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MAPPING CHEMICALLY HETEROGENEOUS POLYMER SYSTEM USING CHEMICAL MODIFICATION AND ATOMIC FORCE MICROSCOPY

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Introduction

Interactions between a film and its external environment are strongly influenced by the surface chemistry and morphology of the film. For example, the exterior surface composition of a film mostly defines its wettability. In recent years, extensive research has been conducted to provide in-depth microstructural information of thin polymer films using analytical techniques such as small-angle X-ray scattering, X-ray photoelectron spectroscopy, neutron scattering, and secondary ion-mass spectrometry.¹⁻³ However, these techniques lack the lateral resolution to detect and map the heterogeneity in polymer films. With the advent of atomic force microscopy (AFM), it is possible to provide direct spatial mapping of surface topography and surface heterogeneity at nanometer resolution. A combination of tapping mode and force mode AFM techniques have been effective in mapping mechanically heterogeneous regions in multi-component polymer system.^{4,5} Recent developments in chemically functionalized AFM tips have allowed mapping of chemically heterogeneous lithographically patterned surfaces by AFM at the molecular scale. This technique is known as the chemical force microscopy.^{6,7} However, mapping chemical heterogeneity in a polymer system by chemical force microscopy pose difficulties because of chain length variation and irregular packing of chains at the probe surface. A solvent-based method in combination with AFM was recently used to study chemically-heterogeneous polymer surfaces.⁸ The solvent-based method is applicable for studies of phase separated structure for phases having different swelling characteristics in a particular solvent. Alternatively, a highly-aggressive chemical medium can be chosen that effectively modifies one component while the other component remains unchanged. The objective of this study is to chemically degrade one component of a model blend and then identify the degraded component by AFM. A model blend consisting of polyethylene acrylate (PEA) and polystyrene (PS) was selected for this study because of the difference in the hydrolysis characteristics of PEA and PS. Acid was selected as the aggressive chemical medium so as to accelerate the hydrolysis of one component in the model blend film.

Experimental

Materials. PEA with $M_w = 119,300$ and PS with $M_w = 250,000$ were used for this study. Blend 1 had mass fractions of both PEA and PS of 50 % (hereafter designated as 50:50); Blend 2 had a mass fraction of PEA of 20 % and a mass fraction of PS of 80 % (hereafter designated 20:80); and Blend 3 had a mass fraction of PEA of 70 % and a mass fraction of PS of 30 % (hereafter designated 70:30). To prepare these blend samples, a 2% mass fraction solutions of PS in toluene and a 2% mass fraction solution of PEA in toluene were mixed in appropriate amounts. The three blends were cast into thin films by spin coating on a silicon substrate. Prior to application of the solutions, the silicon wafers were cleaned first with acetone, then with methanol, and dried with nitrogen. All of the cast films were conditioned for 24 h at $24 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ before analysis. Some of the conditioned samples were analyzed using AFM while the remaining samples were exposed to acid vapors. In addition to the blend samples, cast films of PEA were prepared using a mass fraction of 5% of PEA in toluene by the spin casting procedure described for the blend films.

Acid Hydrolysis. The cast PEA and cast PEA/PS films were exposed to 2M HCl acid vapor by placing them on a dessicator grid, which was kept several centimeters away from the acid solution. The hydrolysis experiment was conducted at $24 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ for up to 500 h. At specified time intervals,

samples were removed from the dessicator and characterized by AFM. Care was taken to image the same region of the sample before and after hydrolysis by AFM. For the current investigation, the exposure time was defined as the time the sample was inside the dessicator.

Atomic Force Microscopy. Tapping mode AFM was used to characterize the polymer blend samples. All AFM images were recorded under ambient conditions ($24 \pm 2 \text{ }^\circ\text{C}$, $45 \pm 5 \text{ } \%$ RH) using microfabricated silicon cantilever probes. Manufacturer's values for the probe tip radius and probe spring constant are in the range of 5 nm to 10 nm and 20 N/m to 100 N/m, respectively. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation, a scan rate of 1 Hz, and a free-oscillation amplitude, A_0 , of $60 \text{ nm} \pm 5 \text{ nm}$. Typically, a set point to free amplitude ratio (rsp) of 0.50-0.75 was used. To study the mechanical response of different regions in the film, force curves were obtained using the same type of silicon cantilever tip. From the slope and shape of the force curve, information about the identity of mechanically different regions was inferred.

Results and Discussion

In the past, assignments of phase separated regions have been based on the topographic image contrast. Using a similar approach, an attempt was made using the 3-D topographic results of 70:30 and 50:50 blend films to assign the bright and dark regions in the topographic image to PS or PEA in the blend (9). In Figures 1a-b, the 3-D topographic images of the 70:30 and 50:50 blend films, respectively, after 24h of ambient conditioning, are shown. For the 70:30 blend, all the domains are protruding, while that for the 50:50 blend all the domains are depressed. This observation suggests that the topographic image contrast is not consistent for different sample compositions. Therefore, the identification of protruded and depressed regions in Figures 1a-b could not be made.

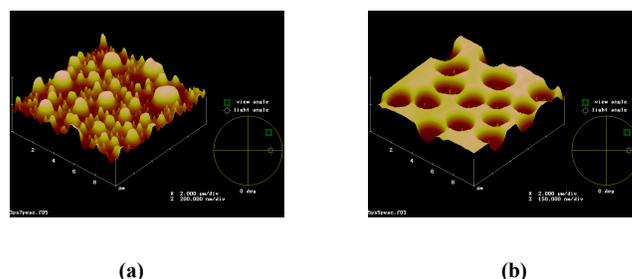


Figure 1. A 3-D representation of the topography for (a) 70:30, and (b) 50:50 PEA/PS blends after exposure to ambient condition for 24h (rsp = 0.7). Contrast variations are 200 nm from white to black for the height image.

For 2-component polymer blend, several other methods were used to identify the composition of the domain and matrix in a phase-segregated system. One method was based on changing the sample composition and comparing the areas occupied by the domain and matrix regions in the phase images of the blend. Computer image analysis of two images each for the 70:30 and 20:80 blends was performed to measure the area fraction of the domain regions. For the 70:30 blend, the area occupied by the bright domains was $24 \text{ } \% \pm 3 \text{ } \%$ of the scan area, while that for the 20:80 blend was $19 \text{ } \% \pm 7 \text{ } \%$ of the scan area. Thus, the area occupied by domains did not increase proportionately with increasing PS content, instead it slightly decreased. Possibly, as the PS content in the blend is increased, phase inversion might occur such that PEA forms domains in a PS matrix. Although this phase inversion may occur, positive identification of the bright and dark regions was not possible.

To assist in the identification of domains and matrix in the blend, the sample was exposed to HCl vapor, as previously described. In Figure 2, a 3-D topographic image and a corresponding line profile of the acid treated 70:30 PEA/PS film is shown for similar tapping conditions as described previously. The preparation of this film was similar to that for the film imaged in Figure 1a, except that this cast film was exposed to an acid environment for 3h. Pits were observed in isolated regions of the matrix,

but the overall size and shape of the domains remained unaltered. The dark regions in Figure 2a represent pits that are formed within the heterogeneous structure. The depth and width of the pits can be read directly from the line profile.

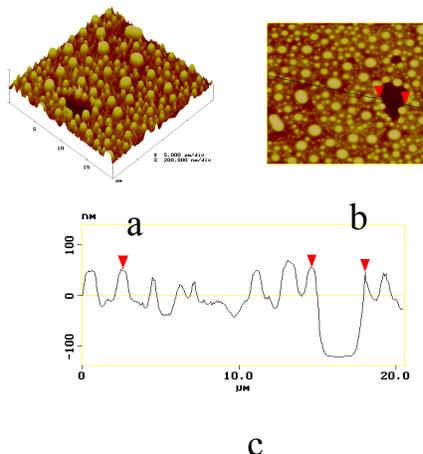


Figure 2. (a) and (b) 3-D and 2-D representations of the topography, respectively and (c) a line profile, for a 70:30 blend sample after ambient conditioning for 24 h and then exposing the film to 2M HCl vapor for 3 h. Contrast variations are 200 nm from white to black for the height images.

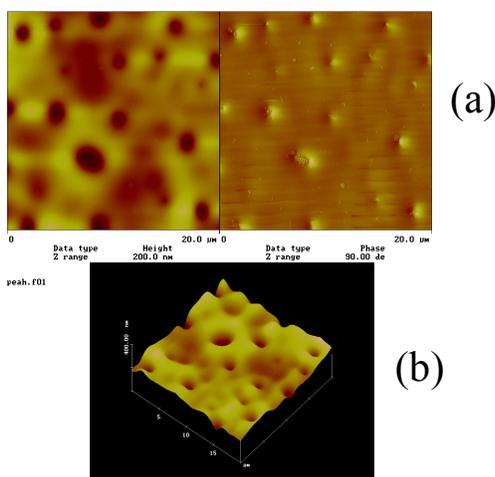


Figure 3. (a) Tapping mode height image (left) and phase image (right), and (b) a 3-dimensional representation of the topography for the PEA film after 24 h of ambient conditioning and exposure to HCl vapor for 40 days. Contrast variations from white to black for the height image are 200nm and 90° for the phase image.

To relate the changes due to acid exposure in the composition of the PEA/PS blend, PEA and PS cast films were similarly exposed to HCl vapor. The changes observed in the matrix material of the blend were assumed to

correspond to changes in either the PEA or PS film with exposure to HCl vapor. In Figure 3a, the AFM topographic image (left) and phase image (right) are shown for a 20 μm x 20 μm scan area of a 110 nm ± 10 nm thick PEA film on Si substrate that has been exposed to an acid environment for 40 days. In contrast to the generally smooth surface of the unexposed PEA film (not shown), the surface of the exposed PEA film shows isolated degradation (dark spots in the topographic image). Much of the degradation occurs at localized sites in the form of pits with lateral dimensions from several nanometers to several micrometers, as observed in the 3-D topographic image shown in Figure 3b. From this study, it was concluded that in 70:30 PEA/PS blend, the domains are PS and the matrix is PEA.

To confirm that the PEA component in the PEA/PS 70:30 blend was indeed the matrix and the PS component in the blend is the domain, force-curve measurements were performed on pure PS, pure PEA, and the 70:30 blend. A force curve is a plot of the deflection of the free end of the AFM probe as a function of z-piezo motion as the probe approaches, contacts, and withdraws from the sample surface. There are several notable similarities in the shape of the force curves for domain and matrix regions compared to that of pure PS and PEA (data not shown). For example, considerable penetration of the probe into the matrix and minimal penetration of the probe into the domain were observed, which was similar to that observed for the pure PEA and pure PS films, respectively. In addition, a strong hysteresis (difference between the loading and unloading region) in the force curve was observed for the matrix region and no hysteresis for the domain region. The significant penetration of the probe tip and strong hysteresis in the force curve are indicative of the extremely compliant PEA rich matrix material, while minimal penetration and no hysteresis are indicative of the stiff PS rich domain material.

Conclusions

The mapping of chemically heterogeneous regions in PEA/PS film was achieved by hydrolyzing the film in a low pH environment and analyzing by AFM. In 70:30 blend, the domains were identified as PS rich regions and matrix as the PEA rich regions, based on AFM images, force curve measurements, and chemical modification study. During the course of hydrolysis of PEA, pits were formed in isolated regions of the matrix, as characterized by AFM.

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