

Degradation of Polyester Film in Alkali Solution

D. RAGHAVAN, K. EGWIM

Polymer Science Division, Department of Chemistry, Howard University, Washington, DC 20059

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ABSTRACT: In recent years there has been a remarkable growth in coatings technology, yet polymer-coated metals still corrode when they are exposed to severe environments. If the effectiveness of polymer coatings is to be increased, it is essential to understand the microstructure of polymer coating film and the changes that occur to the film upon environmental exposure, and relate the changes to the protective performance of coatings. The degradation of a polyester immersed in alkali solution has been investigated using a number of analytical techniques including atomic force microscopy (AFM), liquid chromatography/mass spectrometry (LC/MS), and Fourier transform infrared spectroscopy (FTIR). AFM was used to characterize the heterogeneous phase in the unexposed films and films exposed to alkali solution. Film roughness was found to increase with aging of the film in alkali medium. Total organic carbon analysis of the leached aqueous medium showed the presence of organic compounds, suggesting a chemical degradation of the film in alkali medium. FTIR analysis of the leached medium showed evidence for the formation of carboxylate species upon degradation of polyester film in alkali solution, while LC/MS analysis of the leached medium confirmed the presence of isophthalic acid and sodium isophthalate. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2454–2463, 2000

Key words: polyester; alkali medium; coating; degradation; atomic force microscopy

INTRODUCTION

Corrosion costs the U.S. about 4.2% of its gross national product, or over 250 billion dollars in 1996. There are many methods to prevent corrosion, but the economical method for protecting metals is by the application of a polymer coating on the surface of the substrate. Coatings are an essential component of engineered materials both for functional and aesthetic reasons. Over the last several decades, organic coatings have been widely used in aerospace, military, and infrastructural applications. Depending on the end use application, the specifications of the organic coat-

ings can vary over a wide range. Generally, the coating systems include multiple layers of different polymer formulations.^{1,2}

Despite recent progress in the formulation of coatings to meet end use applications, problems continue to prevail in providing protection to the substrate from long-term exposure to aggressive environment.³ During exposure of coating film to aggressive environments, surface coatings become damaged. Therefore, to improve longevity of the engineered material, the surface coatings must be refurbished to meet the original design requirements. Recoating of the surface involves paint stripping and application of a fresh paint coating. In order to alleviate the impact of stripped paint waste on the environment and to minimize the cost of refurbishing, surface coatings must be developed that meet durability and performance requirements in aggressive environments. If the effectiveness of the coating in ag-

Correspondence to: D. Raghavan (draghavan@howard.edu).

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gressive environments is to be increased, it is essential to understand the microstructure and properties of the complex coating film, the mechanism of degradation of coating in aggressive environments, and develop tools to quantify organic coating degradation.⁴

Resins commonly used in coatings are alkyd, epoxies, and urethane. A recent survey of paints and coatings estimates that alkyd resins account for 15% of the total coating.³ A typical polyester resin is the condensation product of fatty acids with polyhydric alcohols.⁵ The polyesters can be used in conjunction with epoxy crosslinkers as powder coatings.⁶ Epoxy-based powder coatings are used in bridges and other structures.⁷ One of the prime concerns in the application of polyester as coating in a highly corrosive environment (say alkali environment) is the degradation.

During service, the coating is constantly exposed to moisture and aggressive chemicals. The amount of water sorbed by the coating film depends on the composition of coating and the morphology of the film.⁸ For some polymer coatings, the sorbed water promotes both physical and chemical aging of film.⁹ Physical aging is often accompanied by changes in the thermophysical properties (such as glass transition temperature and moduli) of the film. Recent studies have shown that physical aging of the film can lead to delamination of the coating from the coated substrate.¹⁰⁻¹²

Leidheiser and Wang found that the rate of coating delamination from a metal substrate is also influenced by diffusion of certain type of cations through the coatings.¹⁰ In highly aggressive media, such as alkali and alkaline medium, polymer films also undergo chemical aging. For example, in a basic environment, the ester units in polyester film react and form carboxylic acid terminated units. The carboxylic acid terminated unit can then combine with the cations in solution to form salt.¹³ The chemical and morphological alteration of the film can eventually lead to a reduction in the properties of the bulk polymer, e.g., a 75% loss of the original strength of the polymer film.¹²

Extensive research has been conducted to provide evidence that polyester film undergo chemical and physical changes when exposed to highly aggressive media; however, these studies have been limited to measurements of film properties before and after degradation. Limited research has been conducted to characterize the nature of degraded substance.^{9,13} Identifying the nature of

the degradation products and their relative abundance can be extremely useful in developing more durable polymeric coatings.

HETEROGENEITY AND CHEMICAL SUSCEPTIBILITY OF A COATING SYSTEM

A coating system is primarily composed of topcoat, primer, and surface treatment structures. The role of topcoat is to provide the structural material protection against chemical, moisture, and mechanical degradation. Certain polymers used in the formulation of coating system are more susceptible to chemical degradation and moisture attack than the others. Furthermore, certain regions within the polymer coating film are more degradation-susceptible compared to the rest of the film. The exact nature of the degradation-susceptible regions is unknown. Research during the past decade has provided indirect evidence to suggest that the small degradation susceptible domains in cured polymeric film may represent the low molecular weight, low crosslinked regions, and the remaining film may represent the high molecular weight high crosslinked regions.^{4, 4,15} The size of the degradation susceptible regions is believed to range from nanometers to micrometers. Mills and Mayne¹⁶ postulated that the degradation susceptible regions are formed of partially polymerized molecules that did not completely crosslink. The behavior of these regions has been compared to that of a hydrophilic membrane, i.e., they have high water sorption capacity and ion conductivity. Although the degradation susceptible regions occupy a small volume of the total polymer film, they control the corrosion protection performance of coating. Corrosion of polymer coated metal have been found to occur directly underneath these regions.¹⁷ It is believed that during exposure to an electrolytic medium, the degradation susceptible regions are leached by the exposure medium.¹³ Upon leaching of degradation-susceptible regions, new pathways/channels are created for corrosive ions to travel through bulk coating film and eventually reach the coating/substrate interface. This leads to the corrosion of the substrate. Analysis of the leachate can provide information about the degradation-susceptible regions in the film.

Attempts have been made to characterize the properties of degradation susceptible regions in polymer coating film, but they have been limited

to indirect measurements.^{13–20} For example, microhardness, DC resistance, and AC impedance measurements have revealed that there are few regions in the polymer films that are mechanically soft and chemically more polar than the rest of the film.^{21,22} Until recently, because of the lack of proper identification tools, there has been difficulty in the direct identification of heterogeneous regions in polymer coating film.

With the advent of analytical techniques such as atomic force microscopy (AFM), it may be possible to obtain direct information of the heterogeneous regions in the coating film. AFM has recently been shown to be highly powerful and useful tool for investigating the nanostructures of fluorinated polyester coating films by studying the outermost free surfaces.²³ Tapping mode AFM is especially useful in correlating topographical and phase information of the various domains in the coating. Furthermore, tapping mode AFM is useful because there is only a short duration of contact between the AFM tip and the sample, causing minimal damage of the sample. The current study attempts to establish the existence of the heterogeneous regions in the coating film using tapping mode AFM, and provide chemical information of the degradation susceptible regions in the coating film using Fourier transform infrared (FTIR), liquid chromatography/mass spectroscopy (LC/MS), and total carbon analytical technique.

AFM was used to characterize polyester coatings before and after exposure of the films to an alkali medium. Due to the physical and chemical complexity associated with organic coatings, the current study is limited to polyester formulation free of pigments and additives. Changes to the near surface regions of the coatings were monitored via the mechanical response of the different domains. An attempt was made to correlate subsurface changes to molecules leached from the coating. The molecules leached from coating film were characterized spectroscopically, and using mass spectrometric techniques.

MATERIALS AND METHOD

The isopolyester resin was synthesized by reacting isophthalic acid, glycols, maleic anhydride, and cobalt dimethyl aniline. The isopolyester was then dissolved in styrene monomer, which promotes free radical reaction to form a cross linked network structure. The specimen was prepared

by hand mixing polyester resin with 2% by mass of methyl ethyl ketone peroxide catalyst containing 9% by mass active oxygen, pouring the mixture into an acrylic plate mold of 670 μm depth, and covering with polyethylene terephthalate film. The polyethylene terephthalate film served as the release film and the plastic mold prevented any oxygen inhibition of the free radical crosslinking reaction and loss of styrenic monomer due to evaporation. The mold was placed between two glass plates. The film was allowed to gel overnight at 24°C and postcured at 130°C for 2 h. Final film thickness was in the range of 600–700 μm .

Film Characterization

The film (undegraded and degraded) was imaged by AFM. Height and phase data were recorded simultaneously on a Dimension 3100 AFM from Digital Instruments, Santa Barbara, CA. Tapping image mode was used in which the cantilever probe is oscillated at its mode-1 bending resonance frequency such that the probe tip taps on the surface of the film while the probe is raster scanned in the x - y directions. Phase refers to the lag signal between the contact and response. Tapping mode AFM allows direct mapping of different domains with high lateral resolution by generating a phase image, in which contrast is provided by the interaction of the tip with various domains of the surface of the film. Changes in the phase of the oscillating probe were used to produce a contrast between harder and softer areas in the film. Mean square roughness of the film was determined from the topographic (height) image data.

Degradation of Polyester Film

Any application of a polymer film in an outdoor environment often involves exposing the film to moisture and aggressive medium attack. Degradation experiments were conducted to simulate the attack of aggressive media (such as alkali) by exposing the film to 3M NaOH solution at 24°C. The film was removed at predetermined time intervals, and an alkali free film was obtained by equilibrating the sample with deionized water. AFM imaging was performed on the dried film.

Total Organic Carbon Analysis

The extraction medium obtained upon degrading the polyester film with 3M NaOH solution was

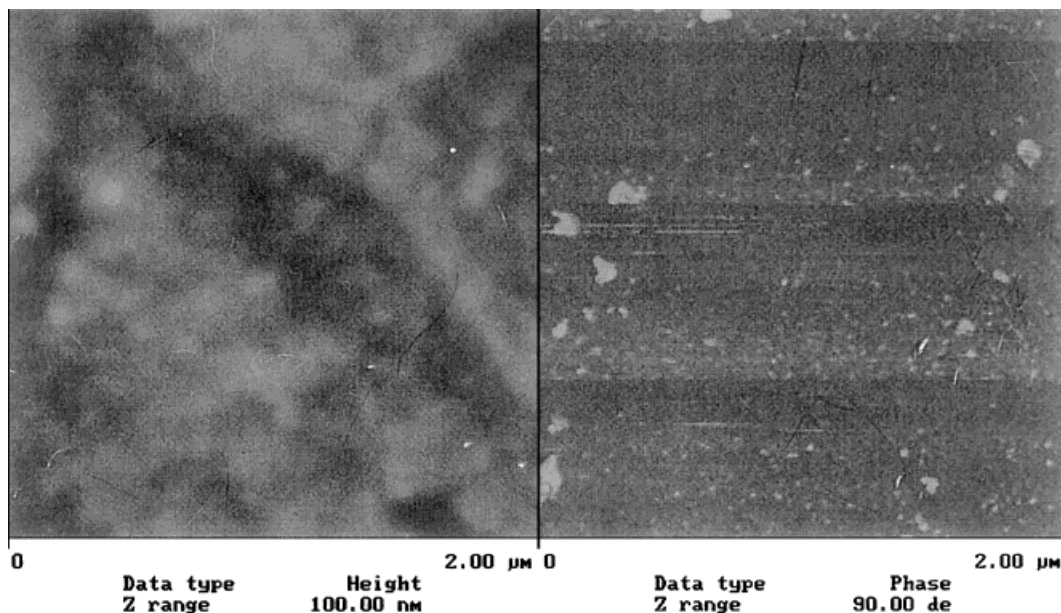


Figure 1 AFM tapping mode data for unexposed polyester film. Left: topographical image; right: phase image. Scan box is $2 \times 2 \mu\text{m}$.

used for total organic carbon (TOC) analysis. TOC analysis was performed on Tekmar-Dohrman Phoenix 2000. Persulfate in the presence of UV light is able to convert organic carbon in the extraction medium into carbon dioxide and the carbon dioxide is detected using a nondispersive in-

frared detector. Phthalic acid from Tekmar-Dohrman served as the calibration standard for the assay. Extracts of control experiments (3M NaOH with no polymer) were analyzed for TOC in a similar manner. The reported results are averages of triplicate measurements.

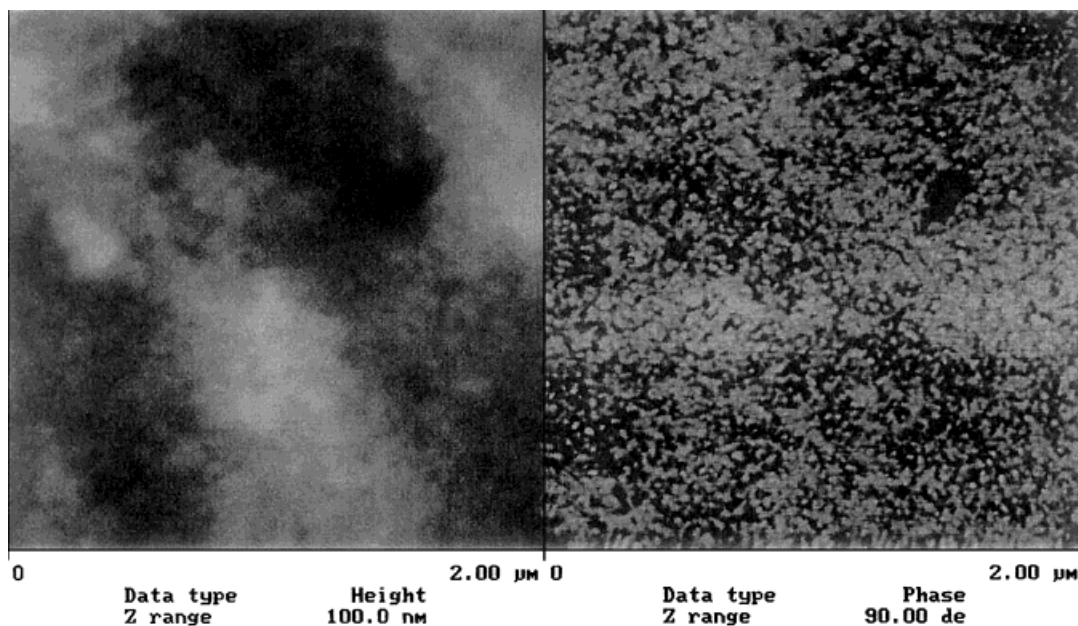


Figure 2 AFM tapping mode data for polyester film exposed to NaOH solution for 21 days. Left: topographical image; right: phase image. Scan box is $2 \times 2 \mu\text{m}$.

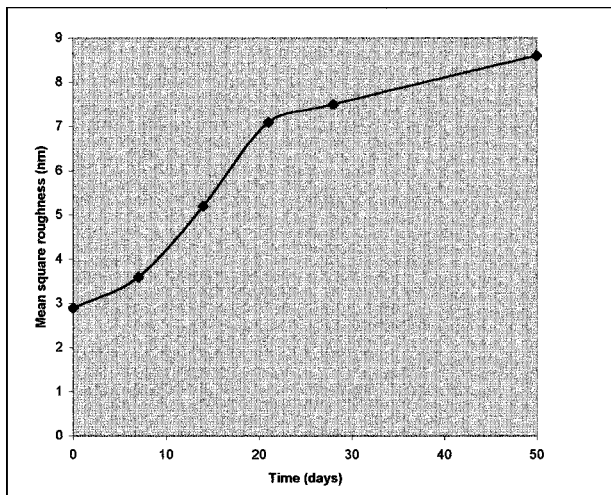


Figure 3 Mean square roughness value of polyester film exposed to NaOH solution as a function of duration of exposure.

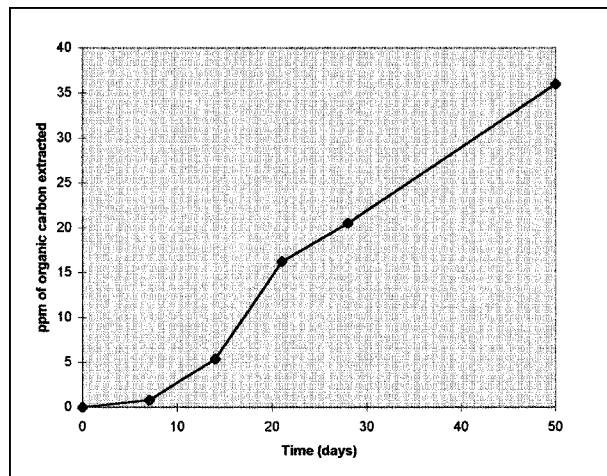


Figure 4 The total organic carbon analysis of leachate solution as a function of duration of exposure.

FTIR Analysis

FTIR analysis was carried out on the alkali solution in which the polyester film had been exposed for 50 days at 24°C. This solution was filtered and dried. The dried extract was mixed with KBr and vacuum packed to obtain pellets of the extracted

material. The pellet was analyzed using a Nicolet Magna IR 560 spectrophotometer.

LC/MS

Organic extract samples were acid neutralized and analyzed with a Hewlett Packard model 1100 Liquid chromatography-mass selective detector

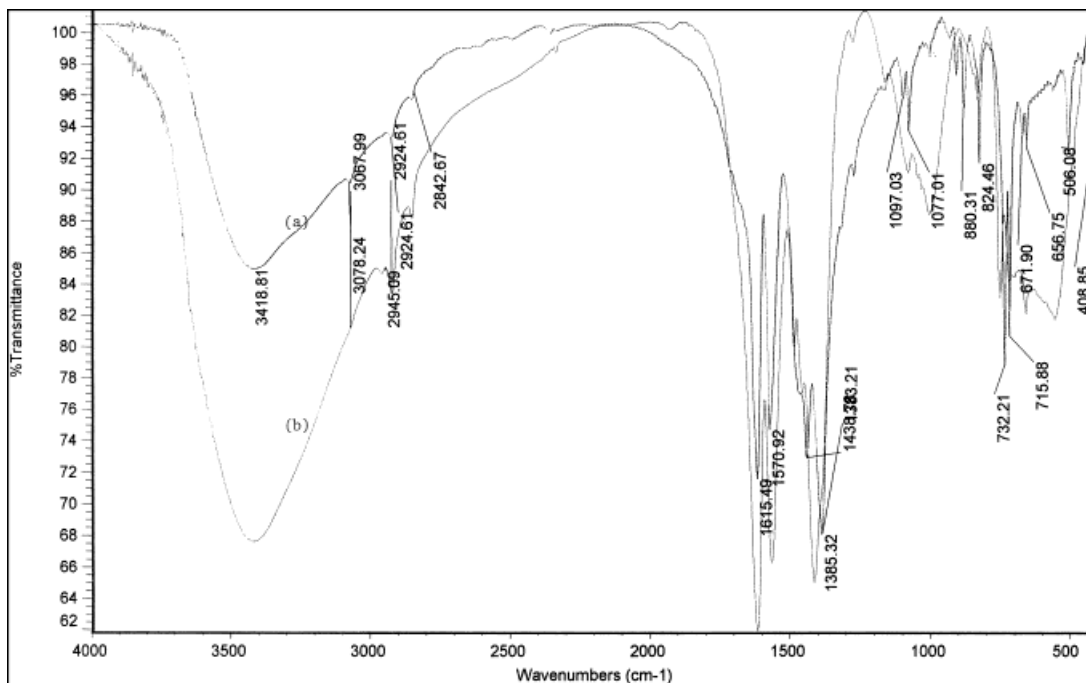


Figure 5 FTIR spectrum of (a) salt of isophthalic acid and (b) extract from polyester film.

equipped with a variable wavelength detector. Five microliters of sample was injected into a Zorbax Eclipse C18 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 1 mL/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 100–600. 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

Figure 1 is the tapping mode AFM image of the untreated polyester film. The left- and right-hand side of the AFM image provides the height data and phase information, respectively. The height scale is 100 nm and the phase scale is 90°. The polyester sample is smooth topographically but has some phase segregation. The presence of lighter and darker features in the phase information suggests that the polymeric film is highly heterogeneous. The shape and spacing of the lighter regions in the phase image vary within the sample. Assigning the light and dark features in the phase image to hard and soft regions in the polymeric sample is not straightforward,²⁴ because the phenomenon affecting phase image contrast is highly complex.^{25,26}

The phase image contrast is highly sensitive to material surface properties such as chemical and mechanical composition. Recently, using phase imaging and nanoscale indentation with the Tapping mode AFM, we showed that it is possible to effectively distinguish the hard and soft regions in a mechanically heterogeneous (polystyrene/polybutadiene) (PS/PB) blend.²⁷ However, when the same method was used along with the unmodified tip to study chemically heterogeneous [nonpolar (oxidized PS)/polar (oxidized PB)] blend, the method was not very effective.

Since we observe a phase image contrast in a polyester formulation free of pigments and additives, this suggests that there may be heterogeneous regions in the film. The heterogeneous regions in the neat polymer film can be a result of the entrapment of oligomers/unreacted molecules

Table I Infrared Vibrations and Assignments for (a) Salt of Isophthalic Acid and (b) Aqueous Extract from Polyester Film

(a) Isophthalic Acid Salt	
Peak Position (cm ⁻¹)	Assignment
3418	O—H stretching
3068	Aromatic C—H stretching (weak)
1615	Benzene ring stretching, might be overlapped with small part of C=O stretching absorption
1570	Asymmetric COO— stretching
1438, 1385	Symmetric COO— stretching
1096, 1077	Benzene ring bending
732, 715	Aromatic C—H out-of-plane deformation
(b) Salt of Extract Medium	
Peak Position (cm ⁻¹)	Assignment
3418	O—H stretching
1615, 1485	Benzene ring stretching, might be overlapped with small part of C=O stretching absorption
1566	Asymmetric COO— stretching
1414	Symmetric COO— stretching
1086, 1003	Benzene ring bending
750, 658	Aromatic C—H out-of-plane deformation

in a sea of cured polymer film.^{15,16, 28} Depending on the extent of cure, the film can have hard and soft regions.

Figure 2 is the AFM image of the dried polyester sample that was exposed to NaOH solution for 21 days at 24°C. In the AFM image of the exposed sample, we notice considerably more lighter features than that of the unexposed sample. Immersion of polyester coatings to alkali environment has caused significant physical changes. Some of the physical changes in the film are in the form of pits with lateral dimensions from tens of nanometers to several micrometers. The microstructure of the material present inside the pit was found to be different from that of the surrounding region. When these pits are connected along the thickness of coating, they provide the channels for corrosive ions to percolate through the film to the coating/substrate interface.

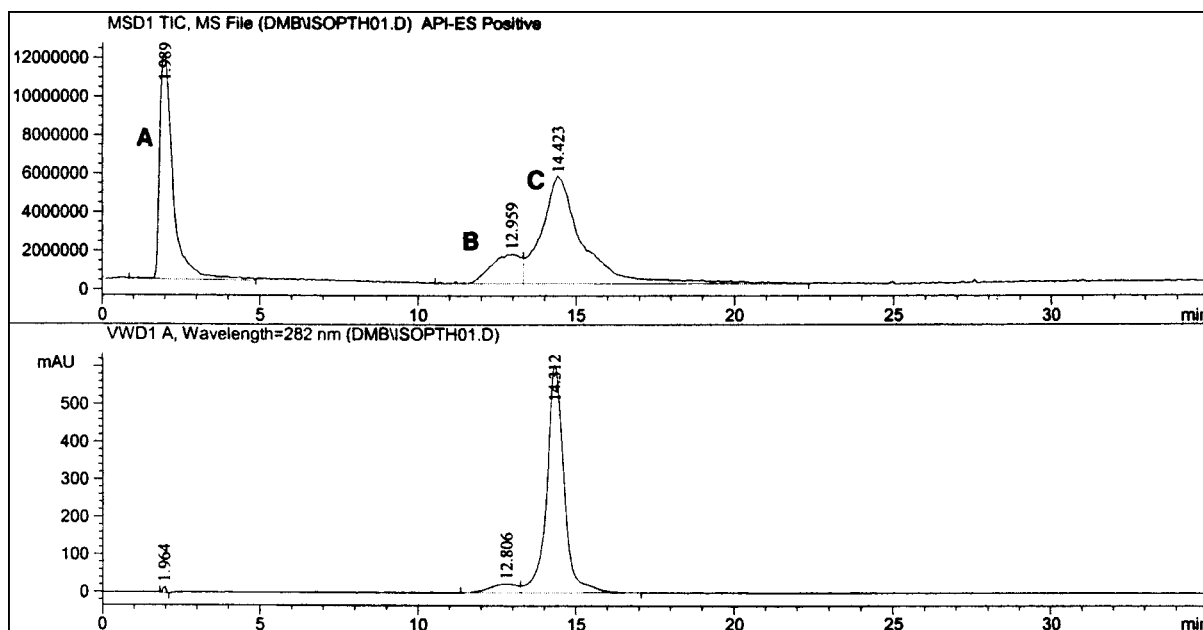


Figure 6 Chromatogram of the extract medium upon exposure of polyester film to NaOH solution

The observation of pits in certain locations of film suggests that these regions are presumably the degradation susceptible region.⁴ Because the saponified material is water soluble, they dissolve in the extraction medium, leaving behind polymer film. Further studies are needed to identify and directly map the degradation susceptible regions in the polymeric film by using chemically modified AFM tips.

To study the extent of subsurface level changes in polyester film due to immersion in alkali environment, roughness was measured. Figure 3 is a plot of mean square roughness of the film as a function of time of aging in NaOH medium at ambient temperature. The roughness rose rapidly within the first week and then leveled off, and at approximately 20 days, we notice a change in the slope of roughness. This suggests that polyester degradation in chemical environment is time dependent.

An attempt was made to correlate subsurface changes (roughness) to molecules leached from the coating film. The molecules leached from the polymer, if they are water soluble, chemical analysis of the leached medium should provide information of the degradation susceptible regions of the film.

TOC Analysis

Figure 4 is a plot of the TOC present in the extract medium upon exposure of polyester to the

alkali medium at different duration of aging. The control measurements had a small constant amount of organic carbon in the leachate, while the measurements of extracted material from polyester had a total organic carbon content which increased with duration of aging. For example, upon 50 day alkaline aging, 36 ppm of organic carbon was present in the extraction medium as compared to 2 ppm of the control experiment. The TOC results suggest that organic molecules are leached from the polyester film. An examination of the TOC data shows a change in the slope (i.e., rate of organic carbon formed in the extraction medium) after about 20 days. A similar change in the slope was also noticed for the roughness results obtained by AFM method.

FTIR Analysis

By FTIR, the chemical nature of degradation susceptible regions was identified. The FTIR spectrum of the organic extract medium is shown in Figure 5(b). The IR vibrations of organic extract medium are shown in Table I(b). Signature peaks of the monomer (acid salt) used in the polyester formulation were noticed in the spectra. The only band that was not necessarily used for spectral comparison was the OH band, due to the dependence of the OH band on the type of monomer and possibly trace amounts of water in the pellet, and the atmospheric conditions. The spectrum of the

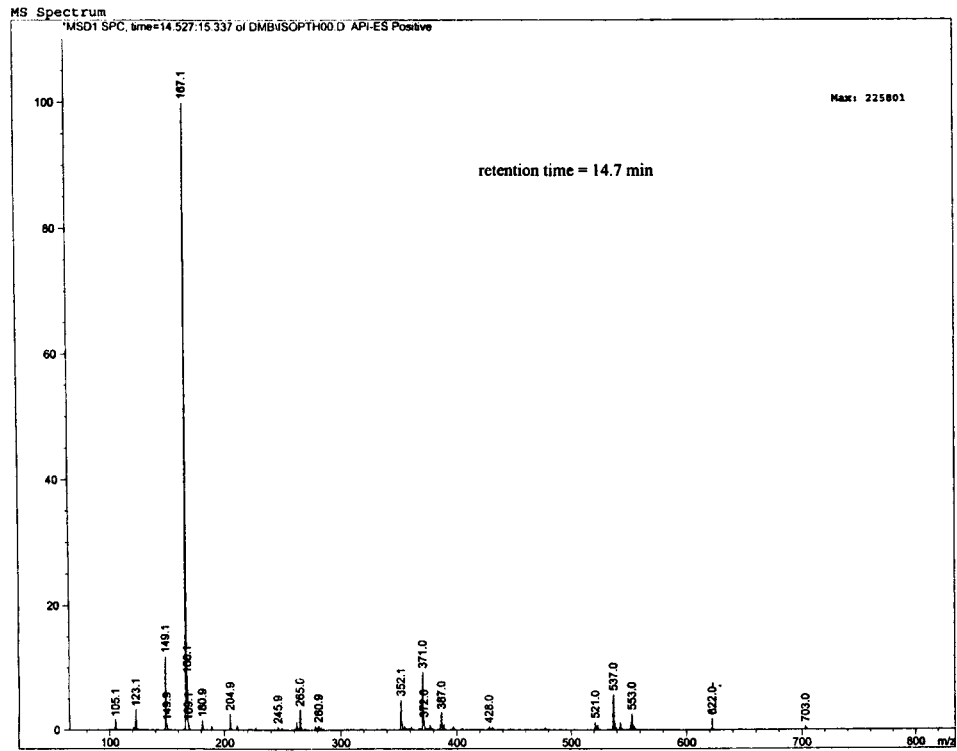
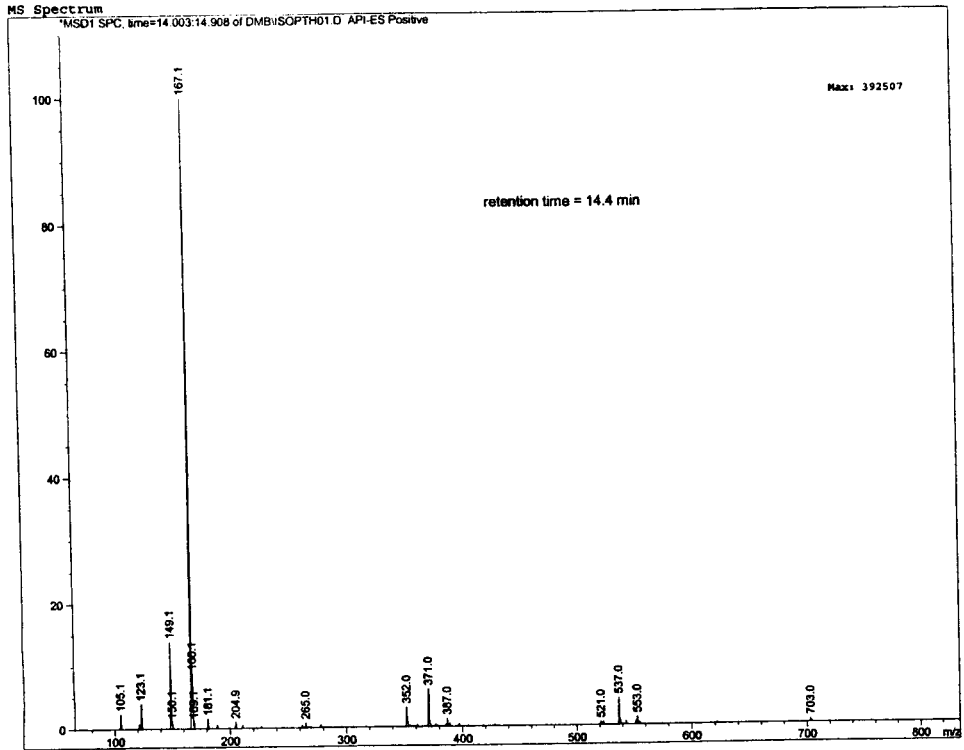


Figure 7 LC/MS of (b) salt of isophthalic acid and (a) extract from polyester film.

Table II LC/MS Identification of Molecular Species from Compounds C and Isophthalic Acid^a

Observed (<i>m/z</i>)	Probable Species ^b
105.1	(M—CO ₂ —H ₂ O + H) ⁺
123.1	(M—CO ₂ + H) ⁺
149.1	(M—H ₂ O + H) ⁺
167.1	(M + H) ⁺

^a Upon neutralization, the salt in the medium is present in the free acid form.

^b M = isophthalic acid (C₈H₆O₄).

disodium salt of isophthalic acid is shown in Figure 5(a). Table I(a) summarizes the peak assignment for salt of isophthalic acid. Isophthalic acid may be present in the polyester film as unreacted molecule or may be formed upon alkali degradation of ester units in polyester film. The formation of salt of isophthalic acid from the alkali degradation of ester units in polyester film has been described in the literature.¹³

Under acidic pH conditions, the hydrolytic degradation of esters is to a large degree reversible and sometimes incomplete. Under basic pH conditions, the hydrolytic degradation of esters is irreversible and complete because of the formation of resonance stabilized carboxylate anion. Similarly, it can be proposed that the reaction of hydroxyl ion with the carbonyl carbon of the ester groups in the polyester film yield carboxylate species and sodium salt of carboxylate. Since the resulting salt (soap) is far more water soluble than the ester counterpart, the salt promotes further solubilization of ester units in polyester film.

Recently, Chin et al.²⁹ performed degradation experiment by exposing polyester to a high pH concrete pore solution at elevated temperature and noticed low molecular weight carboxylate salt formation in the leached solution. This is in agreement with our observation that polyester film, upon exposure to alkali medium form low molecular weight carboxylate salts.

The formation of carboxylate salt due to the base-catalyzed hydrolysis of the ester, was confirmed by FTIR/attenuated total reflectance analysis of the unexposed and exposed polyester film.³⁰

LC/MS Analysis

Using LC/MS, we observed several components in the extraction medium. Figure 6 is the chromatogram of the acid neutralized extract medium upon degradation of polyester. We discuss the identification of one of the predominant species eluted upon injection of the extraction medium into the C18 column. Compounds A, B, and C elute at retention times of 1.98, 12.96, and 14.42 min, respectively. Compound A is not UV active at 282 nm, while the other two compounds are UV active. This suggests that compound A may not contain aromatic chromophore in the molecule, while compound B and C may contain chromophore in the molecule. Figure 7 is the mass spectrum of compound C. Compound C had similarities in their mass spectra with major peaks (greater than 5% of total abundance) at *m/z* = 105.1, 123.1, 149.1, 167.1. The peaks below 5% were not assigned because the spectrum was not corrected for background. Table II gives the probable identification for some of the peaks found in the positive ion spectrum of compound C. The spectral pattern of compound C had characteristics similar to the spectral pattern found in standard isophthalic acid. Since the LC/MS analysis was conducted on a neutralized extract using an acid modifier (CH₃COOH) in the mobile phase, any salt present in the extract would be present in the free acid form in the extract. Although the neutralized extract showed the presence of free isophthalic acid, salts of isophthalic acid is likely to be also present in the leachate of polyester film.

Compounds A and B from the extraction medium are currently being analyzed for chemical composition. The results revealed that the materials leached out from the films during immersion were mostly monomers. These materials were probably present in the degradation-susceptible regions (hydrophilic regions) as unreacted material and/or formed during alkali degradation of polyester.

CONCLUSIONS

We investigated the degradation of polyester films in an alkali environment. The following conclusions were drawn from the work:

1. The unexposed and exposed polyester film was characterized using AFM images. The presence of lighter and darker features in the AFM phase image suggests that the polymeric film is highly heterogeneous. The film exposed to NaOH solution was found to increase in roughness with expo-

- sure time. Pits were observed at certain locations in the degraded film, suggesting that these locations may possibly correspond to the degradation susceptible regions in the film.
- The leachate from the polyester film degradation studies showed the presence of organic species and the amount of organic carbon in the leachate was proportional to the duration of aging.
 - The FTIR spectrum of the extraction medium suggests the formation of carboxylic acid salts, following exposure of polyester to the alkali medium.
 - LC/MS analysis of the extraction medium shows the leaching of organic components from the polyester film. One of the components is isophthalic acid. The identification of isophthalic acid in the extract suggests the leaching of residual monomers (isophthalic acid) from the polyester film or the leaching of monomers that are formed upon chemical degradation of polyester film.

The findings are preliminary, but they do provide a benchmark for more exhaustive study of heterogeneous regions in polyester coatings.

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