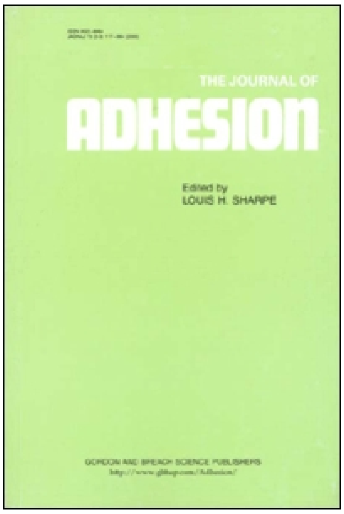

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Quantifying Water at the Organic Film/Hydroxylated Substrate Interface

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A method, based on Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy, for determining the amount and thickness of water at an organic film/hydroxylated substrate interface has been developed. The analysis uses a two-layered model, which takes into account: 1) water at the organic film/hydroxylated substrate interface, 2) water taken up by the organic film within the penetration depth of the evanescent wave and 3) change of the penetration depth as water displaces the organic film from the substrate. Experimentally, the method requires the application of an organic film, transparent or opaque, of sufficient thickness on a hydroxylated internal reflection element, which is used as the substrate. A water chamber is attached to the organic-coated specimen. After adding water to the chamber, FTIR-MIR spectra are taken automatically at specified time intervals without disturbing the specimen or the instrument. Water uptake in the organic films and FTIR-MIR spectra of water on the substrates are also obtained and used for the analysis. Results of examples of three organic films: a clear epoxy, an unmodified asphalt, and a pigmented ester, on a hydroxylated SiO_2-Si substrate were presented to demonstrate the method. The water layer at the interface for the ester and asphalt specimens was found to be much thicker than that for the epoxy, and this was attributed to the presence of a water-sensitive layer accumulated at the interface for the formers. The method should be equally applicable to studies of organic and inorganic compounds at the organic film/hydroxylated substrate interface and their transport rates through films adhered to a substrate.

KEY WORDS ATR; FTIR; interface; internal reflection spectroscopy; *in-situ* measurement; quantitative; water.

INTRODUCTION

Water at the interface is the primary cause of degradation of an organic film/substrate system. Probably the most severe effect of water at the organic film/substrate interface is the cathodic delamination and blistering that occurs near a defect when an organic-coated steel panel is exposed to electrolytes.[1-5] Water at the interface also causes the loss of adhesion of organic-coated substrates, adhesive bondings and paved asphalts when these materials are exposed to water or high relative humidities.[6-12] Finally, water at the interface is essential for corrosion to occur and spread on a metal surface under an organic protective coating. Consequently, measurement of water at the organic film/substrate interface is the subject of great interest in

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many industries including organic coatings, adhesives and asphalt pavements. Water and hydroxyl groups on surfaces can be studied effectively by a number of techniques.[13–15] However, until recent research at the National Institute of Standards and Technology that has led to a technique for measuring water *in situ* at the polymer coating/substrate interface, there has been no suitable technique available for organic-coated substrates.

Previously, we have described a technique based on Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy for studying *in situ* water at the coating/substrate interface.[16,17] We also gave expressions, which were derived rigorously from the theory of the internal reflection spectroscopy, for quantitatively studying water at the interface between an organic coating and an infrared-transparent substrate.[18] In this technique, an organic coating is applied to the surface of a plain or metallic-coated internal reflection element. A water chamber is attached to the organic-coated substrate and FTIR-MIR spectra of water accumulated in the coating/substrate interfacial region are collected at specified time intervals without disturbing the specimen, the conditions of the experiment, or the optical alignment of the instrument. FTIR-MIR offers a number of advantages for studying water at the organic film/substrate interface: 1) it is sensitive toward molecular water, its dissociated OH group, and its degrees of hydrogen bonding, 2) it can be used at ambient conditions, and is, thus, suitable for *in situ* measurement, and 3) it detects water from the substrate side, therefore, preventing the interference of water from the environment. This paper describes an empirical method based on FTIR-MIR spectroscopy to estimate the amount and thickness of the water layer at the interface between an organic film and a hydroxylated substrate. Since the surface of most common metals is covered with a hydroxyl-rich oxide layer,[19] quantitative information on water at the organic film/hydroxylated substrate interface will enhance our understanding of the mechanisms of the adhesion loss, delamination, and corrosion of organic-coated and adhesive-bonded substrates.

BACKGROUND

Fourier transform infrared spectroscopy has been recognized as a powerful technique to provide qualitative as well as quantitative information on complex molecules. On the other hand, the use of multiple reflections increases the sensitivity of internal reflection spectroscopy. In internal reflection, commonly known as attenuated total reflection (ATR), spectroscopy, the evanescent electric field penetrates the surface of the sample to a depth on the order of one wavelength of the radiation. The evanescent field, which decays exponentially with distance into the sample, interacts with the material of interest and causes an attenuation of the reflection of the propagating beam. Detection of the attenuated radiation at the exit of the substrate yields an infrared spectrum of the sample. This unique mode of interaction has made possible a large number of applications and new applications are being developed each year. These applications take advantage of the technique's ability to probe the near-surface layers of solids and liquids. Harrick[20,21] has developed the quantitative aspects of internal reflection spectroscopy and Mirabella[22,23] and

Iwamoto and Ohta[24,25] have provided experimental data for a variety of applications to validate the quantitative capability of this technique. The applications of this technique for studies of adsorbed species, ultrathin organic films and monolayer Langmuir-Blodgett films on substrates have been reviewed.[26-31]

When an organic-coated specimen is exposed to water, water will eventually enter the film/substrate interfacial region, interact with the evanescent wave and be detected. The model in which water at the organic film/hydroxylated substrate interface is quantified by the FTIR-MIR technique is illustrated in Figure 1. The substrate in this case is a hydroxylated internal reflection element (IRE) having a refractive index greater than those of organic films and water. The problem is treated as a two-layered sample model. The first layer consists of a water layer having thickness, l, in contact with the substrate. The second layer contains the water uptake in the organic film within the penetration depth of the evanescent wave, d_p, which is given by[21]

$$d_p = \frac{\gamma}{2\pi n_1 [\sin^2\theta - (n_2/n_1)^2]^{1/2}} \tag{1}$$

where γ is the wavelength of the infrared radiation in vacuum, n_2 and n_1 are the refractive indices of the sample and the substrate, respectively, and θ is the incident angle. d_p is defined as the point at which the amplitude of the evanescent field decays to $1/e$ of the value at the substrate surface. Most of the intensity of an absorbance band obtained by the FTIR-MIR technique derives from this depth.[24,25] Equation 1 is generally valid for non-absorbing or weakly-absorbing materials. For absorbing functional groups, Muller *et al.*[32] have derived a more exact equation for d_p, which uses the complex refractive index, $n_2/n_1(1 + i\kappa)$ (κ is the extinction coefficient), in place of the simple refractive index, n_2/n_1. Further, due to the rapid change in the magnitude of n_2 around the center of an absorption band (dispersion effect), d_p in the vicinity of the peak maximum may be different from that at or away from it, particularly for low n_1 and low θ,[21] as demonstrated recently by simulation.[33] However, Nguyen *et al.*[18] have shown that, for high refractive index substrates, *e.g.*,

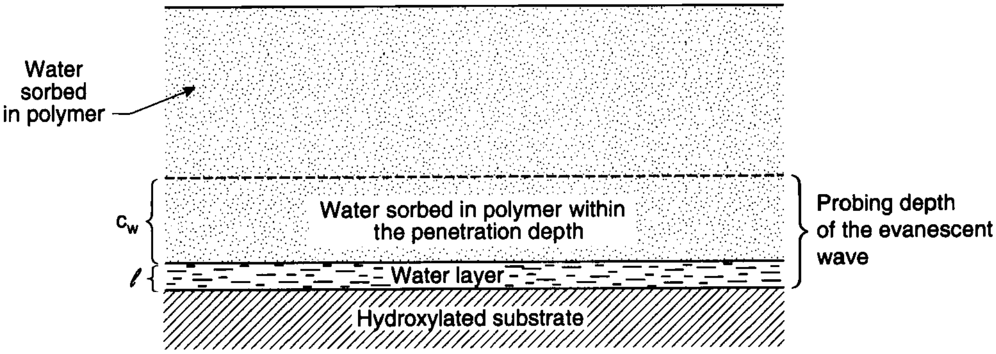

FIGURE 1 The two-layered model used for quantifying water at the organic film/hydroxylated substrate interface.

Si, the effect of absorption on d_p at the band center is negligible. For these substrates, Equation 1 is valid for determining d_p in water and polymers.

Figure 1 indicates that the total water detected consists of the water layer at the organic film/hydroxylated substrate interface and the water sorbed in the organic film within d_p. This statement can be mathematically written

$$W_t = W_{wi} + W_{wf} \tag{2}$$

where W_t is the total amount of water in the specimen detected by the FTIR-MIR technique, W_{wi} is the amount of the water layer at the organic film/substrate interface, and W_{wf} is the amount of water uptake in the organic film within d_p. All of these quantities vary with time, *t* and thickness of the water layer at the interface, *l*. If water is taken up only in the bulk of the film and does not enter the interface ($l = 0$), then $W = W_{wf}$. This means that the water detected is the water sorbed in the organic film only. On the other hand, if the thickness of the water layer at the interface is very large (*i.e.* $l > d_p$), then $W = W_{wi}$, indicating that only water at the interface is detected.

Equation 1 is more conveniently expressed in terms of fractions

$$F_w = c_w(1 - x) + x \tag{3}$$

where F_w is the fraction of water detected within d_p (mass of water detected within d_p/mass of the water layer having a d_p thickness), c_w is the fraction of water sorbed in the organic film within d_p (relative to initial weight of the organic film), and x is the thickness fraction of d_p occupied by water, which is given by

$$x = \frac{l}{d_p(x)} \tag{4}$$

where l is the thickness of the water layer at the organic film/hydroxylated substrate interface, as defined earlier, and $d_p(x)$ is the penetration depth as a function of the relative thickness of the water layer, x. Equations 3 and 4 are still valid for cases where the water layer is not continuous, *e.g.*, discrete droplets, provided that the height of the droplet is not greater than the d_p.

Since the refractive index of water is generally different from that of the organic films, d_p will vary as the organic material at the interface is gradually replaced by the water. This variation of d_p can be approximated by the simple linear relation

$$d_p(x) = d_{pf} - x(d_{pf} - d_{pw}) \tag{5}$$

where d_{pf} and d_{pw} are the penetration depths in water-free organic film and water, respectively. Assuming water is uniformly distributed on the entire surface area of the specimen, the amount of water at the organic film/hydroxylated substrate interface, w_i, is determined by

$$w_i = lA\rho \tag{6}$$

where A is the area of the specimen in contact with water and ρ is the density of water at the interface.

By using Equations 3 through 6, the thickness and amount of the water layer at the organic film/hydroxylated substrate interface are determined. F_w, the total amount of water detected, is obtained by combining the data of an FTIR-MIR *in situ* experiment of organic-coated specimens exposed to water and an FTIR-MIR intensity-concentration calibration curve for water. c_w, the mass of water uptake in the organic film within d_p, is derived from a water uptake study of organic free films. Values of d_{pf} and d_{pw}, the penetration depths in the organic film and water, respectively, at the bands of interest, are calculated from Equation 1. In this study, the thicknesses and amounts of water at the interfaces of three organic films applied on a hydroxylated silicon substrate were determined using the above equations to demonstrate the method.

EXPERIMENTAL SECTION

Three separate experiments were conducted to provide quantitative information on the water layer between an organic film and a hydroxylated substrate: 1) FTIR-MIR *in situ* measurement of an organic film applied on a hydroxylated substrate exposed to water, 2) FTIR-MIR analysis of water at different concentrations in contact with a bare hydroxylated substrate, and 3) water uptake in the bulk of the organic films.

FTIR-MIR *In situ* Measurement of Water in Organic-Coated, Hydroxylated Substrate

Specimens of three organic films on a hydroxylated substrate were used in this study. The three organic films were a phthalate ester (hereafter referred to as ester), an epoxy and an asphalt. The ester film was an opaque material containing 47.5 percent (by mass) pigment. The epoxy was a stoichiometric mixture of a low molecular weight, diglycidyl ether of bisphenol A and a polyethertriamine curing agent. The asphalt was an unmodified type. The substrates were 50 × 10 × 3 mm spectroscopic grade, 45° parallelogram Si internal reflection elements (IRE). At a 45° incident angle, these elements produce 17 reflections inside the substrates. When received, each IRE was wrapped in a soft cloth and hermetically sealed in a plastic envelop inside a rigid box containing desiccant and packaging foam. The Si IRE surfaces had an oxide (SiO_2, refractive index = 1.460) layer 2.25 nm thick on them, as determined by ellipsometry. The time between unwrapping and applying the organic films on the IRE was about one hour. This was the duration required to prepare the IRE before the organic film application. During this period, the IREs were exposed to ambient conditions (24°C and 45% relative humidity). The key characteristics of the SiO_2 surface are that it reacts readily with water and that, at ordinary temperature, its surface is covered with silanol (SiOH) groups.[34,35] Since the silanol group is energetic and hygroscopic, the $SiOH—SiO_2$ surfaces are generally covered rapidly with sorbed water.[19,34] The physically-adsorbed water can be removed by degassing at room temperature. However, even after heating up 400°C, more than half of the hydroxyl groups still remain on the SiO_2 surface. Most of these surface hydroxyl groups are adjacent to one another and are favorably positioned for preferential water adsorption.[35] Based on the above information, the surfaces of the substrate used in this study were presumed to have the chemical structure illustrated in Figure 2. This structure is similar to that proposed on a silica surface.[34,35] The SiO_2-covered Si IRE having sorbed water-SiOH groups on its surfaces was used as the hydroxylated SiO_2—Si substrate. No attempt was made to determine the SiOH coverage or the amount of sorbed water on the substrate surface.

Specimen preparation and FTIR-MIR *in situ* analysis of water at the organic film/hydroxylated substrate interface were similar to those described previously for polymer coatings on a germanium substrate.[16] Briefly, liquid ester and epoxy coatings and molten asphalt (at 60°C) were flooded on one end of one of the 50 x 10 substrate surfaces, then firmly pulled down toward the other end using a round glass rod. Masking tape strips of 1-mm width, placed along the length of the IRE, were used to control the thickness of the organic film. Four hours after the coatings were applied, the 1-mm masking tape strips were removed from the substrate. The bare areas (where the strips were removed) were covered (by brushing) with the same coatings. The film thicknesses were measured, using a micrometer, on dried, free films removed from the substrates after completing the experiment. The thickness result for each film was the average of five measurements. The quality of the specimens was good and no visible pinholes or air bubbles were observed (by the naked eye) on the coated specimens. After curing, a water chamber, with two ports for introducing and removing water, was mounted on the coated side of the substrate using a silicone adhesive. Figure 3 illustrates the specimen configuration for the measurement of water at the organic film/hydroxylated SiO_2—Si substrate interface by the FTIR-MIR technique. With this configuration, the only pathway for migration of water from the outside to the organic film/hydroxylated substrate interface is through the thickness of the film within the walls of the water chamber.

In situ measurements of water in organic-coated specimens were carried out using an FTIR spectrometer (Perkin Elmer 1760X*) with a variable angle ATR accessory

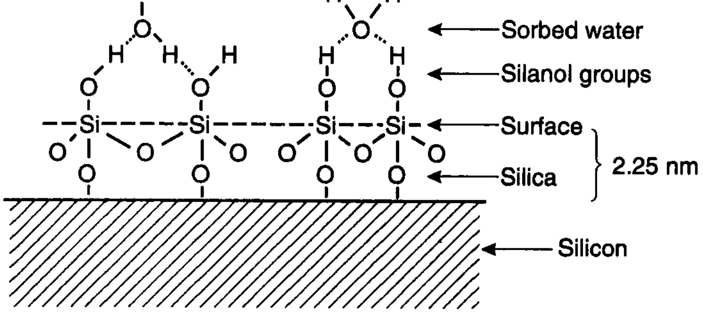

FIGURE 2 Postulated surface chemical structure of the substrates used in the study.

(Spectra Tech*). The spectrometer was equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The specimen with the water chamber attached was placed vertically in an ATR accessory holder (Fig. 3). After placing the ATR holder with the mounted specimen in the spectrometer, and prior to filling the chamber with water, the spectra of the specimens before water exposure (unexposed) were taken. Distilled water was then added to the chamber and inlet and outlet ports were sealed to prevent water evaporation. FTIR-MIR spectra of the water-exposed specimens were taken automatically at every 15 minutes until the experiment was complete. This was done without disturbance to the spectrometer or to the specimens. The spectrum obtained was the ratio between the single beam spectrum taken at each exposure time and that of the background (specimen-free spectrometer). Spectra were collected at 4 cm^{-1} resolution using purged dry air, 32 scans, and unpolarized radiation at 45° incident angle. The peak height method was used for quantitative analyses.

FTIR-MIR Analysis of Different Concentrations of Water in D_2O

An FTIR-MIR analysis of eight different H_2O concentrations in D_2O solutions (w/w) was conducted to establish an FTIR-MIR intensity-concentration curve for

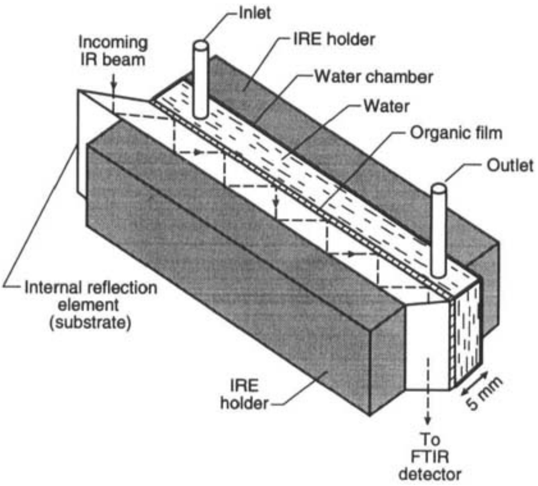

FIGURE 3 Experimental setup for measuring water at the organic film/hydroxylated substrate interface.

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* Certain commercial equipment is identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

water. Distilled water and reagent grade D_2O were used. In this study, a water chamber was attached to a bare (no organic film) hydroxylated IRE (substrate). The chamber was filled with each water/D_2O solution and FTIR-MIR spectra were taken using the same procedure for exposed, organic-coated specimens. The FTIR-MIR spectrum was the ratio between the single beam spectrum of water in contact with the bare, hydroxylated substrate and that of the water-free, bare, hydroxylated substrate.

Water Uptake in Organic Films

Water uptake of the organic films (detached film for ester and epoxy, and film applied to an aluminum plate for asphalt) was determined using the gravimetric method. Free films of ester and epoxy coatings were acquired by applying the coatings onto a polished poly(tetra fluoroethylene) substrate. The water uptake in the ester free film was obtained from a one-faced water absorption experiment, as described in Reference 36. Data of water uptake in the asphalt film was taken from Reference 37. For the epoxy, free films were prepared, weighed and immersed in distilled water. They were taken out, blotted and reweighed at specified time intervals. The thicknesses of the ester epoxy and asphalt films were 109 ± 10, 145 ± 18 and $65 \pm 8\,\mu m$, respectively. Water uptake is expressed as a fraction of the mass of the initial, dry specimen. Three specimens of each organic film were used.

RESULTS AND DISCUSSION

FTIR-MIR *In situ* Measurement

Figure 4 presents typical, unprocessed FTIR-MIR spectra of an organic film (phthalate ester) on a hydroxylated SiO_2—Si substrate before and during exposure to water for different time intervals. The effect of exposure to water for different times on the specimen is evident in these spectra. However, these spectra still contain the absorbance bands of the organic films. To provide quantitative information on the water layer at the organic film/hydroxylated substrate interface, the FTIR absorbance of the organic films before exposure must be nullified. This was done by subtracting the spectra collected before exposure to water from those acquired at different exposure times. The subtraction was carried out after adjusting for the baseline shifts, some of which may be seen in the spectra in Figure 4. Figures 5a–5c display the FTIR-MIR difference spectra in the 2700–3800 and 1500–1800 cm^{-1} regions of ester, epoxy and asphalt films on a hydroxylated SiO_2—Si substrate for several representative exposure times. The thicknesses of the ester, epoxy and asphalt films were $143 \pm 8, 429 \pm 24$ and $63 \pm 12\,\mu m$, respectively. As emphasized earlier, there were no mirror or sample adjustments throughout the measurements. If there were no effect from the exposure to water, all difference spectra would be straight lines, with the exception of the intensity fluctuations of the bands near 2350 cm^{-1}, due to CO_2, from the dry air in the spectrometer. Difference spectra,

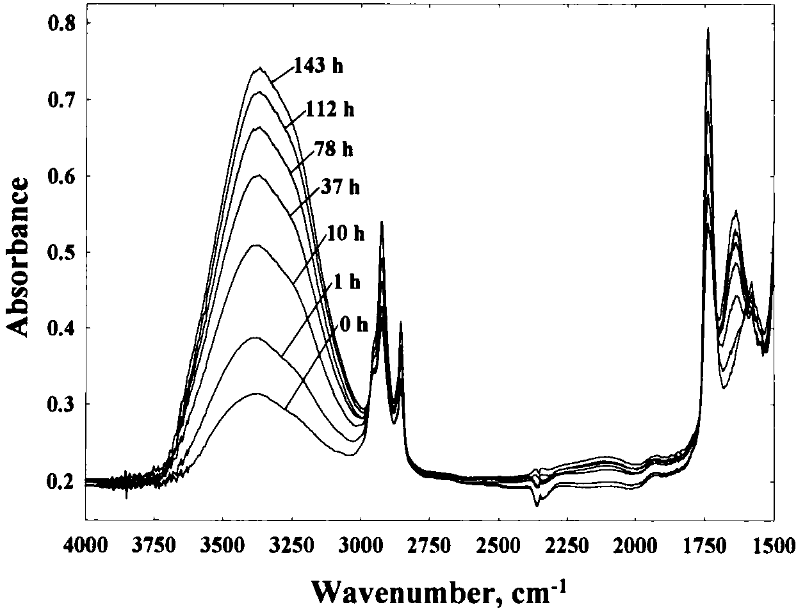

FIGURE 4 Typical unprocessed FTIR-MIR spectra for several exposure times of *in situ* measurement of water at the organic film/hydroxylated substrate interface.

such as those shown in Figure 5, were used for quantitative studies of water at the organic film/hydroxylated substrate interface.

Figures 5a–5c clearly illustrate the effect of water on the organic-coated specimens. The intensity of the bands in the 3100–3650 and 1625–1645 cm^{-1} regions increased, and the intensity of the organic film bands, *e.g.*, at 1737 cm^{-1}, due to C=O stretching, for the ester and at 2925 cm^{-1}, due to CH stretching for all three films, decreased with exposure time. The decrease has been found to depend on the band absorption strength: the stronger the band, the larger the decrease.[16] These changes are the result of water entering the organic film/hydroxylated substrate interfacial region and interacting with the evanescent wave, and not due to swelling of the organic films caused by water uptake. Because the penetration depths of the evanescent wave in water-saturated and in water-free organic films are essentially the same, any swelling of the organic films will result in a decrease, and not an increase, in the intensity in the 3100–3650 cm^{-1} region of the organic film spectrum. The results strongly indicate that intensity increase in the OH—stretching region, and the intensity decreases of the organic film bands at other regions, were due to water entering the organic film/hydroxylated substrate interface and pushing the film away from the substrate surface.

The bands near 3400 and 1640 cm^{-1} in Figures 5a to 5c, whose intensities increased with exposure time, are due to molecular water. This is verified by Figure 5d, which exhibits an FTIR-MIR spectrum of double distilled, liquid water on the same hydroxylated SiO_2—Si substrate. This spectrum was acquired using the

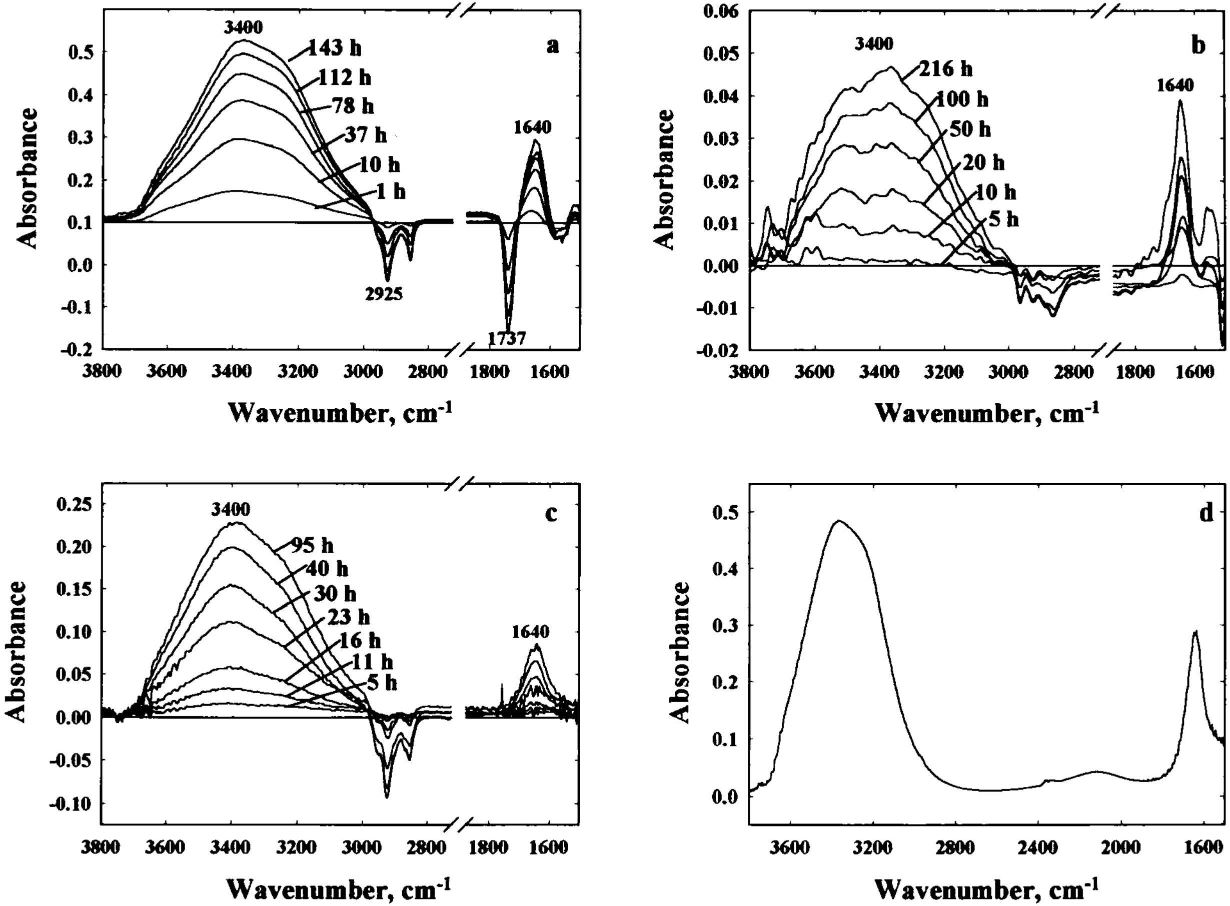

FIGURE 5 FTIR-MIR difference spectra for several times of exposure to water: a) ester, b) epoxy, c) asphalt, and d) FTIR-MIR spectrum of liquid water in contact with a hydroxylated SiO_2—Si substrate.

same procedure used for collecting the FTIR-MIR spectra of organic-coated specimens during water exposure, except that there was no organic film on the substrate. This is considered the spectrum of bulk water because the probing depth of the evanescent wave in the sample is several hundred nanometers. Except for the intensity difference, the peak positions and band shapes of this spectrum resemble those of the water spectrum obtained using a Ge internal reflection element.[16] The intensity difference is due to the difference in the refractive indices between the Si and Ge substrates, which produces a difference in their d_p values in water. The FTIR-MIR spectrum of liquid water shows a broad band peaking near 3400 cm^{-1}, due to hydrogen-bonded H—O—H stretching, and a band near 1640 cm^{-1}, due to H—O—H bending. These peak positions are similar to those of the liquid water spectrum obtained by infrared spectroscopy in the transmission mode.[38,39] It is noted that the stretching band of an adsorbed H_2O molecule on a substrate surface is similar to that of an isolated H_2O molecule, *i.e.*, above 3700 cm^{-1} frequency, because the adsorption only slightly perturbs the bond lengths and force constants of the molecule in the gas phase.[15] The presence of the bending mode at 1640 cm^{-1} in the spectra of the organic-coated specimens during the *in situ* measurement (Figs. 4 and 5a–5c) strongly indicate that molecular water was detected. If water in the specimen is present in any of its dissociated forms, *e.g.*, O—H, the 1640 cm^{-1} was not observed.

Figure 6 depicts the intensity (peak height) changes of the water OH-stretching band at 3400 cm^{-1} as a function of exposure time for the three specimens. All three

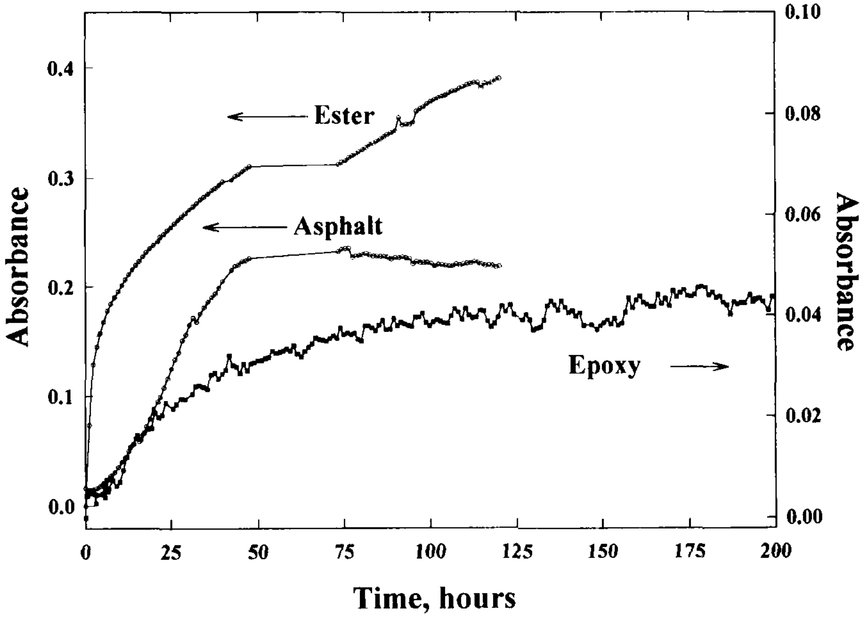

FIGURE 6 Intensity changes of water OH-stretching band as a function of exposure time to water for three specimens (each dot represents a data point). Note, for clarity, a different scale is used for the epoxy.

specimens show a rapid increase in intensity at short exposure times. Thereafter, it rose at a slower rate. The increase was much greater for the ester and asphalt specimens than for the epoxy specimen. These curves will be used for deriving F_w values in Equation 3.

QUANTITATIVE ANALYSIS

FTIR-MIR Intensity-Concentration Calibration Curve for Water

In order to translate the FTIR-MIR intensity (Fig. 6) to the amount of water, an intensity-concentration correlation for water using the same analytical technique must be established. This was accomplished using water at different concentrations in D_2O solvent. Figure 7 presents FTIR-MIR spectra of water at eight different concentrations in D_2O. It is noted that when H_2O and D_2O are mixed, HDO is formed and the solutions comprise HDO, H_2O and D_2O. Accordingly, the FTIR-MIR spectra of the solutions will contain contributions from H—O—H, D—O—D and D—O—H bonds. Since for every two H—O—D molecules formed, one molecule of water is consumed, the intensity of the OH group in the spectra should be proportional to the concentration of water in the solutions. Any deviation from this proportionality is due to factors other than the mixing of the two solutions, *e.g.*, the degrees of hydrogen bonding.

The bands at 3400 and 1640 cm^{-1} of Figure 7 are due to molecular water, as discussed earlier, and the band near 2510 cm^{-1} is due to D_2O molecules. Figure 7

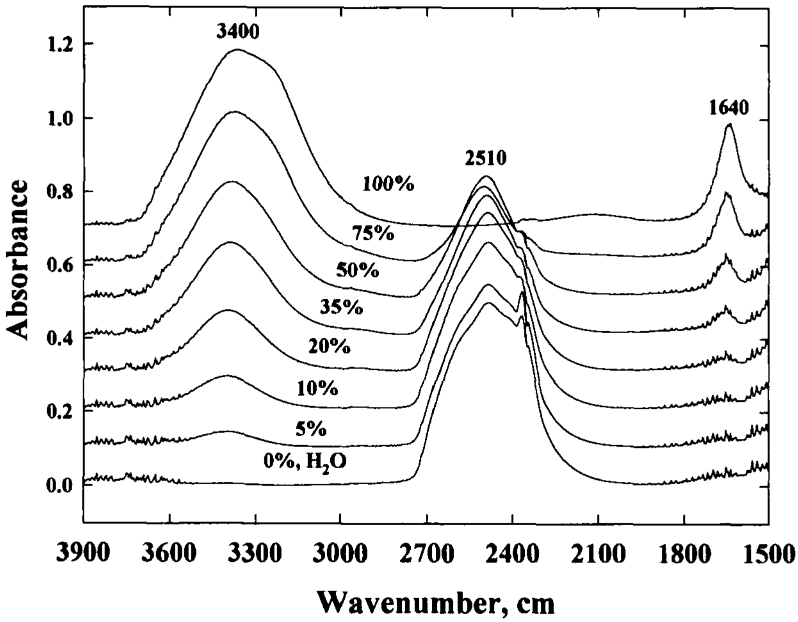

FIGURE 7 FTIR-MIR spectra of water at eight different concentrations in D_2O.

shows that the OH-stretching bands for water concentrations from 5 to 35% are mostly symmetrical while those at higher concentrations are not. The OH bending mode at $1640\,cm^{-1}$ only becomes visible at water concentrations $>20\%$, indicating that this band is not useful for detecting water at low concentrations. Careful examination of the 100% water spectrum reveals a very weak shoulder at around $3625\,cm^{-1}$. This band is believed to be due to the non-hydrogen-bonded OH stretching of liquid water. This assignment is consistent with the results obtained by infrared transmission spectroscopy of liquid water.[38] Liquid water at room temperature contains from 5 to 30% non-hydrogen-bonded molecules (depending on the method of study).[40] However, because non-hydrogen-bonded OH is much less effective in absorbing infrared radiation than hydrogen-bonded OH, the intensity of the $3625\,cm^{-1}$ shoulder is very low. Figure 7 also discloses that the shoulder around $3250\,cm^{-1}$ of the OH stretching, which is not visible at concentrations below 50%, becomes pronounced at 75 and 100% water concentrations. This shoulder is probably due to the contribution of the overtone of the $1640\,cm^{-1}$ band.[38,40] Due to the asymmetrical shape of the OH stretching band at high water concentrations and the lack of sensitivity of the OH bending mode at low water concentrations, the peak height (instead of peak area) of the OH stretching band was chosen for quantitative analysis.

Figure 8 illustrates the FTIR-MIR intensity changes of the water OH stretching as a function of the fractional water concentration. The lower horizontal axis of Figure 8 also gives the corresponding amounts of water within the penetration depth. The amount was calculated using a d_{pw} value of $0.224\,\mu m$ at the OH stretching frequency ($3400\,cm^{-1}$, $2.94\,\mu m$) (see Fig. 10). It is obvious from Figure 8 that the intensity-concentration relationship for water obtained by the FTIR-MIR technique does not follow the well-known Beer-Lambert law. The deviation from linearity starts at approximately 20% water and increases as the concentration of water increased. Figure 8 will be used for converting the FTIR-MIR intensity of Figure 6 into water fraction (F_w).

Water Uptake in Organic Films

The total water detected in the sample is the sum of, i) the amount of sorbed water in the organic film within d_{pf} and, ii) the amount of water layer at the organic film/hydroxylated substrate interface, as depicted in Figure 1. By accounting for (i), the amount of the water at the organic film/hydroxylated substrate interface can be deduced. The amount of water sorbed in the organic films within d_{pf} was determined from the water uptake in the bulk of the organic films, which are given in Figure 9 for the three films. All three films took up water rapidly in the first 10 hours; thereafter, the rates of uptake of the ester and epoxy films fell to a very low value by about 100 h. The rate of uptake for the asphalt slowed down between 10 and 50 h, then rose again thereafter up to the time the experiment was terminated (300 h). The maximum fractional uptakes in the ester, epoxy and asphalt (taken at 150 h for ester and epoxy and 300 h for asphalt) films were about 0.04, 0.019 and 0.052, respectively. The mass fractions of water sorbed in the bulk of the organic films within d_{pf} (c_w in

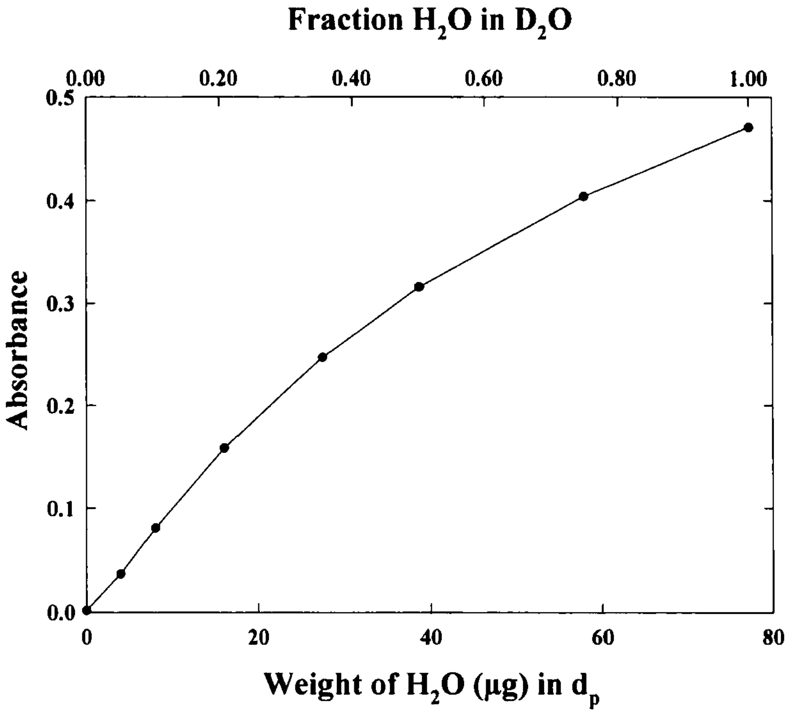

FIGURE 8 FTIR-MIR intensity-concentration calibration curve for water on a hydroxylated SiO_2—Si substrate.

Equation 3) were extrapolated from Figure 9, assuming that all sorption sites in the films must be occupied by the same amount of water before the next layer of water is sorbed. There is no information available to validate this assumption for polymers; however, it is in agreement with adsorption of water on oxide surfaces.[15]

Evanescent Wave Penetration Depth in Water and Organic Film

The determination of water at the organic film/hydroxylated substrate interface using the method described here also requires the values of the penetration depth of the evanescent wave in the organic films (d_{pf}) and in water (d_{pw}) at the wavelength of interest (Equation 5). These values were computed from Equation 1 and the results as a function of wavelength are displayed in Figure 10. The calculations were made using an angle of incidence of 45° and refractive indices of the substrate of 3.5 for Si[21], 1.30 at 2.94 μm wavelength for water,[41] 1.5 for ester and epoxy films, taken from the value for a typical polymer[42] and 1.55 for asphalt, which was extrapolated from data of Reference 43. Note that although the refractive index of a pigmented film is a composite of the polymer and the pigment,[44] we used a refractive index

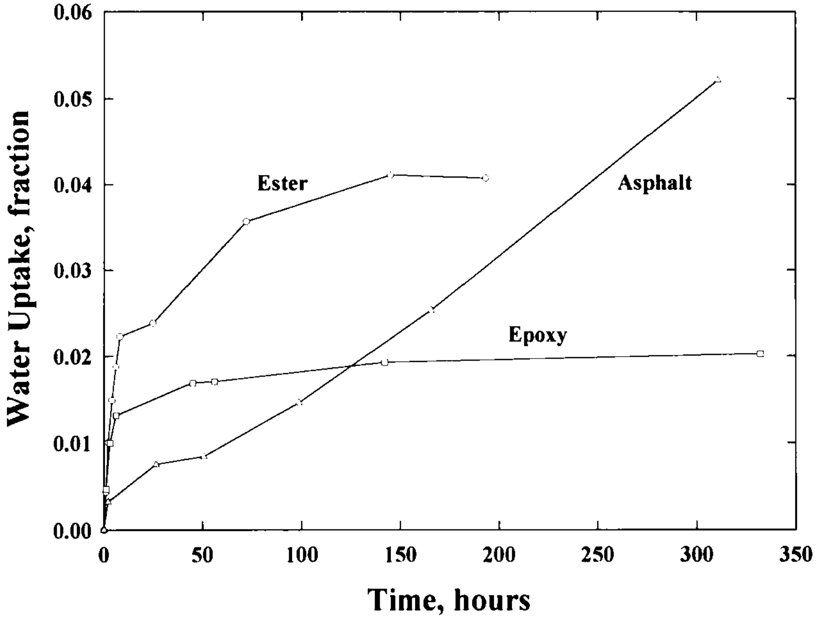

FIGURE 9 Water uptake in organic free films.

value of an unpigmented polymer for the calculation of the ester film. The use of this value is correct for the present study because water is primarily sorbed in the polymers with, perhaps, some at the polymer/pigment interface but not in the bulk of the pigment particles. In the calculation, we also ignored the effect of the SiO_2 layer on the surface of the Si substrate, because this layer is not only very thin (2.25 nm) but also because it has a refractive index (1.46) close to that of the organic films. Thus, it has little effect on d_p. Figure 10 demonstrates that, at long wavelengths, the MIR technique can probe rather deeply into the organic films and water in contact with a Si substrate. There is only a slight difference in d_p of asphalt and polymer, particularly at high wavelengths. Further, d_p in the organic films is greater than in water. This difference varies with wavelength, being smaller at shorter wavelengths. For the water OH-stretching band (3400 cm^{-1}, 2.94 μm), there is only a small difference in the d_p values, regardless of whether an organic film or water is in the interfacial region. At this wavelength, d_p values in ester or epoxy, asphalt and water on a Si substrate were 0.239, 0.242, and 0.224 μm, respectively (Fig. 10). These results, which will be used in Equation 5, indicate that the signals observed (Fig. 4) were mostly derived from water close to the organic film/hydroxylated substrate interface. It should be mentioned that the peak maxima of the OH stretchings of both ester and epoxy films before exposure also occurred at the same position of that of water, 3400 cm^{-1}. Further, there was little evidence of absorption in the OH stretching region for the asphalt sample. Thus, Equation 1 is valid for obtaining d_p at the OH stretchings in water as well as in organic films, as stated earlier.

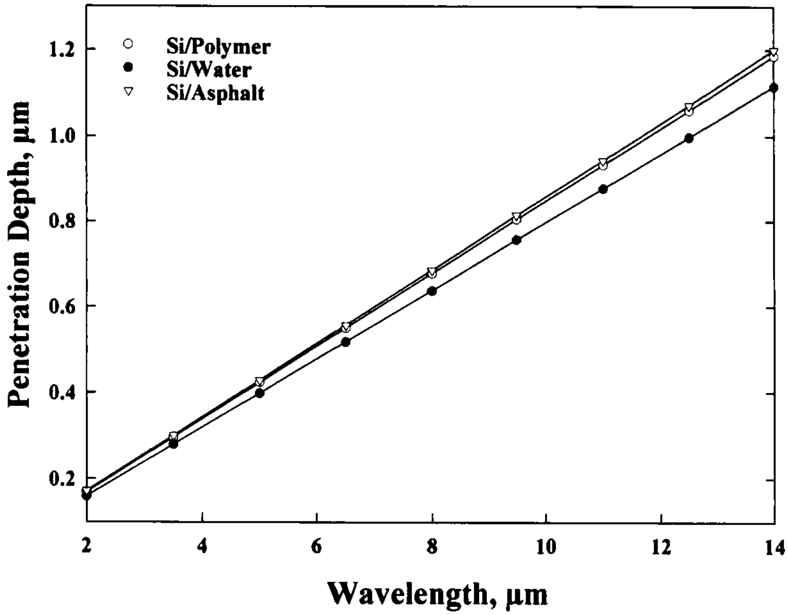

FIGURE 10 Penetration depths of the evanescent wave in organic films and in water on a Si substrate as a function of wavelength. Unfilled symbol: organic film; filled symbol: water.

Thickness and Amount of Water at the Organic Film/Hydroxylated SiO_2—Si Substrate Interface

The thickness of the water layer at the organic film/hydroxylated substrate interface was determined using Equations 3 through 5 and all the information presented above. F_w, the total amount of water detected within d_p, was derived using the experimental data of Figure 6 and the intensity-concentration calibration curve of Figure 8. c_w, the mass fraction of water uptake in the organic film, was obtained from linear interpolation from the data given in Figure 9. It should be mentioned that the water sorption process in the ester and asphalt films was from only one face of the specimen. This process simulates the experiment used for quantifying water at the organic film/hydroxylated substrate interface. On the other hand, the water uptake in the epoxy free films took place on both faces of the film. Accordingly, to provide a rough correction for the difference in the experimental conditions, c_w values of the epoxy were derived after multiplying by two the time scale of the water uptake in the epoxy free films. Values of d_{pf} and d_{pw}, the penetration depths in organic films and water, respectively, at 2.94 µm wavelength, were taken from Figure 10. The amount of water was determined by Equation 6 using an area value of 329 mm^2, the surface area of the organic-coated substrate within the water chamber, and a density of water at the organic film/hydroxylated substrate interface of 1 Mg/m^3.

Figures 11a–c present the thickness and the amount of the water layer at the organic film/hydroxylated SiO_2—Si substrate interface as a function of exposure time for the ester, epoxy and asphalt specimens, respectively. Figure 11 also includes the total amount of water detected (upper curves). The difference between the upper curve and lower curve of each specimen is the mass of water absorbed in the organic film within d_{pf}. There are some fluctuations in the data of the epoxy specimen, probably due to experimental errors resulting from the baseline adjustment and spectra subtraction procedures. These errors are normal in FTIR spectroscopy when dealing with minute concentrations, as in the case of the epoxy specimen. However, the deviations are very small and do not affect the general trend of the data. Figure 11 shows that, for the ester and asphalt films, the amounts of water uptake in the bulk

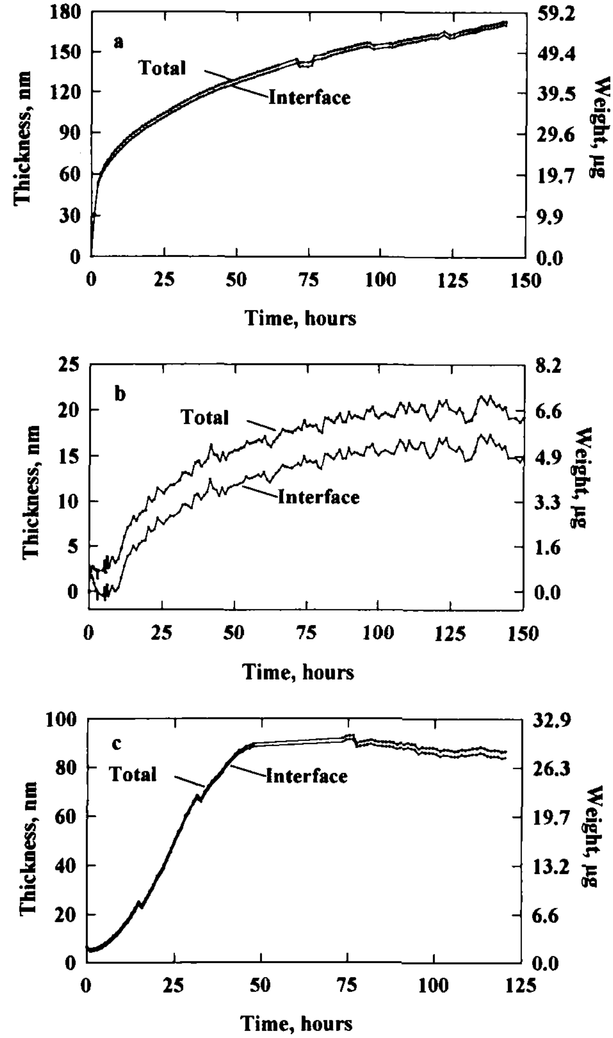

FIGURE 11 Amount of water and thickness of the water layer at the organic film/hydroxylated substrate interface: a) ester, b) epoxy and c) asphalt. (Each dot represents a data point.)

of the organic films detected by the FTIR-MIR technique was small compared with those at the interfaces. However, for the epoxy, because the amount of water at the interface was low, the relative contribution of water sorbed in the film with respect to the total water detected was substantial. The water layers at the ester/hydroxylated SiO_2—Si and asphalt/hydroxylated SiO_2—Si substrate interfaces were much thicker than that at the epoxy/hydroxylated SiO_2—Si substrate interface. Further, the initial rates of increase of the thickness of the water layers for the ester and asphalt-coated specimens were also much higher than that for the epoxy specimen. The results suggest that the epoxy/hydroxylated SiO_2—Si system was more resistant to displacement by water than the ester or asphalt/hydroxylated SiO_2—Si system.

Discussion

The use of variable water uptake in the bulk of organic films as a function of exposure time in Figure 9, instead of using the water uptake at equilibrium, for the quantitative analysis of water at the organic film/hydroxylated interface deserves some comments. The use of these data implies that, at steady state, all sorption sites in the organic films must be occupied by the same amount of water before the next layer of water is sorbed. This means that after a steady state was reached, the concentration of water remained constant at all points of the organic films. This assumption is analogous to that used in the derivation of the diffusion equations of materials in polymers based on the permeation approach.[45] Brown[46] also made a similar assumption in his analysis of water clustering in polymers. Although there has been much work on the sorption of water in polymers,[47,48] there is no information available that could be used to test this hypothesis. However, the premise that each sorption site in the organic film was occupied before the next water layer was formed is in agreement with adsorption of water on oxide surfaces.[15] For these materials, water does not generally favor multiple occupancy of sites at low coverage until almost all sites are occupied. Apparently, the tendency to "cluster" is overridden by the oxide-H_2O interaction, which ties the H_2O to specific oxide sites. This is in contrast to the adsorption of water on clean metals, which tends to form multilayers at low coverage.[15] For these substrates, the adsorption of water directly on the metal sites and on other water molecules are energetically equivalent. Consequently, multilayers of water can start to form on a clean metal surface even before the first layer is saturated.

The use of the variable water uptake/time curve for the analysis also denotes that water breaks the organic film/hydroxylated substrate bonds as it reaches them. This assumption is consistent with the analysis by Wu,[49] and the results of Kinloch,[50] Comyn[51] and Nguyen and Byrd,[52] who showed that the thermodynamic work of adhesion between a polymer and an untreated, high-energy substrate in the presence of an aqueous liquid is negative. The negative work of adhesion indicates that the interfacial bonds are not stable in the presence of water and that water is capable of displacing the organic film from the substrate. This means that water is likely to enter the interface when an organic film/untreated, high energy substrate system is exposed to a humid environment. The assumption that water enters the organic film/hydroxylated interface is substantiated by the results of Figure 11. This figure shows not only that liquid water entered the interface but also that it entered very early in the exposure. For the ester and asphalt specimens, we detected water within one hour of exposure. For the epoxy film, molecular water did not appear until after seven hours. Further, since d_p in water-free and water-saturated organic films is essentially the same, the decrease of the coating bands with exposure time (Fig. 5) may only be explained by the fact that water had entered the interface and pushed the organic film from the substrate. For the organic film/hydroxylated SiO_2—Si system used here, water probably entered the interface by breaking the water-silanol bonds and building up the water layer on the silanol-terminated surface. This occurred because the hydrogen bonds between the first water layer and the silanol groups on a silica surface have been found to be substantially weaker (about 25 kJ/mol) than the bonds between the first and second layer of water (> 40 kJ/mol).[53]

The accumulation of molecular water at the organic film/hydroxylated substrate interface is further corroborated by comparing the water uptake in free films and that of films applied to a substrate.[54–56] These studies have shown that the water uptake in the films applied to a substrate is higher than that in the free film. Funke and Haagen[55] noted a cross over in the water uptake-time curve between the applied film and free films and attributed the excess water in the applied film to water at the interface.

What would be the effect on the thickness of the water layer at the organic film/hydroxylated substrate interface if these two assumptions did not hold or were only partially correct? That is, if the interfacial bonds are relatively strong, *e.g.*, due to mechanical hooking or strong ionic interactions, and water is absorbed in voids and cavities of the organic films, or by water-soluble impurities in it. In such a case, a substantial amount of water might be absorbed in the organic films before entering the interface. To address this question, we analyzed the extreme case where water completely saturated the organic film before entering the interface. In this situation, we used the maximum (equilibrium) fraction values (instead of the variable fraction/time) of water uptake from Figure 9 for c_w in Equation 3. This would give a lower limit on the thickness of the water layer at the interface. The results obtained showed essentially no difference between the two cases for the ester and asphalt specimens. This is because the amount of water sorbed in the penetration depth of the evanescent wave is small compared with that of the water layer at the interface. For the epoxy specimen, due to the low concentration of water at the interface, there is a slight difference, particularly at the low water thickness values (Fig. 12).

The results of Figure 11, which showed that at long exposure times many monolayers of water had accumulated at the organic film/hydroxylated substrate interface (one water monolayer is approximately 0.3 nm), also requires some discussion. Indeed, this was the case because we observed substantial amounts of liquid water beneath the ester and asphalt films as they were peeled from the hydroxylated SiO_2—Si substrate at the conclusion of the experiment. The presence of a substantial amount of water underneath the epoxy film was also evidenced by the wetness, which disappeared instantaneously, on the substrate at the peeling front. These results strongly indicate that the intensity increase of the water bands and intensity decrease of the organic bands observed in Figure 4 were due to the increase of the thickness of the water layer at the organic film/substrate interface. As the thickness

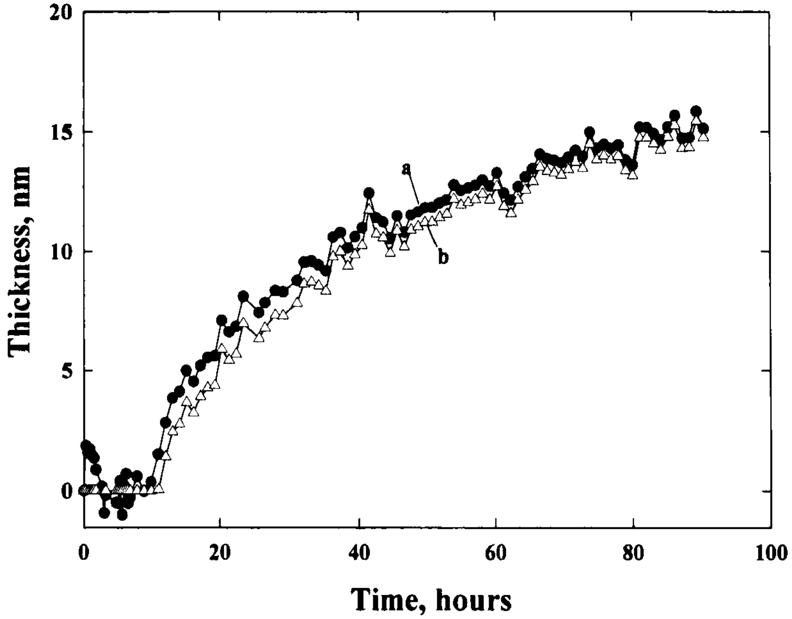

FIGURE 12 Thicknesses of the water layer at the epoxy film/hydroxylated substrate interface for a) c_w varies with exposure time and b) c_w at maximum (equilibrium).

of the water layer at the interface increased, the amount of organic material within the probing depth decreased because the coating was pushed further away from the substrate. Leidheiser and Funke[8] have given examples and cited references to support the evidence of the presence of multilayers of water at the organic coating/metal interface. Another piece of evidence comes from water adsorption studies on high-energy surfaces. For example, Zettlemoyer and coworkers[57,58] noted that a monolayer of water on ferric and nickel oxides occurs at low relative humidities, but multilayers exist at a relative humidity of 90%. Bowden and Throssell[59] found that up to 20 molecular layers of water were on aluminum, iron and SiO_2 surfaces at ambient temperatures and humidities. Similarly, Debye and van Beek[60] reported that silica powder, washed with water and then dried at 100°C, retained a water adsorbed layer tens of nanometers thick. The presence of multilayers of sorbed water on the surface of different types of glass has been discussed briefly by Bascom.[61]

The amount of water at the coating/substrate interface is greatly increased if the interface also contains hydrophilic contaminations. Bowden and Throssell[62] found that, even at a relative humidity of 50%, a metal contaminated with 10^{-7} g/cm^2 of potassium hydroxide would sorb the equivalent of five monolayers of water. It should be noted that, in the presence of salt contamination, a liquid phase of water at the interface can be formed at humidities far below the saturation point of water (humidity of liquification). For some salts, this humidity of liquification is quite low. For example, the humidities of liquification of LiCl and $CaCl_2$ are only 15 and 32%, respectively.[63] Thus, if the interface is contaminated with these salts, it is likely to hold molecular water even at low relative humidities. Unfortunately, water soluble inorganic and organic salts are almost ubiquitous contaminants at the organic film/substrate interface, either present before the film application or migrating there during the exposure.

The thickness of the water layer at the interface increases rapidly if there are osmotic driving forces existing between the interface and the outside.[8] This phenomenon may explain the much thicker water layers observed for the ester and asphalt specimens than for the epoxy specimen (Fig. 11). The ester coating was a commercial material, which would normally contain surfactants, flow-enhancing agents and other additives. Some of these materials are hydrophilic and may have leached out of the film and accumulated at the interface during exposure. These materials may also have migrated to the film/substrate interface during the coating application and curing process. Such a migration would likely result in the formation of a water-sensitive layer at the organic film/substrate interface. The presence of such a layer was documented by Walker,[6] who found that the concentrations of the water-soluble products accumulated at the coating/substrate interface of alkyd and epoxy ester coatings were substantially higher than those for polyurethane coatings. Walker postulated that this water-sensitive boundary layer was responsible for the differences in the adhesion loss of different coatings exposed to water. When applied on steel and quartz substrates, we observed that the ester coating blistered readily in distilled water. Based on these results, we believe that there was probably a layer of hydrophilic materials at the ester/hydroxylated SiO_2 interface and that this layer was probably the main reason for the much thicker water layer at the interface as compared with that for the epoxy specimen. Similarly, asphalts are also known to contain many water soluble impurities and salts. Indeed, we observed that the asphalt used in this study emulsified and turned grey upon exposure to water. On the other hand, both the epoxy resin and its curing agent were relatively pure products supplied directly by the manufacturers. The cured epoxy film probably contained little or no water soluble materials. Specimens of this epoxy coating on a quartz substrate did not show any evidence of blistering after two weeks immersion in water. It is noted that osmotic force, produced by the difference in the water activity between the outside and the interface, is the primary mechanism responsible for the blistering of organic coatings on substrates. If the outside environment is distilled water, the water activity difference is greatest and is controlled by the type and concentration of the hydrophilic materials at the organic film/substrate interface.

When the water layer at the interface is many monolayers thick, the bonding strength between an organic film and a substrate would decrease substantially. Indeed, this was observed experimentally. The ester and asphalt films were readily lifted from the substrate at the conclusion of the experiment. By using a scalpel to initiate a separation between the coating and the substrate, the epoxy was also easily peeled from the substrate at the conclusion of the experiment. Leidheiser and Funke[8] believed that the formation of a water film many layers thick at the coating/substrate interface is the main mechanism responsible for the disbondment of organic-coated metals. Similarly, Lefebvre *et al.*,[64] in an intensive study on the mechanism of adhesion loss in high water activity, postulated that water condensation on the hydroxyl groups of the polymer at the interface is the main cause for the sudden loss of adhesion of polymer/metal systems exposed to humid environments. Further backing for the adhesion loss of organic-coated substrates in water comes from extensive results on the durability of adhesive bondings,[10] organic coatings on metals[6-9] and asphalt pavements.[11,12] These studies demonstrated that the bonding strength of an organic film/untreated, high energy substrate system decreases significantly after exposure to water and high humidities. Further, the decrease is accelerated with increasing temperature. From these results and the data presented in this paper, we suggest that the FTIR intensity changes of the water and organic films during exposure of the specimens to water may be related to the loss of adhesion of the coatings on the substrate. If further work confirms that such a relationship exists, the method may be useful for studying "wet adhesion" (adhesion in the presence of water) .

The magnitude of the chemical bonds which water forms with metal and oxide surfaces are typically in the range of 40 to 65 kJ/mol.[15] Thus, compared with adsorbates such as CO or O_2, water is a weakly-sorbed species. The fact that water entered the interface and that most of the bonding strength between the organic film and the hydroxylated substrate was lost during water exposure indicated that the organic film/hydroxylated substrate bonds are weak (< 65 kJ/mol). These results suggest that, except for a few special cases where the organic films contain strong acidic groups, either present initially[65] or formed during oxidative curing,[66-68] the majority of organic films interact with the hydroxylated, untreated inorganic oxide and metal surfaces by means of secondary forces (dispersion and polar forces). The contention that the interactions between most organic films and a high energy, inorganic surface are weak is supported by a comprehensive analysis by Bolger and Michael.[69] They showed that there are only a few organic/substrate combinations, *e.g.*, strong acidic organic/strong basic substrate or strong basic organic/strong acidic substrate, that can resist the displacement by water. The reason for this is mainly that most common metals are considerably more electropositive than the carbon atoms in organic compounds. Consequently, the electron density on the oxygen atom in the oxide surface group (-MOH, where M is the metal) is considerably greater than that on the oxygen in water or in most organic compounds. Therefore, covalently-bonded interfaces are not commonly formed in organic film/unmodified oxide systems, and the secondary-force bonds that do occur are too weak to resist the affinity of water for the polar, high-energy substrate. Thus, if the high-energy surfaces are not modified, water is likely to form a layer at the interface when a organic film/high-energy substrate system is exposed to water or a high humidity. This will, in turn, lead to one or more of disbondment, corrosion and blistering of the system.

Water can reach the interface by a number of pathways, by diffusing through the matrix organic material, and by migrating through pinholes, pores, defects, and local inhomogeneities in the films. For some coatings, the interface of the polymer with the fillers and pigments also serves as the transport pathway for water from the environment to the interface.[70] Organic coatings are known to be heterogeneous and the transport through this type of morphology plays an important role in the protective performance of organic coatings.[71] Using selective resistance and microhardness measurements, Mayne and coworkers[72,73] have identified areas of poor and high-crosslink density in coating membranes, including epoxy/amide systems.

The DC resistance of the poor-crosslink areas varies counter to the external water activity but directly with the dissolved ion activity. The estimated defect size that gives rise to the observed behavior is in the range of 50–500 nm. This type of "cellular" microstructure, in which regions of low crosslink density separate highly-crosslinked areas, was also believed to be responsible for the rapid transport of water through a glass-epoxy composite.[74] The rapid transport caused a sharp drop in the DC resistance of the specimen but had little effect on its mass gain. Evidence from microscopy also revealed that polymer films are not homogeneous but consist of micelles or granules of high density polymer separated by narrow boundary regions of lower molecular weight material.[75] Bascom[61] surmised that this low molecular weight material may exist as a thin, continuous film or as channels between micelles at the interface and that the low-density regions provide pathways for easy entry of water to the film/substrate interface. Once entering the interface, water can transport along the film/substrate interface. The transport through the organic films greatly increases if the swelling stresses in the films are high. In this case, the diffusion is no longer a function of square root of time but rather a linear function of time.[71] The transport also increases if there is an osmotic force between the outside environment and the interface.[8]

The examples given in this paper utilized an infrared transparent material as the substrate. For studying water at the interface between an organic film and an industrial metal, such as aluminum or steel, a thin film (<10 nm for iron) of the desired metal is evaporated on the IRE prior to the application of the organic film. *In situ* measurement of water at the organic coating/iron substrate using this type of arrangement has been demonstrated.[17] However, care must be exercised for quantitative analysis of water at the interface using this organic/metal film/internal reflection element configuration. For this arrangement, the effects of the metal film on the penetration depths in the organic film and water must be taken into account. Further, for low reflective and oxidizable metals, such as iron, the loss of the metal due to corrosion during the *in situ* measurement likely complicates the analysis.

Another point that should be mentioned is that since the method described here detects water after it has penetrated through the thickness of the film, it can be used for measuring the diffusion of water through a film that is still adhered to a substrate.[76] This information on water transport through a film adhered to a substrate better represents the transport of water in organic coatings in actual practice than do the values obtained for water transport through a detached film. The transport of water through a film applied to a substrate should be used for interpreting water disbondment and corrosion of organic-coated metals, and not that of the free film. Finally, although the method was developed for liquid water, it should be equally applicable for quantifying organic and inorganic compounds and ions at the organic films/substrate interface, or measuring their transport through a film still adhered to a substrate.

SUMMARY AND CONCLUSIONS

Exposure to water causes disbondment of an organic film from a hydroxylated substrate and may cause corrosion of the metal under a protective organic coating.

Quantitative information on the water layer at the organic film/hydroxylated substrate interface is crucial for understanding and preventing the failure of organic-coated substrates. A method, based on Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy, for determining the amount and thickness of water at an organic film/hydroxylated substrate interface, has been developed. The analysis uses a two-layered model, which takes into account: 1) water at the organic film/hydroxylated substrate interface, 2) water taken up by the organic film within the penetration depth of the evanescent wave, and 3) change of the penetration depth as water displaces the organic film from the substrate. Experimentally, the method requires the application of an organic film, transparent or opaque, of sufficient thickness on a hydroxylated internal reflection element, which is used as the substrate. A water chamber is attached to the organic-coated specimen. After adding water to the chamber, FTIR-MIR spectra are taken automatically at specified time intervals without disturbing the specimen or the instrument. Water uptake in the organic films and FTIR-MIR spectra of water on the substrates are also obtained and used for the analysis. Results of examples of three organic films, a clear epoxy, an unmodified asphalt and a pigmented ester, on a hydroxylated SiO_2—Si substrate were presented to demonstrate the method. The water layer at the interface for the ester and asphalt specimens was found to be much thicker than that for the epoxy, and this was attributed to the presence of a water-sensitive layer accumulated at the interface for the formers. The method should be equally applicable to studies of organic and inorganic compounds at the organic film/hydroxylated substrate interface and their transport rates through films adhered to a substrate. Quantitative information on water at the organic film/substrate interface and the transport of water through films on a substrate is essential for the development of models for predicting the service lives of organic protective coating systems.

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