polymeric systems including adhesives and coatings on plastics and metals. Interphase formation is affected by processing conditions that control chemical kinetics, diffusion, and volumetric changes. In addition, the interphase often includes impurities, unreacted molecules, and additives. The resulting interphase can be a very complex structure, which is not easily analyzed. This study presents examples to demonstrate the usefulness of phase shift in tapping mode atomic force microscopy (AFM) for the characterization of polymeric interfaces/interphases.

Tapping mode AFM is particularly attractive for polymer surface and interface studies because it exploits the high-resolution of the contact mode while minimizing sample damage due to the lateral forces inherent to contact mode. In tapping mode, the cantilever on which the tip is mounted is oscillated at a frequency near its resonance, typically, a few hundred kHz, so that the tip makes contact with the sample only for a short duration in each oscillation cycle. As the tip approaches the sample, the tip-sample interactions alter the amplitude, resonance frequency, and phase angle of the oscillating cantilever. Detection of phase changes of the cantilever probe during scanning provides an image, called a phase image. Phase changes during scanning are related to energy dissipation during tip-sample interactions [1], and can result from changes in a number of parameters including topography, sample-tip interactions, deformation of sample-tip contact area, and experimental conditions [2-4]. The phase image often provides significantly more contrast than the topographic images, and is useful for compositional mapping of surfaces and interfaces of polymeric materials [5].

EXPERIMENTAL CONDITIONS**

Three types of interfaces were investigated: film/air (film surface exposed to air), film/substrate (film surface exposed to the substrate) and cross sections. For film/air interface, both thin and thick films were investigated, and for film/substrate, only thick film was used. Thin films (< 15 nm) were prepared by spin coating of 0.08 % mass fraction of the polymers in solvent on cleaned silicon wafers using a spinner. Thick film samples were prepared by applying polymer solutions to the substrates by draw down or spraying. Cross sections of thermoplastic olefin (TPO) bulk and TPO/paint systems were prepared following the usual procedures for preparing cross sections for microscopic study. Strips of PTO and painted TPO were imbedded in a molding compound. Cross sections were obtained by cutting the embedded samples with a diamond saw, and followed with several polishing steps. Final polish was with a 0.25 μm diamond paste.

Unless otherwise stated, AFM measurements were performed using the Dimension 3100 Digital Instruments under ambient conditions. Both AFM topographic (height) and phase images were taken in tapping mode. For most of the images, a set point amplitude of between 50 % and 70 % of the free amplitude was used. Silicon tips having a drive frequency of about 300 kHz and a radius of approximately 5 nm were used. To obtain mechanical responses of different regions of the surface, nanoscale indentation was performed using the same silicon tip.

RESULTS AND DISCUSSION

One example to illustrate the advantage of phase over height AFM imaging for nanoscale characterization of polymer interfaces is illustrated in Figure 1. This sample was prepared by applying a thick film (~300 μm) of a stoichiometric amine/epoxy on silicon wafer. The epoxy was a low viscosity resin comprising a 190 g/mol epoxide equivalent mass material and reactive diluents; the curing agent was a polyalkoxyamine. After completely curing, the films were lifted up, and these images were taken from the surface that was in contact with the silicon substrate during film formation. The height image barely shows the dark and bright regions corresponding to the valleys and hills of the surface. However, the phase image clearly reveals the microstructure of the film, which consists of the nodular domains surrounding by the matrix regions.

Similar microstructure has been observed in other amine-cured epoxies [6,7]. The domain has been attributed to the high-crosslinked region and the matrix as due to the low molecular mass material. Although still showing an heterogeneous structure, the microstructure of the surface facing the air (not shown) is much less defined than that of the surface facing the substrate. This observation suggests that the surface chemical composition of the film at the film/substrate interface is different from that at the film/air interface. One contributing factor may be the depletion of amine on the air/surface due to amine-CO_2 side reactions [8] and preferential adsorption of amines on the hydrophilic silicon substrate side [9]. Both processes would affect film surface chemical composition and microstructure. The

result is also consistent with the extensive literature that the film/air interface is generally enriched with a lower-surface free energy component to minimize the polymer-air interfacial energy. The observed microstructural difference between the interior and exterior surfaces has strong implication in epoxy/substrate adhesion and wettability, paintability, and glueability of epoxy surfaces.
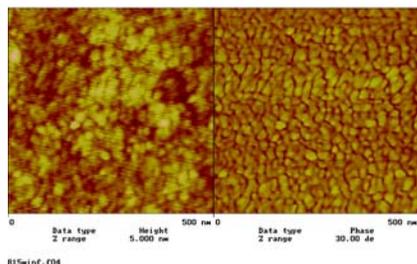

Figure 1. 500 nm x 500 nm height (left) and phase (right) AFM images of the amine-epoxy film surface that was in contact with a silicon substrate during cure.

Poly (vinylidene fluoride) (PVDF) blended with amorphous polymers to improve the optical property is commonly used for industrial coatings. One example of the use of phase imaging for interfacial microstructure study of PVDF blends is displayed in Figure 2. This sample was a blend of 50/50 mass fraction of PVDF and PMMA-co-PEA (poly(methylmethacrylate)-poly(ethylacrylate) copolymer) applied to a glass substrate at 246 °C for 10 min and cooled down slowly to 24 °C. The films were peeled off after immersing the coated glass plates in boiled water for 10 min. These images were taken from the surface that was in contact with the glass substrate. Both height and phase images for the large-size scan (Figure 2a) exhibit similar topographic features, showing the presence of 200 nm to 300 nm deep holes on the surface.
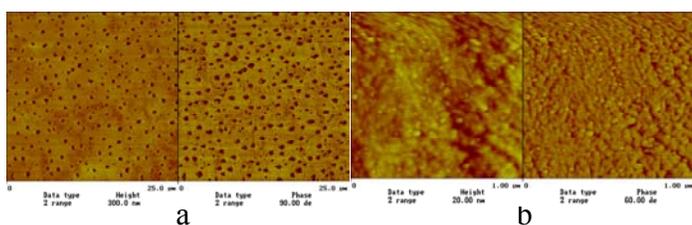

Figure 2: (a) 25 μm x 25 μm and (b) 1μm x 1μm AFM images of the surface that was in contact with glass substrate for a 50/50 blend of PVDF/PMMA-co-PEA film. (In both a and b, height image is on the left and phase image is on the right.)

However, the fine microstructure at the film/glass interface of this film is best visualized in the magnified phase image displayed in Figure 2b for the smooth area away from the holes. It reveals the nanofibrils oriented in orthogonal directions. It should be mentioned that both height and phase image results show that the surface exposed to air of these films (not shown) is covered almost

completely with crystallites of the PVDF. The result indicates a large difference in chemical composition and microstructure between the film/air and film/substrate interfaces. This difference has a strong implication in the adhesion, wettability, and cleanability of PVDF-base coatings.

Thermoplastic olefins consisting of polypropylene blending with rubber are used increasingly in the automotive industry [10]. Molded TPO surface tends to have a poor adhesion with paints used to increase the durability and enhance the appearance of exterior TPO parts. For that reason, primer is commonly used for painting TPOs. The following two examples demonstrate the use of phase imaging AFM for characterization of TPO and its interphases with coatings. Figures 3a and 3b are the height and phase images of the polished surface of bulk TPO. The height image exhibits the bright and dark areas, corresponding to the peak and valleys, respectively, of the surface. However, the phase image shows the presence of dark particles having a dimension ranging from 50 nm to a few micrometers embedded in a matrix. Analyses of the force curves (Figures 3c and 3d) obtained by nanoindentation on the particle and on the matrix indicate that the particle has characteristics of a compliant material while the matrix behaves as an elastic body. Similar behaviors have been observed for hard/soft polymer blends [2,11]. Based on the combined phase image and force curve results, the dark particles are assigned to the rubber material and the bright matrix is the bulk polypropylene.
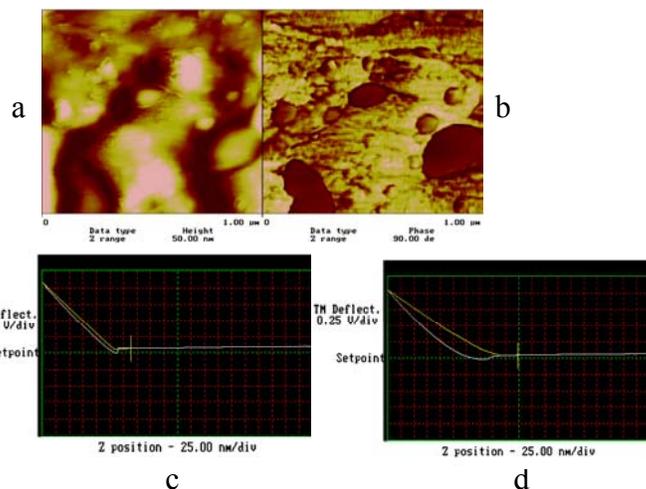

Figure 3. (a) Height and (b) phase AFM images of a polished bulk TPO, (c) force curve of the dark particle, and (d) force curve of the bright matrix of Figure 3b.

The good contrast of the phase image would allow an effective investigation of rubber particle size and distribution in the TPO bulk material as a function of processing conditions. An example is illustrated in Figures 4a and 4b, which show height and phase images of polished cross sections for good-adhesion and poor-adhesion

TPO/paint systems. The paint layers consist of a primer in contact with the TPO substrate, a basecoat and a topcoat. While the height images exhibit little difference in the polished surface structure between the two specimens, the phase images show the presence of numerous rubber particles near the TPO/paint interphase of the good-adhesion system. This phase image result is consistent with a recent fluorescence and Raman imaging study, which provided evidence of rubber migration to the TPO surface after primer application [12]. However, phase images of Figure 4b, and also at higher magnifications, show little evidence of rubber particles near in the TPO surface of the poor-adhesion TPO/paint system.
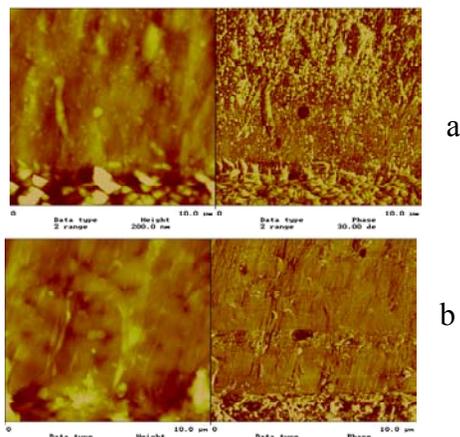

Figure 4. Height (left) and phase (right) AFM images of (a) good-adhesion TPO/paint system, and (b) poor-adhesion TPO/paint system.

Another example to demonstrate the usefulness of phase imaging AFM is illustrated in Figure 5. This is a patterned self-assembled monolayer (SAM) sample consisting of hydrophilic regions separated by hydrophobic regions. The images were taken using a NIST-developed relative humidity (RH) chamber attached to the AFM. Except for the high spots of the surface defects, the height images are essentially featureless at low or high RH. However, the phase images at different RH levels reveal the bright hydrophilic regions separated by the hydrophobic areas. Further, the phase image contrast difference increases with increasing RH. AFM using chemically-modified tips are increasingly used for probing surface chemical heterogeneity [13]. However, most studies are carried out in liquid to eliminate the effects of environment-induced capillary forces. This study provides the first evidence to indicate that indeed AFM can be used in air to effectively probe hydrophilic and hydrophobic domains of polymer interfaces.

CONCLUSIONS

While the contrast mechanism in phase imaging in tapping mode AFM is not well understood, the examples given in this study have demonstrated that the enhanced contrast of phase imaging often allows for distinguishing different material phases and constituents in the polymer interface region.
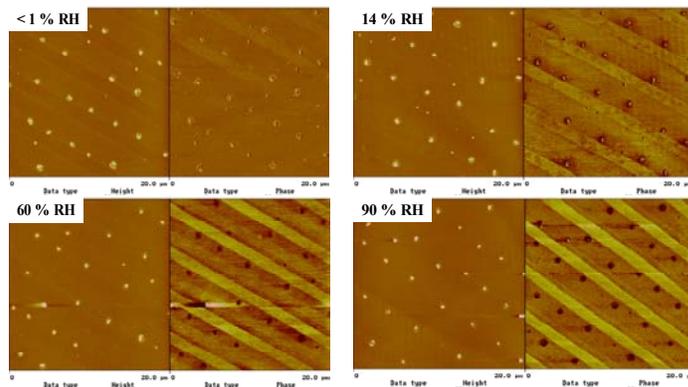

Figure 5. Height and phase AFM images of a patterned SAM taken at different relative humidities, showing the effect of moisture on the phase image contrast. (In each RH, height image is on the left and phase image is on the right.)

**Certain commercial product or equipment is described to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that it is necessarily the best available for the purpose.

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