

MAPPING CHEMICALLY HETEROGENEOUS POLYMER SYSTEM USING SELECTIVE CHEMICAL REACTION AND TAPPING MODE ATOMIC FORCE MICROSCOPY

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SUMMARY: The mapping of chemically heterogeneous regions in PEA/PS film was achieved by reacting 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, FTIR 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.

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 photo-electron spectroscopy, neutron scattering, and secondary ion-mass spectrometry¹⁻³⁾. 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 surfaces⁸⁾. 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 medium can be chosen that chemically react with one component while the other component remains unchanged. The objective of this study is to perform a selective chemical reaction of one component of a model blend and then identify the reacted 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 reaction 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 and cast films of PS 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, cast PS, 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 1450 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 ($24 \pm 2^\circ\text{C}$, $45 \pm 5\%$ 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

(a)

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. 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 Figure 1a-b could not be made. For two-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.

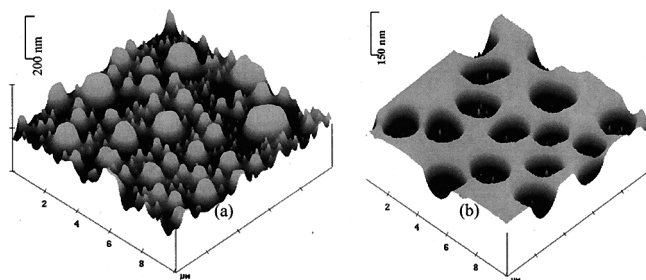


Fig. 1. A 3-dimensional representation of the topography for (left) 70:30, and (right) 50:50 PEA/PS blend after 24 h of ambient conditioning ($r_{sp} = 0.70$). Contrast variations are 200 nm from white to black for the height images.

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 $24 \% \pm 3 \%$ of the scan area, while that for the 20:80 blend was $19 \% \pm 7 \%$ 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.

Another method for identifying different regions in a heterogeneous system is based on the use of force curve measurements. The force curve can be used to provide information on the local elastic properties. Numerous studies have shown the usefulness of force curve in distinguishing hard and soft regions in multiphase polymer systems^{4,5,9,10,11}. In the present study, force curve measurements were made on the phase separated regions to identify the domains as PS-rich or PEA-rich regions. However, force curve measurements on this system were not always reproducible and the force curves of domain and matrix regions were difficult to distinguish, even though the T_g values of the two materials were vastly different. Perhaps for the phase-separated regions, a thin layer of the PS resided above and/or below the PEA regions and similarly PEA may have resided above and/or below some PS regions. Also, as commented previously, small regions of PEA were observed in the PS domains. The presence of the matrix phase as tiny droplets within

the domains during the late stages of phase separation has been previously observed for other blends⁽¹²⁾. In any case, the force curves were not helpful in distinguish the PS and PEA region in the blend.

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.

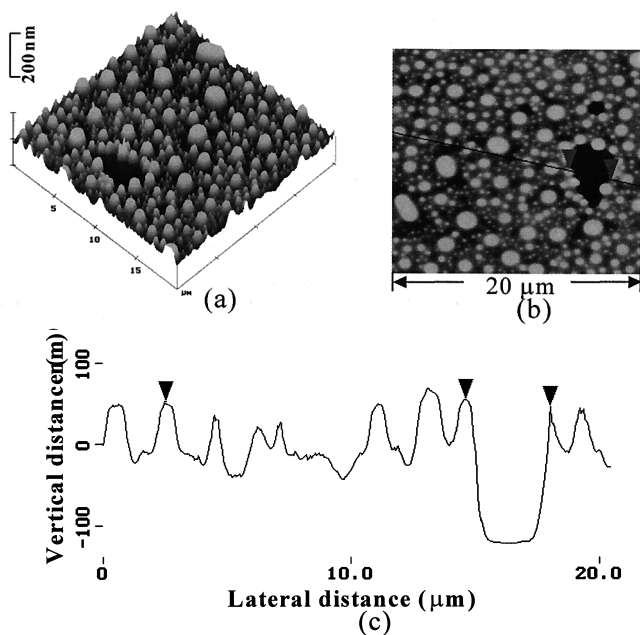


Fig. 2. (a) A 3 D representation of the topography image, (b) tapping mode height images and (c) line profile for a 70:30 blend sample after 24 h of ambient conditioning and exposing the film to HCl vapor for 3h. Contrast variations are 200 nm from white to black for the height images.

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.

Although PS is essentially a hydrophobic polymer, it is necessary to determine the susceptibility of PS to the same hydrolytic conditions as that for the blend. Little visible change was observed in the topographic image contrast of the cast PS film after 60 days exposure; a roughness of $0.47 \text{ nm} \pm 0.045 \text{ nm}$ for the exposed and $0.446 \text{ nm} \pm 0.004 \text{ nm}$ for unexposed polystyrene film. These results indicate that, under the conditions used in the hydrolysis experiment of the PEA/PS blend, the changes observed in the matrix material were due to the hydrolysis of the PEA regions in the blend and not from the PS domains.

In Figure 3a, the AFM topographic image (left) and phase image (right) are shown for a $20 \mu\text{m} \times 20 \mu\text{m}$ scan area of a $110 \text{ nm} \pm 10 \text{ nm}$ 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

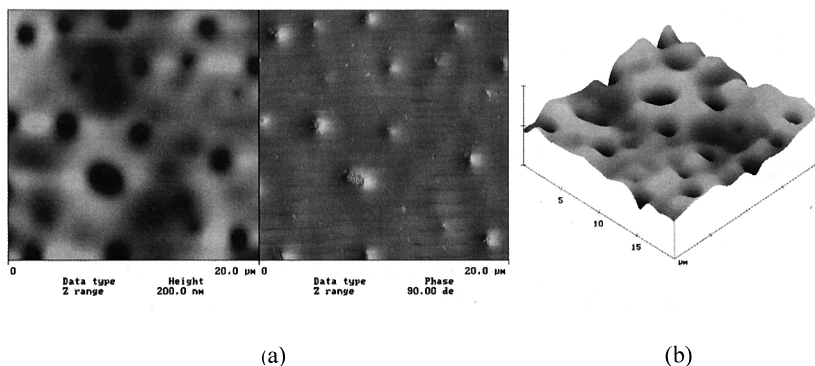


Fig. 3. (a) Tapping mode AFM height image (left) and phase image (right) and (b) a 3-dimensional of the topography for the PEA film after 24 h of ambient conditioning and exposing the film to HCl vapor for 40 d. Contrast variations are 200 nm from white to black for the height image and 90° from white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

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 component that hydrolyzed during acid exposure, fresh PEA film was subjected to the same acid hydrolysis and temperature conditions (as for the blend) and the composition of the film was studied by FTIR. In Figure 4a, the FTIR transmission spectra of a spin coated PEA film on CaF_2 are shown for the region from 3800 cm^{-1} to 1200 cm^{-1} as a function of exposure time to HCl vapor. Peak attributable to pure PEA is observed at 1732 cm^{-1} and is assigned to the ester $\text{C}=\text{O}$ stretching. The difference spectra (Figure 4b) between the film exposed to different times and the unexposed film was used to measure the ester group consumption and formation of the acid group for the entire $110\text{ nm} \pm 10\text{ nm}$ film thickness. Hydrolysis of PEA is catalyzed by the presence of HCl. Hydrolysis of the polyester (e.g., PEA) film results in the formation of alcohol and carboxylic acid-terminated polymer chains. Two bands that are attributable to the OH stretching (3400 cm^{-1}) and acid $\text{C}=\text{O}$ stretching (1710 cm^{-1}) appear in the difference spectra. This indicates that acid and alcohol were formed upon hydrolysis of the PS/PEA film. From the difference spectra, the loss of ester peak and the growth of acid and alcohol peaks in the PEA/PS film with exposure time can be clearly noticed.

Although the time scales of ester conversion, as monitored by FTIR, and that of the morphological alteration of the PEA film as studied by AFM are only qualitatively comparable, all information is consistent with hydrolysis of the PEA in the blend upon exposure to HCl vapor and dissolution of the PEA component from the blend leading to the formation of pits. Pits were observed to grow and reach the film/substrate interface, upon exposure of the film for longer periods. These pathways could have occurred either by hydrolysis of continuous PEA regions or by a combination of hydrolysis of non-continuous PEA regions and structural rearrangement of PS regions. A detailed explanation to pit/pathway formation process in thin film of PEA/PS blends can be found

13).

The underlying information from these results is that the changes observed in the PEA film correspond to the changes in the matrix material of the blend when both are exposed to HCl vapor. This information can be useful for identifying different phases in chemically heterogeneous polymeric systems. The AFM/selective chemical reaction approach can be helpful in providing a better understanding of the degradation of coating materials.

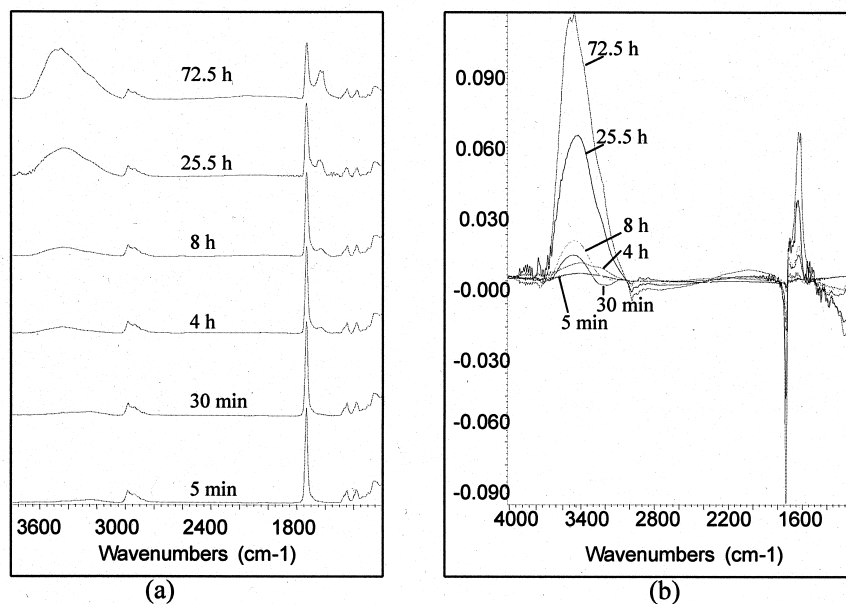


Fig. 4. (a) Unprocessed and (b) difference FTIR-transmission spectra in the 3800 cm⁻¹ to 1200 cm⁻¹ regions showing the effects of exposure of PEA film to HCl vapor.

Conclusions

The mapping of chemically heterogeneous regions in PEA/PS film was achieved by reacting 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, FTIR 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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