Characterization of Polyester Degradation Using Tapping Mode Atomic Force Microscopy

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Introduction

Polymer coatings are heterogeneous and often contain sub-micron scaled degradation-susceptible regions. Mapping and identification of heterogeneity in polymer coatings would provide a better understanding on degradation mechanism and help to improve the coating performance.

Tapping mode atomic force microscopy (AFM) has emerged as a powerful technique to provide direct spatial mapping of surface topography and surface heterogeneity with nanometer resolution. Phase contrast in tapping mode AFM often reflects differences in the properties of individual components of heterogeneous materials[1], and is useful for compositional mapping in polymer blends, copolymers and coatings[2]. Additionally, force curves in tapping mode AFM have also been explored to provide local mechanical property information in multi-component materials[3]. A combination between phase imaging and force curve measurement would allow the heterogeneous regions in polymer systems to be identified.

One of the major drawbacks of polyester coatings is their sensitivity to hydrolysis. In this paper, AFM was used to examine microstructural changes of the polyester film after exposure to an alkaline solution. Changes in AFM images and force curves were correlated to direct chemical information obtained from attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The chemical species leached from the coating film were characterized by liquid chromatography.

Experimental

Materials The polyester resin was a commercial product obtained by reacting isophthalic acid, glycols, maleic anhydride and cobalt dimethyl aniline. The polyester resin was dissolved in styrene monomer, which promotes free radical reaction to form a crosslinked network structure. The polyester coating was prepared by mixing 100 parts of an isophthalate ester resin and 2 parts of a methyl ethyl ketone peroxide catalyst. Dry free films of approximately 670 μm were prepared by molding the mixture between two sealed acrylic plates and by covering with polyethylene terephthalate film. Films were allowed to gel at ambient conditions (22 °C and 45% relative humidity) overnight followed by post-curing at 150 °C for 2 h in an air-circulating oven.

Degradation of Polyester Film The mass of free-standing films having dimension 1cm x 1cm was determined prior to exposure. Films were immersed in 3 M NaOH solution contained in screw-top plastic containers placed in a water bath at ambient temperature. Specimens were removed at predetermined time intervals from the solution. After being washed with deionized water for 15 minutes, the film was then dried in a dessicator to a constant mass. The percentage of mass loss was expressed as a change in mass with respect to the initial mass. The dried degraded films were saved for AFM and ATR-FTIR measurements. The solution was neutralized by 2 M HCl solution and analyzed by liquid chromatography (LC).

Atomic Force Microscopy Tapping mode AFM was used to characterize the polyester films before and after exposure to alkaline environment for different times. A scanning probe microscope was operated in tapping mode under ambient conditions with commercial silicon microcantilever probes. Manufacturer's values for the probe tip radius and probe spring constant are in the ranges 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 and a free-oscillation amplitude of 60 ± 5 nm. A set-point ratio (r_{sp}) in the range of 0.70-0.90 was used. To obtain mechanical response of different domains in the films, force curves were performed utilizing the same type of silicon cantilever described previously. While more in-depth analysis of the force curves can be used to measure relative modulus values, the identity of mechanically different regions can be inferred simply from the slope and shape of the repulsive or contact portion of the force curve[4]. This technique was thus used to provide heterogeneity information in degraded polyester coating films.

ATR-FTIR Analysis ATR-FTIR spectra of the films were obtained using a Fourier transform spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. The single reflection horizontal ATR accessory with a germanium crystal was used, the crystal face angle is 45°. The diameter of the sampling area is approximately 5 mm, thus this technique provides "point-to-point" contact with the pressure device when analyzing solid samples. All spectra were acquired as 256 scans with a resolution of 4 cm^{-1}. The spectrometer was constantly purged with dry air.

Liquid Chromatography-Mass Spectrometry (LC-MS) Organic extract solution samples were acid neutralized and analyzed with a LC-MS equipped with a variable wavelength detector. Five microliters of the solution was injected into a HPLC column with a diameter of 2.1 mm and 150 mm in length. The LC mobile phase consisted of approximately 75% water, 25% methanol, and 0.075% acetic acid; isocratic elution was used. The mobile phase flow rate was 1ml/min. The UV absorbance of eluted species was monitored at 282 nm by the variable wavelength detector, in series with the mass spectrometer. Electrospray ionization was used in positive polarity to analyze the LC column effluent. Ions were monitored in the range m/z 100 to 600. The threshold on the mass spectrometer was set to 100; the gain was 3; a fragmentor voltage of 70 V was used.

Results and Discussion

Unexposed Polyester Film A heterogeneous structure with an average domain size around 40 nm was clearly observed on length scales less than 1 μm in AFM images (Figure 1). In both the topographic and phase images, compact domains are visible. All the domain structures are relatively bright in color in the phase image with interstitial regions distinguished by a relatively dark color. The compact domains appear to be similar to the so-called "microgel-like" particles formed during the curing reaction of unsaturated polyester resins[5]. An important feature of the curing of polyester resin through the microgel mechanism is the formation of a heterogeneous structure through strong intramolecular reactions and phase separation[6]. The strong intramolecular reaction among the pendant C=C bonds of polyester molecules might lead to a higher crosslinking density for nodular domains; while, the interstitial regions between the microgel particles might form a less crosslinked structure. Some unreacted monomers and free polystyrene and polyester chains may remain in this interstitial region, thus, the property difference between brigh-colored nodules and dark-colored surrounding matrices in AFM phase images could be quite significant.

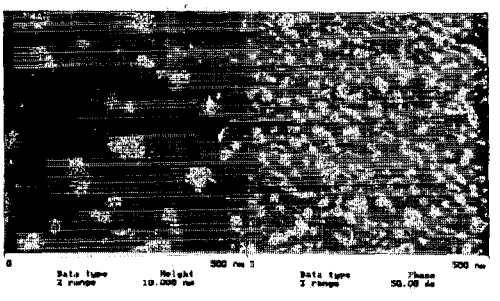
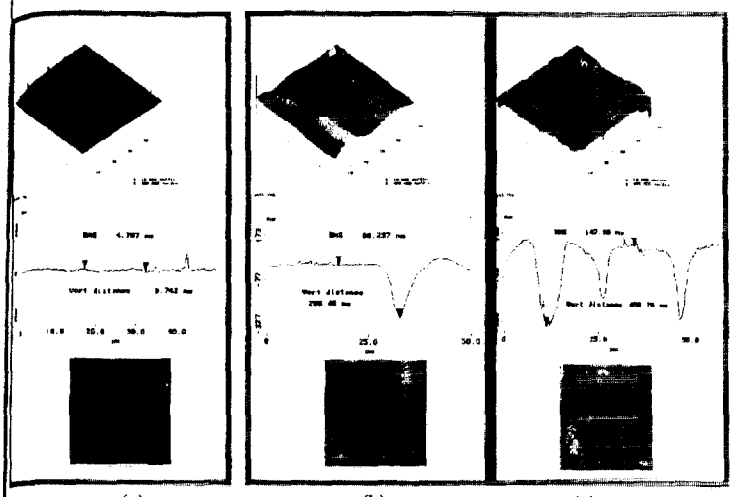


Figure 1. Tapping mode AFM height images (left) and phase images (right) of the polyester film before exposure to NaOH solution. Contrast variations from white to black are 10 nm for the height images and 50 ° for the phase images.

Exposed Polyester Film 3-Dimensional representations of the topographic images of the polyester samples after exposure in 3 M NaOH solution for different times are displayed in Figure 2, along with their corresponding line profiles. In contrast to the generally smooth surface of the unexposed film, pitting is visible for the surfaces after exposure, and the relative number of the pits increases with the exposure time. As can be seen in the line profiles of the topographic images, the pit depth and diameter also increase as the alkaline solution attack proceeds. These topographic changes are consistent with the mass loss of the exposed polyester samples, the liquid



(a) (b) (c)

Figure 2. 3-D topographic images and line profiles of polyester film exposure to NaOH solution for different times: (a) 0 day, (b) 28 days, (c) 50 days. Contrast variations are 400 nm from white to black for the height images.

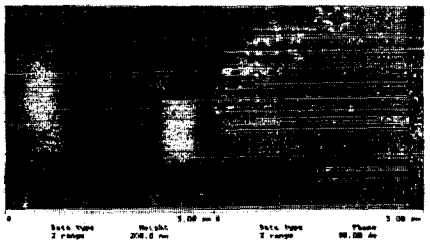


Figure 3. AFM height image (left) and phase image (right) of an area with a pit in the polyester film exposed to NaOH solution for 28 days. Contrast variations from white to black are 200 nm for the height images and 90 ° for the phase images.

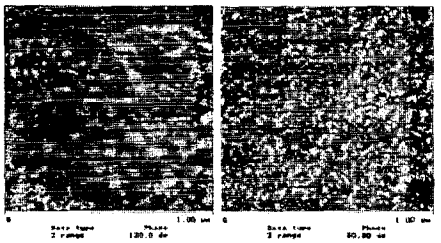


Figure 4. Phase images of an area inside the pit (left) and an area outside the pit (right) for the polyester film exposed to NaOH solution for 28 days. Contrast variations from white to black are 120 ° for the left image and 50 ° for the right image.

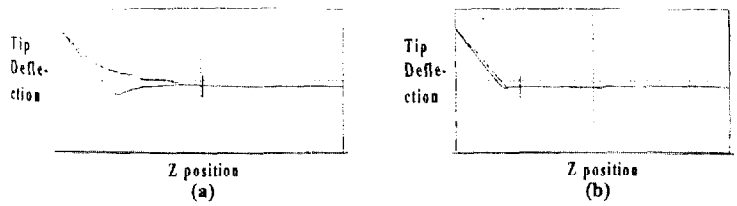


Figure 5. Force curves of (a) dark-colored region inside the pit and (b) bright-colored nodules outside the pit. One division is 20.00 nm for Z position and 0.25 V for tip deflection, respectively.

chromatography results on the immersed solutions, and the FTIR intensity decrease of the ester groups. These changes are due to the hydrolysis of ester groups and the subsequent leaching of low molecular mass and water-soluble fragments of polyester material in the alkaline environment.

To provide a better understanding of the microstructure change in polyester film during exposure to NaOH solution, a region (5 μm × 5 μm) containing one deep pit was selected for further AFM analysis (Figure 3). From topographic data, one prominent large pit is observed, and numerous small and shallow pits are also visible. Marked changes in the microstructure are clearly noticed in the area around the pit. For the area within the pit, the phase contrast appears darker. The increased heterogeneity around the pit indicate that the polyester microstructure has changed substantially after exposure. Figures 4 displays 1 μm scaled phase images of one region inside the pit and another outside the pit. Compact two-phase structure with bright domains and dark interstitial regions is shown in the unpitted region, which is similar to the microstructure of the unexposed sample. On the other hand, in the region inside the pit, a higher percentage of dark-colored area is noticed. The force curve performed on dark-colored regions inside the pit also shows a higher hysteresis than that on bright-colored nodules outside the pit (Figure 5). These results indicate that the microstructure and the chemical/mechanical properties between these two regions are significantly different. The dark-colored regions in the phase image inside the pit might be large fragments of degradation products.

The inherent presence of inhomogeneities and phase separation on the surface of the polyester films are postulated to affect the initiation and development of the pits. Hydrophilic regions that contain mostly low crosslinked materials or unreacted monomers are susceptible to hydrolysis and would become the sites to initiate the degradation and pit formation. As degradation progresses, the hygroscopicity inside the pits will increase with an accumulation of acidic and alcoholic chains from the degradation products. Further, the salts of carboxylic acid, which are observed in ATR-FTIR spectra, could effectively accelerate the hydrolysis rate[7]. Therefore, the degradation would occur in localized regions and the pits would tend to become deeper and larger.

Conclusions

Tapping mode AFM was used to examine the microstructure of the polyester film before and after exposure to an alkaline solution. Bright-colored microgel particles and dark-colored interstitial regions were observed in phase images of the unexposed samples. The microstructure of polyester film was substantially changed after exposure. More and deeper pits were observed on the sample surfaces with increasing exposure time. Phase imaging and force curves indicated that the properties of the regions with the degradation pits are significantly different from those of undegraded regions. The localized nature of pit initiation and propagation is believed to result from the heterogeneity of the polyester film.

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