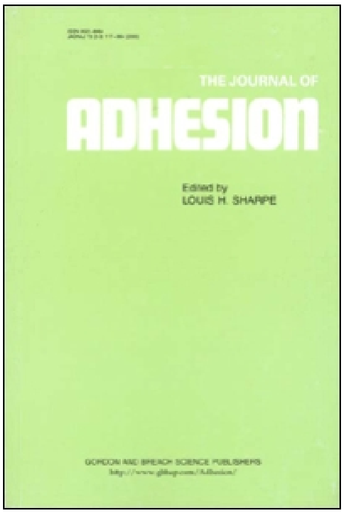

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In Situ Spectroscopic Study of Water at the Asphalt/Siliceous Substrate Interface and Its Implication in Stripping

Tinh Nguyen[a]; Eric W. Byrd[a]; Dale Bentz[a]; Jon Martin[a]
[a] National Institute of Technology, Gaithersburg, Maryland, USA

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In Situ Spectroscopic Study of Water at the Asphalt/Siliceous Substrate Interface and Its Implication in Stripping

Tinh Nguyen
Eric W. Byrd
Dale Bentz
Jon Martin
National Institute of Standards and Technology, Gaithersburg, Maryland, USA

Water at the asphalt/aggregate interface is the major contributor to the debonding of asphalt from mineral aggregates (stripping). A technique based on Fourier transform infrared (FTIR) spectroscopy in the multiple internal reflection (MIR) mode to measure in situ the water layer at the interface between an asphalt and a model siliceous aggregate is described. An asphalt layer of approximately 70 µm thick was coated to an SiO_2-covered Si prism, which serves as the model siliceous substrate. A water chamber was attached to the asphalt-coated substrate. FTIR-MIR spectra were taken automatically at specified time intervals without disturbance to the specimen or the optical alignment of the instrument. The amount and thickness of the water layer at the interface between an asphalt and a siliceous substrate were determined based on a two-layer model derived from the internal reflection spectroscopy theory. The application of this technique for measuring the thickness of the water layer at the asphalt/model siliceous interface for several asphalts is presented. Based on interfacial water data, the mechanism of the stripping of an asphalt from a siliceous aggregate and the transport processes of water from the environment to the asphalt/aggregate interface are discussed.

Keywords: Adhesion; Aggregate; Asphalt; Attenuated total reflection (ATR); Fourier transform infrared spectroscopy (FTIR) *in situ* measurement; Interface; Internal reflection spectroscopy; Quantitative; Siliceous substrate; Stripping; Water; Water susceptibility

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Address correspondence to Tinh Nguyen, National Institute of Standards and Technology (NIST), 100 Bureau Drive, 226/B350, Gaithersburg, MD 20899-8621, USA. E-mail:tinh.nguyen@nist.gov

INTRODUCTION

The debonding of asphalt from mineral aggregates in the presence of water (stripping) "has been observed at times ever since asphalt paving came into existence" [1]. Since stripping was first recognized as a problem, many studies have been devoted to the search for a solution to this problem, as evidenced in several reviews [2–4]. The Strategic Highway Research Program (SHRP) in the early 90s also devoted a good portion of its resources to solve this problem [5]. Still, stripping continues to occur in many areas, particularly, for asphalts on siliceous (SiO_2) aggregates. This problem is magnified if there are hygroscopic contaminants at the asphalt/aggregate interface or osmotic driving forces existing between the interface and the outside. Unfortunately, water-soluble inorganic and organic salts are almost ubiquitous contaminants at the asphalt/aggregate interface, either present on the aggregate surface before the asphalt application or migrating there during exposure. The presence of a monolayer of water at the interface probably would not interfere with the adhesion of an asphalt/aggregate mixture. However, increasing the coverage of water will, at some point, affect the bonding strength of the asphalt/aggregate mixtures.

Whether asphalts fail prematurely or in the range of their expected service lives, they require large replacement costs that probably could be reduced through development of effective methods for studying the water resistance of an asphalt/aggregate system. A major technical barrier to overcoming the problem of stripping is the lack of an effective technique for measuring the stripping resistance of an asphalt from an aggregate. If such a technique were available, it would make possible direct studies of the effects of water on the asphalt/aggregate interaction and, ultimately, predict the stripping characteristics of an asphalt/aggregate pair in the presence of water. The current method for assessing the effects of water on asphalt pavement [6], which measures the residual tensile strength of compact asphalt concrete after exposure to moisture, does not separate the cohesive strength loss of the asphalt from that of the adhesive loss of asphalt/aggregate mixture. Stripping is due to the latter phenomenon, that is, the removal of asphalt from an aggregate in moisture environments is due to the breaking or weakening of the bonds between the asphalt and the aggregate. This assertion is confirmed by a recent, extensive theoretical and experimental study, which concluded that the main mechanism of moisture damage of asphalt mixtures is the loss of adhesion between the asphalt and the aggregate [7]. If asphalt is separated from the aggregate by cohesive failure of the asphalt material, for example, because of plasticization or emulsification, a layer of asphalt still covers the aggregate surface.

The main objectives of this paper are 1) to describe a spectroscopic technique for measuring water *in situ* at the asphalt/model siliceous substrate interface, 2) to present results on the application of this technique for measuring the thickness of the water layer at the interface between an asphalt layer and a model siliceous substrate, and 3) to discuss the mechanism of the stripping of an asphalt from a siliceous aggregate and the transport processes of water from the environment to the asphalt/aggregate interface, based on spectroscopic information provided by this technique.

BACKGROUND

In situ measurement of the water layer (amount and thickness) at the organic film/substrate interface is the subject of great interest in many industries including asphalt pavements, organic coatings, adhesives, and electronic packagings. Water and hydroxyl groups on oxide surfaces can be studied effectively by a number of spectroscopic methods [8–10]. Similarly, techniques for studying *in situ* chemical reactions at an aqueous electrolyte/electrode interface have been developed [11]. A technique for measuring the viscosity of thin films of aqueous solutions between two closely spaced mica or silica surfaces has been reported [12, 13]. However, until research at the National Institute of Standards and Technology [14–17], no technique has been available for measuring *in situ* and quantifying water at the polymer/substrate interface.

In situ measurement of water at the asphalt/siliceous aggregate interface is accomplished using Fourier transform infrared (FTIR) in the multiple internal reflection mode (FTIR-MIR). FTIR internal reflection spectroscopy, commonly known as FTIR-ATR (attenuated total reflection) spectroscopy, is a powerful technique that provides qualitative, as well as quantitative, information on complex molecules at surfaces and interfaces. In internal reflection, the evanescent electric field (produced on total reflections at the substrate surfaces) penetrates the surface of the sample to a depth generally on the order of one wavelength of the radiation. The evanescent field, which decays exponentially with distance in 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. Thus, when an asphalt-coated specimen is exposed to an aqueous environment, water eventually will enter the asphalt/substrate interfacial region, interact with the evanescent wave, and be detected. This unique mode of interaction between the evanescent wave, and material has made possible a large number of applications that take advantage of the technique's ability to probe the near-surface layers of solids and liquids. Harrick [18, 19] has developed the quantitative aspects of the internal reflection spectroscopy, and its quantitative capability has been verified by experimental data from a variety of applications [20–22]. The uses of this technique for the studies of adsorbed species, ultrathin organic films, and single-monolayer Langmuir–Blodgett films on substrates have been reviewed [23–26]. The applications of FTIR-MIR for measuring the diffusion coefficient of solvents and water in polymers adhered to a substrate [27–29] and the transport of water along the polymer/substrate interface have been demonstrated [30]. Nguyen *et al.* [15] have expanded the internal reflection theory for quantitative analysis of water at the polymer/inorganic substrate interface and have used this approach for studying water resistance of polymer coatings on substrates [14–17] and epoxy/glass fiber composites [31, 32].

FTIR–internal reflection spectroscopy 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, thus, is suitable for *in situ* measurement, 3) it detects water from the substrate side, therefore, preventing the interference of water from the environment, and 4) it can be quantitative, under proper conditions.

The theoretical basis of the model for quantifying water at the asphalt/substrate interface is derived from the penetration-depth concept of internal reflection spectroscopy developed for thin and thick films. The physical model in which the thickness of the water layer at the asphalt/substrate interface is measured by the FTIR-MIR technique is illustrated in Figure 1. The substrate in this case is a silicon (Si)

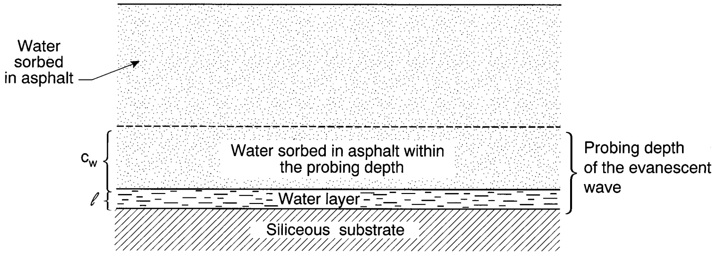

FIGURE 1 The two-layer model used for quantifying water at the asphalt/model siliceous aggregate interface.

prism that has a refractive index greater than those of asphalt and water. The problem is treated as a two-layered sample model (Figure 1). The first layer consists of a water film having thickness, *l,* in contact with the substrate, and the second layer contains the water sorbed in the asphalt material that is detected by the evanescent wave.

The total water detected by the FTIR-MIR technique is the sum of the amounts of water accumulated at the asphalt/substrate interface and that taken up in the asphalt layer probed by the evanescent wave. Using infrared absorption to express the concentration (amount) of water, this statement may be written [15]

$$A = \frac{n_2 \alpha_2 E_o^2}{n_1 \cos\theta} \int_0^l e^{\left(\frac{-2z}{d_{\mathrm{pw}}}\right)} dz + \frac{a_{\mathrm{w}} n_3 \alpha_3 E_o^2}{n_1 \cos\theta} e^{\left(\frac{-2l}{d_{\mathrm{pw}}}\right)} \int_l^\infty e^{-\left(\frac{-2z}{d_{\mathrm{pa}}}\right)} dz \tag{1}$$

where A is FTIR intensity (in absorbance units), θ is incident angle, z is depth from the interface, E_{o} is amplitude of the evanescent wave at the surface, n_1 is refractive index of the substrate, n_2 and α_2 are refractive index and absorption coefficient of water at the asphalt/substrate interface, n_3 α_3 are refractive index and absorption coefficient of water sorbed in the asphalt, l are thickness of the water layer at the asphalt/substrate interface, d_{pw} and d_{pa} are penetration depths of the evanescent wave in water and asphalt, respectively, and a_{w} is fraction of water sorbed in the asphalt within the probing depth.

The first term of Equation (1) corresponds to the amount of water at the asphalt/substrate interface, and the second term represents the amount of water in the asphalt film within the probing depth of the evanescent wave; d_{pw} and d_{pa} can be obtained from Harrick [19]

$$d_{\mathrm{p}} = \frac{\lambda}{2\pi n_1 \left[\sin^2\theta - \left(\frac{n_2}{n_1}\right)^2\right]^{\frac{1}{2}}} \tag{2}$$

where λ is the wavelength of a infrared radiation in a vacuum. Variable d_{p}, commonly defined as the penetration depth of the evanescent wave, is the depth at which the amplitude of the evanescent field has decreased to 1/e of its value at the surface. Although the probing depth could be up to three times of d_{p} [33], because of the rapid decay of the evanescent wave, more than 85% of the total absorption intensity of a MIR band is from one d_{p} [21]. Thus, the majority of water detected in the asphalt-coated specimen may be assumed to be within one d_{p}. Equation (2) explicitly indicates that the penetration depth of the evanescent wave in the sample is a function of the angle of incidence, the wavelength of the radiation, and the refractive indices of the substrate and the sample.

Equation (2) is generally valid for nonabsorbing or weakly absorbing materials. For strongly absorbing chemical species, a more exact equation for d_p has been derived, 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 [34]. Further, because of 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 α. However, previous analysis has shown that the effect of absorption on d_p is negligible at the OH vibrational bands of water molecules [15]. Thus, at the band of interest (water OH stretching) and for the asphalt materials used in this study, Equation (2) is valid for calculating d_p.

Assuming that the refractive index and absorption coefficient of water at the asphalt/substrate interface are the same as those for water sorbed in the asphalt, that is, $n_2 = n_3$ and $\alpha_2 = \alpha_3$ (a reasonable assumption), integrating and rearranging Equation (1) yields an expression for calculating the thickness of the water layer at the coating/substrate interface, l:

$$l = \frac{d_{pw}}{2}\left[-\ln\frac{1-\frac{A}{A_\infty}}{1-a_w\frac{d_{pa}}{d_{pw}}}\right] \tag{3}$$

where

$$A_\infty = \frac{n_2\,\alpha_2\,E_o^2\,d_{pw}}{2\,n_1\ \cos\theta} \tag{4}$$

and A_∞ is the infrared absorbance when the water layer at the asphalt/substrate interface is very thick ($l \to \infty$, *i.e.*, $l > d_{pw}$). Physically, this means that the water layer at the interface is so thick that the amplitude of the evanescent wave decays to a negligible value within it. In this instance, only the first term of Equation (1) remains. On the other hand, if there is no water entering the interface, only the second term is needed. Equation (3) is still valid for the case where the water layer at the asphalt/substrate interface is not continuous, for example, discrete droplets, provided that the height of the droplet is not greater than the probing depth of the evanescent wave in water. Complete details on the derivation of Equation (3) is given elsewhere [15].

If we assume water is uniformly distributed over the entire surface area of the specimen, the amount of water at the asphalt/substrate interface, Q_i, will be given by

$$Q_i = l\,a\,\rho \tag{5}$$

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

To obtain the thickness, l, and amount, Q_i, of water at the interface using Equations (3) and (5), A, A_∞, a_w, d_{pc}, and d_{pw} must be known. A, A_∞, and a_w are obtained from three separate experiments: 1) FTIR-MIR *in situ* measurement of asphalt/model siliceous aggregate specimens exposed to water, 2) FTIR-MIR analysis of liquid water in contact with the asphalt-free substrates, and 3) water uptake in asphalt films, respectively. Values of d_{pa} and d_{pw}, the penetration depths in asphalt and water, respectively, were calculated from Equation (2) using a 45-deg incident angle and appropriate values of the refractive indices of the substrate, asphalt, and water.

EXPERIMENTAL PROCEDURE

This section briefly describes the experimental procedure used to detect and measure *in situ* the thickness of the water layer at the interface between an asphalt and a model siliceous substrate by the FTIR-MIR technique. Complete details on the materials used, specimen preparations, and experimental setup are given in Nguyen *et al.* [35]. The asphalts were AAC-1, AAD-1, AAG-1, AAK-1, and AAM-1, which were used by the Strategic Highway Research Program (SHRP). Selective properties of these asphalts are summarized in Table 1 [36]. The asphalts were selected based on their wide range of properties, including dispersibility (or compatibility), asphaltene contents (polar fraction), and heteroatomic nonhydrocarbon constituents (*e.g.*, N, O, and S).

The model siliceous substrates were 50 mm × 10 mm × 3 mm spectroscopic grade, 45-degree parallelogram silicon (Si) prisms. The as-received Si prisms had a 2.25-nm-thick layer of native oxide

TABLE 1 Properties of Five Core SHRP Straight Asphalts Selected for the Study

	Asphaltene (heptane)		Element, mass fraction %			
Asphalt	content, %	compat. index	N	O	S	Viscosity kPa.s., 25°C
AAC-1	9.8	2.40	0.7	0.9	1.9	94.540
AAD-1	20.2	1.44	0.8	0.9	6.9	40.570
AAG-1	5.0	3.97	1.1	1.1	1.3	354.000
AAK-1	20.1	1.22	0.7	0.8	6.4	107.700
AAM-1	3.7	5.93	0.6	0.5	1.2	112.300

(SiO_2, refractive index = 1.46) on their surfaces, as measured by ellipsometry. The surface chemical structure of this SiO_2-covered Si substrate has been illustrated previously [16]. The key characteristics of the SiO_2 surface are that it reacts readily with water to form silanol (SiOH) groups. Because most of these OH groups are adjacent to one another and are favorably positioned for preferential water adsorption [37], under ambient conditions (24°C and 45% relative humidity), the SiO_2 surfaces are generally covered rapidly with sorbed water. The physically sorbed water can be removed by degassing at room temperature. However, even after heating up to 400°C, more than half of the OH groups still remain on the SiO_2 surface [38]. The hydrated, SiO_2-covered, 50 mm × 10 mm × 3 mm, 45°, parallelogram Si substrate used in the study is designated as the model siliceous substrate. No attempt was made to determine the SiOH coverage or the amount of sorbed water on the model substrate surface.

Specimens were prepared by applying hot asphalt (at ~ 60°C) to one face of the substrate using the draw-down technique. Masking tape strips placed along the substrate were used to control the asphalt film thickness. A water chamber, which has an inlet and an outlet to introduce and remove water, was attached to each asphalt-coated specimen. The specimen with the water chamber attached was positioned vertically in an accessory holder. The specimen configuration and experimental setup for measuring *in situ* water at the asphalt/aggregate interface is shown in Figure 2. With this configuration, the only pathway for water migration from the environment to the

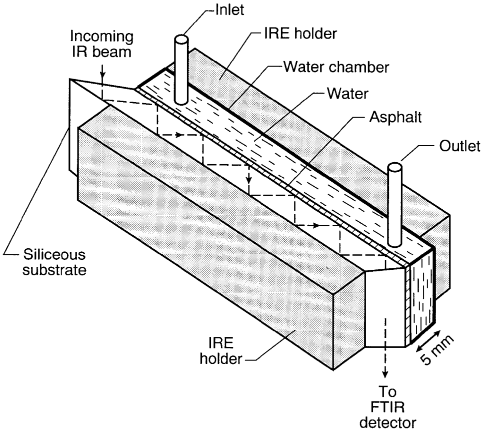

FIGURE 2 Specimen configuration and experimental setup for *in situ* measurement of water at the asphalt/model siliceous aggregate interface.

interface is through the thickness of the asphalt film within the walls of the chamber. Further, because the infrared radiation entered and propagated within the substrate, there was no interference of liquid water from the environmental chamber or water vapor in the spectrometer compartment. Note that with the prism thickness and length and the 45-deg incident angle used, 17 reflections were generated within the substrate before exiting. The use of a thinner prism, a longer prism, a smaller angle of incidence, or a combination of these factors would increase the detectability of water at the asphalt/substrate interface by the FTIR-MIR technique.

After adding water to the chamber and placing the specimen assembly in the spectrometer, FTIR-MIR spectra were taken automatically every 15 min without disturbance to the instrument until the experiment was complete. All spectra were the result of 32 co-additions and were collected at a 4 cm^{-1} resolution throughout the 1200–4000 cm^{-1} range. Unpolarized light at an incident angle of 45 degree was used. All spectra were plotted in the absorbance (A) mode. Difference spectra were obtained by subtracting the spectrum of the specimen before exposure from the spectrum of the same specimen but after exposing to water at a particular time interval. Quantitative analyses were performed using the peak height method, which measures the absorbance at the maximum of the bands of interest. It should be noted that, except for a few cases where two specimens were used, results on the quantity of the water layer at the asphalt/substrate measured by the analytical FTIR-MIR technique were determined from only one specimen; therefore, there are no uncertainty values accompanying these data.

Because this is an *in situ* measurement, errors resulting from the accessory adjustment, specimen changing, spectrometer and environmental chamber conditions, and optical realignments were minimized. Thus, any changes in the spectra were a direct result of the effect of water entering the asphalt/aggregate specimen. Further, because the asphalt was applied directly to the prism, errors resulting from variations in the contact between them were avoided. Until now, lack of control of the contact between the sample and the element has hindered the broad application of the FTIR-MIR technique for quantitative studies.

RESULTS

FTIR-MIR Analysis of Water in the Asphalt/Substrate Interfacial Region

To monitor changes resulting from water entering the interface between an asphalt and a model siliceous substrate, it was necessary to examine the FTIR-MIR spectral characteristics of water and of the asphalt/siliceous substrate system before water exposure. Figure 3a presents a typical FTIR-MIR spectrum in the 1200 to 4000 cm^{-1} region of a typical asphalt (AAD in this case) applied to the model siliceous substrate before exposure to water. FTIR-MIR spectra of the other four asphalts can be seen in Nguyen *et al.* [35]. Because SiO_2-covered

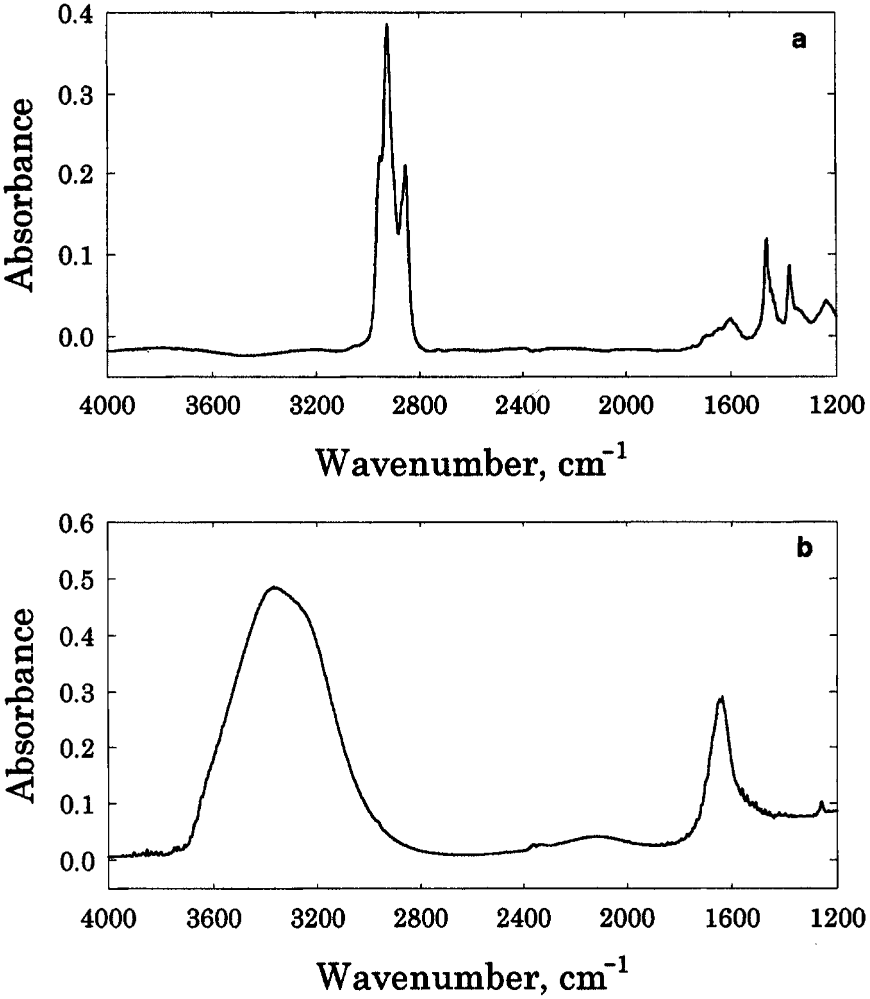

FIGURE 3 a) Typical FTIR-MIR spectrum of a straight asphalt on the model siliceous substrate before exposure to water, and b) FTIR-MIR spectrum of liquid water on the model siliceous substrate.

Si absorbs infrared radiation strongly in the region below 1200 cm^{-1}, bands below this frequency were deemed not reliable for analysis and, therefore, were not included. The thickness of this asphalt film was 60 μm ± 13 μm, as measured by a thickness gage. Typical straight asphalts show four main bands associated with the CH groups in the 2800–3000 cm^{-1} and 1350–1500 cm^{-1} regions. Figure 3a shows little evidence of infrared (IR) absorption resulting from the polar OH/NH groups, which generally occur in the in the 3100–3700 cm^{-1} region. This is probably because of the combination of low concentration of these groups in the asphalts and the shallow probing depth of the MIR technique in this frequency region. On the other hand, the FTIR-MIR spectrum of liquid water on the same substrate (Figure 3b) shows a broad strong band in the 3000–3650 cm^{-1} region, because of the OH stretching, and at 1640 cm^{-1}, because of HOH bending, of molecular water. The shoulder (around 3250 cm^{-1}) on the right side of the water OH stretching band is due to the contribution of the overtone of the bending mode [39].

Figure 4 illustrates one example of a series of typical unprocessed FTIR-MIR spectra for an asphalt applied to the model siliceous aggregate before and after exposure to water for different times. The thickness of the asphalt film of this specimen was 70 μm ± 10 μm. These spectra were obtained by ratioing the spectra of the exposed specimen against the corresponding spectrum of the background (the spectrum of the environment in the spectrometer). Although the effect of water is evident in the 3000–3650 cm^{-1} and 1625–1645 cm^{-1} regions, these spectra still include information of the asphalt material. To provide data for quantitative analysis of water molecules at the asphalt/substrate interface, difference spectra were acquired by subtracting the spectrum collected before exposure from those obtained at different water exposure times. One example of the difference spectra in the 1500–4000 cm^{-1} region of an asphalt (AAC in this case) on the SiO_2-Si model substrate after exposure to distilled water for different times is displayed in Figure 5. If water has not entered the asphalt/substrate interfacial region, all difference spectra would be straight lines, with the exception of the intensity fluctuations of the CO_2 bands from the air in the spectrometer. Bands above or below the baseline of a difference spectrum indicate an increase or a decrease, respectively, of the concentration of a chemical functional group as a result of water exposure.

Figure 5 clearly shows that the intensity of the water band in the 3000–3650 cm^{-1} region increased, while the intensity of the asphalt bands, for example, at 2922 cm^{-1}, decreased with time of exposure to water. Similar results were observed for a variety of polymeric

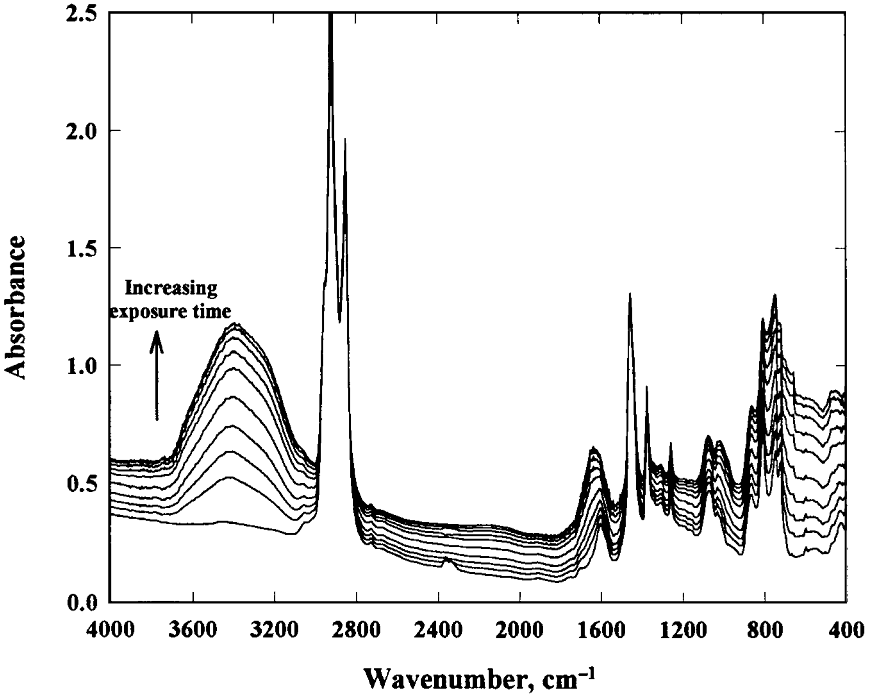

FIGURE 4 Typical FTIR-MIR spectra of an asphalt/model siliceous aggregate specimen after exposure to water.

coatings applied to silicon and germanium substrates [14–17]. The decreases in intensity of the asphalt bands, together with the intensity of the water bands as a function of exposure time, may be explained only by the water entering the asphalt/substrate interface. This is because the probing depths of the evanescent wave in water-saturated and water-free asphalts are essentially the same. As the thickness of the water at the interface increased, the amount of the asphalt material within the probing depth decreased because the asphalt film was pushed further away from the substrate surface. The intensity, expressed as peak height, of the water OH stretching band at 3400 cm^{-1} is suitable for quantitative analysis of water at the asphalt/model siliceous aggregate interface. The water bending mode at 1640 cm^{-1} was found not suitable for the analysis, because it is not visible for low water concentrations [16].

Figure 6 shows intensity changes of the water OH stretching band as a function of exposure time for the five asphalts. Although there are some minor fluctuations of some data points, the trends of water

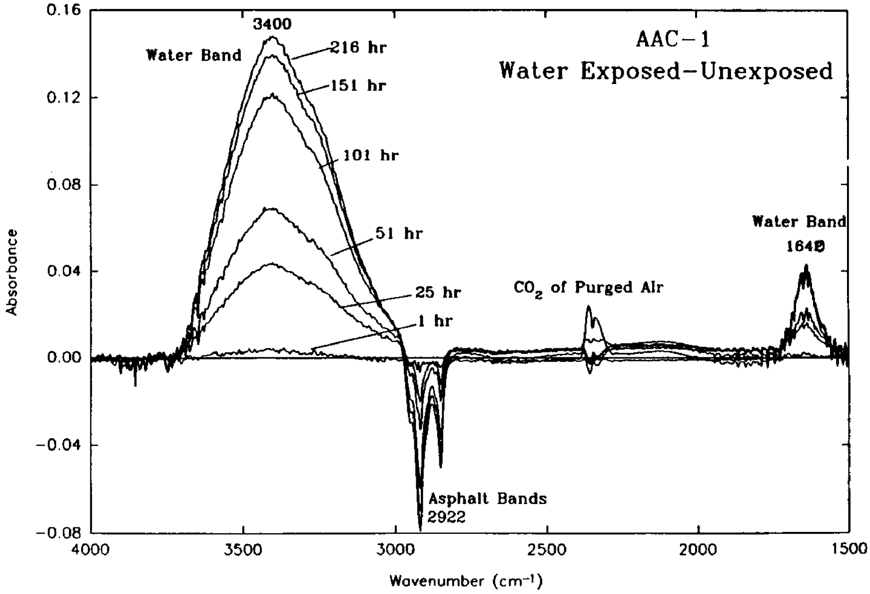

FIGURE 5 An example of FTIR-MIR difference spectra (water exposed–unexposed) of an asphalt/model siliceous aggregate specimen exposed to water for different times.

accumulated in the interfacial region are evident. In general, except for the AAD, which did not appear to take up any more water after 50 h, samples of all other asphalts continued to pick up water for more than 100 h. Water initially entered the interfacial region at a high rate, but then slowed down. The rates at which water entered the interfacial region were quite different for the five asphalts. Further, the rates of intensity loss of the bands associated with the asphalt (*e.g.*, band at 2922 cm^{-1}) also followed the same trend with the water bands.

Model Verification

The FTIR-MIR intensity displayed in Figure 6 corresponds to the total amount of water detected. This quantity comprises water at the asphalt/substrate interface and water in the asphalt film within the evanescent wave probing depth, as depicted in Figure 1 and mathematically expressed in Equation (1). Subtracting the water uptake within the evanescent wave depth in the asphalt from the total water detected yields the values on water at the asphalt/substrate interface.

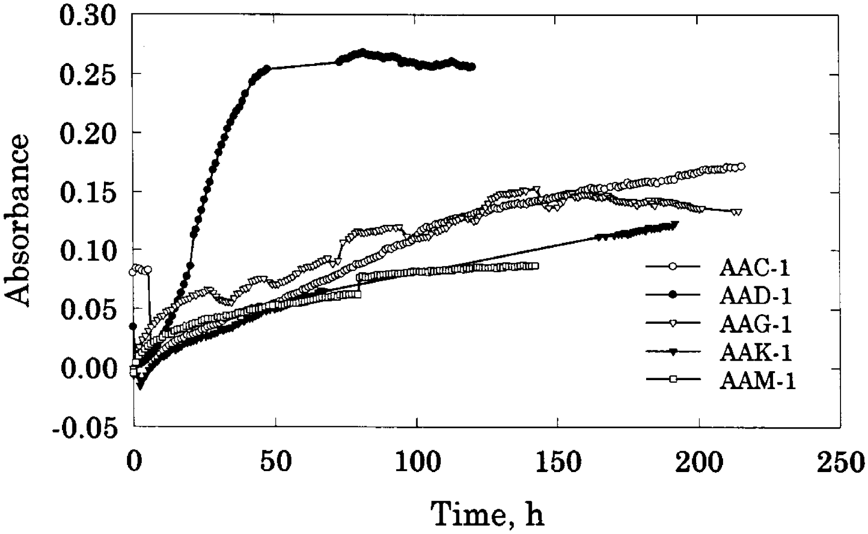

FIGURE 6 Intensity increase of water OH stretching as a function of exposure time for five SHRP asphalts on a model siliceous aggregate (each symbol represents one data point).

Before using Equation (3) for quantifying water at the interface between an asphalt and a siliceous aggregate, the main question must be addressed: how good are the assumptions and model used for deriving this equation? One way to answer this question is to measure the buildup of water in a water-resistant interface of an organic film/substrate system during exposure to an aqueous environment. From the well-known mechanism of molecular adhesion and the shear strength performance of epoxy/silane treated E-glass fiber composites in aqueous environments, such an organic film/substrate system may exist. Consequently, specimens made of a two-part epoxy applied to an amino silane-treated SiO_2-Si substrate were prepared. Details on the chemical structure of the epoxy, silane coupling agent, and procedure for silane treatment on substrate surface are given elsewhere [31].

The results (average of two specimens) on the amount and thickness of the water layer at the epoxy film/silane-treated substrate interface calculated using Equations (3) and (5) are presented in Figure 7. This figure clearly shows that essentially no or little water had entered the interface of this specimen. (The negative value of FTIR intensity upon immersion [between 0 and 20 h] observed in Figure 7 was probably due to the relaxation/expansion of the film, which may cause a debonding in some local areas. Because the epoxy OH stretching band also occurs

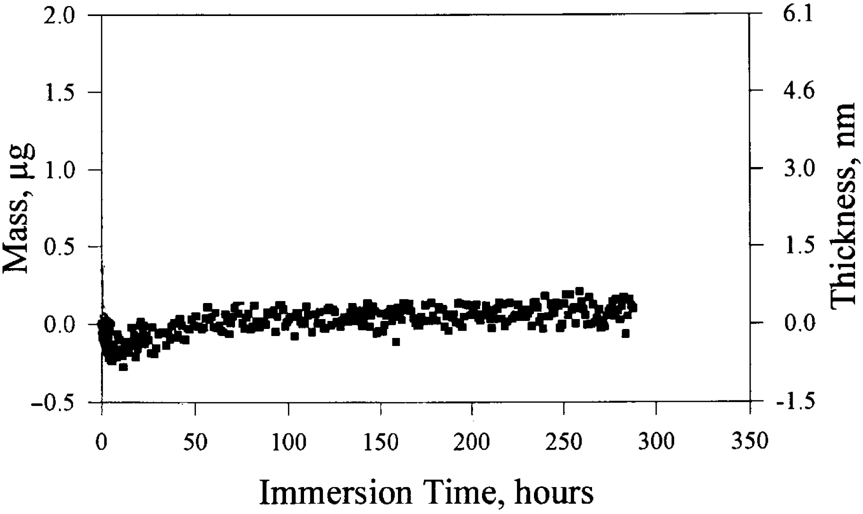

FIGURE 7 Amount and thickness of the water layer at the interface between a model epoxy and an amino silane-treated siliceous substrate as a function of exposure to water, showing essentially no water molecules entering the interface of this specimen (each symbol represents one data point).

in the same infrared absorption region of water molecules, the debonding pushed the epoxy film away from the substrate. This results in a negative value of the intensity.) The interfacial water layer result obtained by the FTIR-MIR technique (Figure 7) is in good agreement with the adhesion data of the same epoxy resin applied to a similar substrate, which showed that epoxy/silane-treated SiO_2-Si substrate system lost little of its bonding strength even after a prolonged exposure to water at 24°C [31]. The result is also consistent with the chemical bonding theory used for explaining the hydrolytic stability of polymer composites made with silane-treated E glass fiber [40]. If no water accumulated at the interface, then the total water detected is solely due to water sorbed in the epoxy polymer layer near the interface. This is predicted by Equation (1) and observed experimentally in Figure 7. For such a case, only the second term of Equation (1) exists. Apparently, the epoxy/silane-treated siliceous substrate system has a hydrolytically stable interface and the water was incapable of replacing either the strong bonds between the silane coupling agent and the siliceous substrate or between the silane agent and the epoxy resin. The result of Figure 7 provides strong evidence to prove that the model developed is suitable for quantifying the water layer at the polymer/substrate or asphalt/substrate interface.

Thickness and Amount of the Water Layer at the Asphalt/Model Siliceous Substrate Interface

As indicated earlier, to obtain the thickness, l, and amount, Q_i, of water at the asphalt/substrate interface using Equations (3) and (5), A, A_∞, a_w, d_{pa}, and d_{pw} must be known. A, the total IR absorbance of water in the specimen at each exposure time, is taken directly from Figure 6. A_∞, the maximum IR absorbance of water is given in Figure 4b. The water fraction in the asphalt film, a_w, is interpolated from the results of water uptakes in asphalts given in Nguyen *et al.* [35]. The uptake experiments were conducted using the gravimetric method for asphalts coated on aluminum sheets. Only the amount of water within the penetration depth of the evanescent wave is used for the calculation. Discussion of the assumptions and errors resulting from the interpolation for polymeric films has been presented in detail elsewhere [16].

Values of d_{pa} and d_{pw}, the penetration depths of the evanescent wave in asphalt and water, respectively, were taken from Figure 8, which shows the penetration depth as a function of radiation wavelength. (For comparison, the penetration depth of a typical polymer [$n = 1.50$] is also included.) The curves on this figure were plotted using Equation (2), a 45-degree incident angle, and the refractive indices of 3.42 for Si substrate, 1.55 for asphalt, and 1.32 for water. The refractive index of asphalt was calculated from the data given in Abson and Burton [41]. As can be seen in Figure 8, the FTIR-MIR technique can probe deeply in the asphalt at long wavelengths. The results also show that d_p in asphalt is slightly greater than in water, and this difference increases with increasing wavelength. At the wavelength of interest, $\sim 2.94\,\mu m$ ($3400\,cm^{-1}$, the OH stretching of water), d_{pa} and d_{pw} values in asphalt and water are $0.243\,\mu m$ and $0.225\,\mu m$, respectively. At this wavelength, there is only a small difference ($0.018\,\mu m$) in the d_p value whether asphalt or water is in the interfacial region. These results indicate that the signals observed in Figure 4 must be from the water molecules close to the asphalt/substrate interface.

Results of the thickness and amount of the water layer at the asphalt/model siliceous substrate interface as a function of exposure time for five asphalts studied are given in Figure 9. The mass of the interfacial water layer was obtained using Equation (5), a water density (ρ) of $1\,Mg/m^3$, and a surface area of $329\,mm^2$ (actual sample area in contact with water). In general, the amounts of water in the asphalt within the penetration depths of the evanescent wave are small ($< 5\%$), as compared with the total water detected. These results are

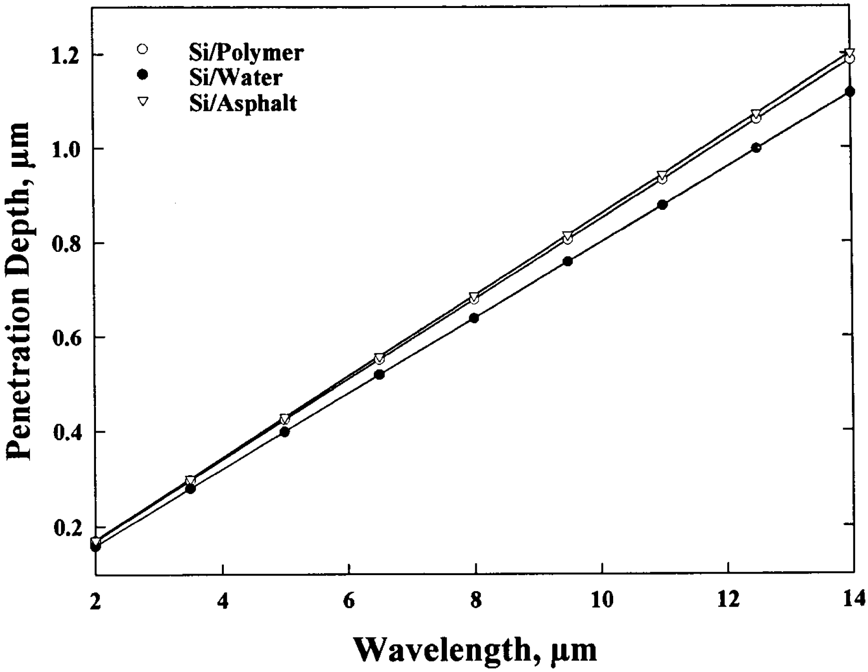

FIGURE 8 Penetration depth of the evanescent wave in asphalt, water, and a typical polymer as a function of radiation wavelength.

consistent with other studies, which show that, for hydrophobic organic and polymer films, the water detected is mainly from the water layer at the film/substrate interface because the amount of water uptake in these materials within the evanescent probing depth is low [15–17].

As seen in Figure 9, the thickness of the water layer at the asphalt/model siliceous substrate interface is different for the five asphalts. The thickness of the water layer for the AAD/substrate interface increases rapidly and remains constant after approximately 50 h of immersion. However, the interfacial water layer for the AAC specimen increases slowly at first and does not level off even after 100 h of exposure. Water layers at the interface of AAG, AAK, and AAM asphalts also increase less rapidly than that of the AAD specimen and seem to slow down after 75 h. For prolonged immersion, for example, 90 h, the water layer at the asphalt/model siliceous substrate interface is thickest for AAD (90 nm) and thinnest for AAM (25 nm). The water thickness values for AAC, AAG, and AAK specimens are 35 nm, 45 nm, and 35 nm, respectively, at the same exposure

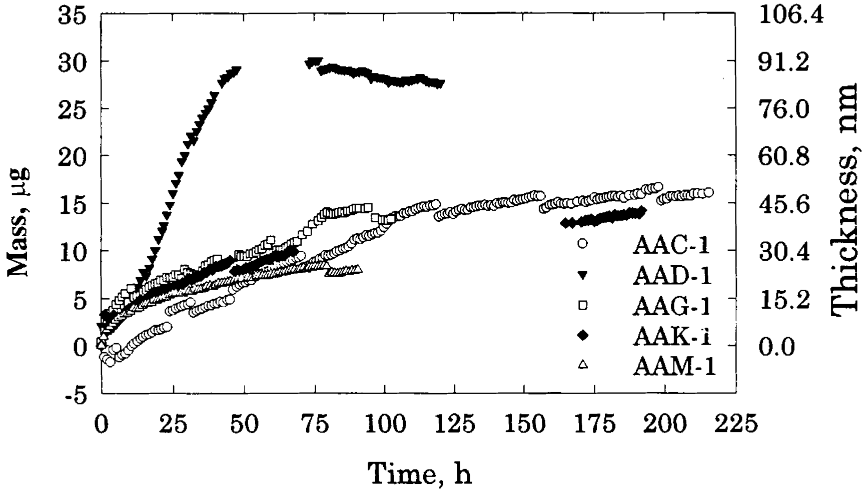

FIGURE 9 Amount and thickness of the water layer at the asphalt/model siliceous aggregate interface for five SHRP asphalts studied (each symbol represents a data point).

time. The results suggest that AAM/siliceous system is more resistant to water stripping than the AAD/siliceous system.

Interfacial water data obtained in this study are consistent with results of water-induced bonding strength loss of asphalt-coated flat siliceous substrates and core SHRP asphalt/aggregate mixtures. For example, at 50-h exposure the thicknesses of the interfacial water layer for AAM, AAC, AAK, AAG, and AAD specimens are 20 nm, 20 nm, 24 nm, 28 nm and 88 nm, respectively (Figure 9). The time-to-failure values of the adhesion loss, which was measured by a pneumatic wet adhesion test, for the same order of the same asphalts on a soda glass substrate were 90 minutes for AAD and approximately 8 h for the other four asphalts [42]. The agreement between thickness of the interfacial water layer and water-sensitive tests of asphalt/aggregate mixtures is also good. For example, data of both the adhesion failure model and mechanical wet test obtained more recently showed that, for the same type of aggregate (either granite or limestone), AAM mixtures are more resistant to water damage than AAD mixtures [7, 43]. Similarly, the numbers of repeated freeze–thaw cycles for AAM, AAC, AAK, AAG, and AAD on the granite aggregate were reported to be 50, 36, 10, 7, and 5, respectively (the longer the number of repeated cycles, the more stripping resistance of an asphalt/aggregate mixture to water) [5]. It is also interesting to note that a fatigue model based on surface free-energy parameters also predicted that AAM mixtures have a better healing property (related to wetting) and longer fatigue life than AAD mixtures for both granite and limestone aggregates [44]. Thus, a comparison of the spectroscopic results obtained in this study and the mechanical test data from the literature indicates that the interfacial water layer not only follows closely with the water-induced adhesion loss of an asphalt/siliceous aggregate system, but its effect on the long-term performance is also in good agreement with the prediction by both the surface energy-based fatigue model [44] and surface energy-based adhesion failure model [7].

A comparison between the interfacial water data of Figures 6 and 9 and asphalt properties given in Table 1 reveals that, except for the AAK asphalt, data on the water layer at the interface appear to follow the same trend with the asphaltene and S contents and the compatibility index. That is, the higher the asphaltene and S contents and the lower the compatibility index, the thicker the water layer at the asphalt/siliceous interface. Although more studies are needed to further verify this finding, the general agreement between the water layer at the interface and S and asphaltene contents is consistent with the affinity of water for the hygroscopic materials. Both S-containing products and asphaltene fraction are the polar components of an asphalt, and these materials tend to migrate to the hydrophilic aggregate surfaces during asphalt application or during exposure to water. Although information on the movement of hydrophilic components to the substrate surface for asphalt/aggregate mixtures is not available, such a phenomenon has been observed in glass fiber-reinforced epoxy composites [45, 46]. In these materials, the amine curing agents have been found to migrate to, and are preferentially adsorbed at, the substrate surface, creating an amine-rich region on the glass fiber surface. As elaborated later in the discussion on the stripping mechanism, the presence of hygroscopic contamination at the asphalt/substrate interface is believed to be the main cause for the presence of many monolayers of water at the asphalt/siliceous interface.

A general agreement between results obtained by the adhesion test or moisture sensitivity test, and data on the thickness or mass of the water layer at the asphalt/siliceous substrate interface obtained by FTIR, suggests that information on the FTIR-MIR spectroscopy may be used for assessing the stripping resistance of an asphalt/siliceous mixture. Thus, instead of carrying out elaborate, destructive water debonding or water sensitive tests, which often require multiple replicates to provide meaningful results, the FTIR-MIR technique may be used for determining the stripping susceptibility at the early exposure stage of an asphalt on a siliceous aggregate. This technique may also be used for conveniently studying the effects of many variables affecting the stripping of asphalts on a siliceous substrate such as asphalt type, antistripping agents and their concentrations, environmental temperature, substrate surface contaminants, salted water, and rained water. It should be noted that, although a silicon substrate is employed in this study, other substrates could be used. For example, the application of this technique for studying the water at the polymer/iron interface has been demonstrated [17]. For infrared opaque substrates such as aluminum or limestones, a thin film of the substrate can be evaporated on a suitable prism, such as ZnSe, prior to application of the organic film. This technique is also applicable to real aggregates as long as the aggregate has a higher refractive index than that of water, has a proper shape to fit in the internal reflection (ATR) accessories, and is of good quality suitable for spectroscopic investigation. Further, because this method detects water after it has migrated through the asphalt film thickness, it is suitable for measuring the diffusion coefficients of water in an adhered film, as demonstrated for asphalt [35] and other polymer films [27–29]. Because interfacial properties of an asphalt/aggregate mixture play an important role in the adhesion loss and rate of water transport to the interface, the diffusion coefficients of the adhered films should be used (instead of the free films) for estimating water transport in asphalts.

MECHANISM OF WATER STRIPPING OF ASPHALT ON A SILICEOUS AGGREGATE

The results of Figure 9 show that, at long exposure times, many monolayers of water have accumulated at the asphalt/siliceous aggregate interface (one water monolayer is approximately 0.3 nm). Indeed, this was the case; we observed substantial amounts of liquid water beneath some of the asphalt films as they were peeled from the model siliceous substrate at the conclusion of the experiment. These results are consistent with extensive data on organic coatings and water sorption measurements on silica surfaces. Leidheiser and Funke [47] had given examples and cited numerous references to support the evidence of the presence of multilayers of water at the organic coating/metal interface. Another piece of evidence is from water adsorption studies on high-energy surfaces. For example, Zettlemoyer and coworkers [48] noted that a monolayer of water on ferric and nickel oxides occurred at low relative humidities, but multilayers existed at a relative humidity of 90%. Bowden and Throssell [49] 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 [50] 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 by Bascom [51].

The adsorbed water layers closest to the surface are strongly bonded and difficult to remove. Therefore, the presence of a monolayer of water at the asphalt/aggregate interface would probably not interfere with the adhesion of an asphalt/aggregate mixture. However, increasing the coverage of water will, at some point, affect the strength of the asphalt/aggregate bonds. This is substantiated by the adhesion loss data for asphalts and epoxy coatings on a siliceous substrate [31, 42]. Further backing for the adhesion loss of organic-coated substrates in water comes from extensive results on the durability of adhesive bondings, which were well documented by Kinloch [52], and organic coatings on metals [47, 53, 54]. 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. Leidheiser and Funke [47], in an extensive review of the water disbondment of polymer-coated substrates, have concluded that a water layer many monolayers thick is responsible for the adhesion loss of these materials when they are exposed to water or high relative humidities.

The stripping susceptibility of an asphalt from siliceous aggregates may be best understood from the interaction energy standpoint. The bonding between asphalt, an organic material, and a siliceous aggregate is governed mostly by weak secondary forces, which are generally less than 25 kJ/mol. On the other hand, the magnitude of the bonds that water forms with oxide surfaces are substantially higher, typically 40–65 kJ/mol [10]. Consequently, the affinity of water for a siliceous aggregate is greater than that of asphalt to the same aggregate. Further, surface free energy analyses by Gledhill and Kinloch [55] and more recently by Cheng *et al.* [7, 43] have also shown that the reversible work of adhesion between an organic film and an oxide, including SiO_2, or between an asphalt and an aggregate, including limestones and granites, is highly negative in the presence of water, implying that the asphalt/inorganic oxide bonds are not stable in water. This means that water is likely to enter the interface and displace the asphalt from a siliceous aggregate when an asphalt/siliceous iceous mixture is exposed to water or to high relative humidities.

This postulation is supported by the acid–base (an electrostatic interaction) concept proposed by Fowkes [56], who used this theory to explain the water susceptibility of asphalt/granite systems and water resistance of asphalt/limestone mixtures. The asphalt, with its low basicity and high acidity, interacts weakly with the acidic SiO_2 but adheres strongly with basic aggregates, such as limestone. The acid–base concept is consistent with several previous reports and with practical observations. For example, for the same asphalt, Texas limestone mixtures have been shown to be more resistant to moisture-induced failure than Georgia granite mixtures [7, 43]. Other related studies showed that carboxylic acids in an asphalt are most easily displaced by water [57] and nitrogen-based chemicals (base characters) are selectively retained on the aggregates during the water displacement test [5]. It (*i.e.*, acid–base interaction concept) is also in good agreement with our observation that the bonds between asphalt and aluminum (aluminum oxide) are highly stable in water. Aluminum oxide, because of its higher isoelectric points (IEPS) than silica, has been shown to have a much stronger interaction with acids than that between silica and acids [58].

Water enters the asphalt/siliceous interface probably by breaking the water–silanol (SiOH) bonds and building up the water layer on the silanol-terminated surface. This occurs because the hydrogen bonds between the first water layer and the silanol groups on a silica surface are substantially weaker (about 25 kJ/mol) than the bonds between the first and second layer of water (>40 kJ/mol) [59].

The contention that the interactions between asphalt/siliceous aggregate bonds are weak and that this weak interaction cannot resist water displacement is also strongly supported by a comprehensive analysis by Bolger and Michaels [58]. They showed that there are only a few organic/substrate combinations, for example, 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 that most common metal elements (including Si) are considerably more electropositive than the carbon atoms in organic compounds. Consequently, the electron density on the oxygen atom in the SiO_2 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 to the polar, high-energy substrate. Thus, if high-energy surfaces (*e.g.*, SiO_2) are not modified, water is likely to form a layer at the interface when an organic film/high-energy solid is exposed to water or to high relative humidities. This assertion is supported by the well-known practice in the polymer/glass fiber composite industry, where the glass fibers are commonly treated with silane coupling agents to improve the durability of the composites used in moist environments.

The amount of water at the coating/substrate interface is greatly increased if the interface contains hydrophilic contaminations or if an osmotic driving force exists between the interface and the outside. Unfortunately, water-soluble inorganic and organic salts are almost ubiquitous contaminants at the asphalt/aggregate interface, either present before the asphalt application or migrating there during service. 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 example, the humidities of liquification of LiCl and $CaCl_2$ are only 15% and 32%, respectively [60]. Thus, if the interface is contaminated with these salts, it is likely to hold molecular water even at low relative humidities.

The presence of a hydrophilic film at the interface may explain the differences in thickness of the water layer for different asphalts on the model siliceous substrate used in this study. Asphalts are known to contain water-soluble species, which probably leached out of the film and migrated to the interface during exposure. Such a water-sensitive layer at the asphalt/model siliceous interface would result in a thick water layer at the asphalt/substrate interface causing the adhesion loss or stripping. The concentration and nature of this water-sensitive layer are also probably responsible for the different rates and quantities of water at the interface of different asphalts on the model siliceous substrate. For a practical asphalt/aggregate mixture, in addition to the water-soluble materials from the asphalts, the nonsilica components of the aggregates and hygroscopic contaminants on the aggregate surface also contribute greatly to the buildup of a thick water layer at the asphalt/aggregate interface. The nonsilica components, such as MgO, K_2O, and N_2O, are known to be so hygroscopic that water adsorption on glass has been characterized by these oxides [51]. Further, it has been verified that the adsorption of tens of molecular layers of water on polar solids at partial pressures just below the saturation point is due to the presence of hygroscopic contaminants. Even at a relative humidity of 50%, a surface contaminated with $10^{-7}\,g/cm^{-2}$ of potassium hydroxide would adsorb the equivalent of five molecular layers of water [49]. The presence of a water-sensitive layer at the organic film/metal interface has been documented by Walker [53], who found that the concentrations of the water-soluble products accumulated at the coating/substrate interface of the alkyd and epoxy ester coatings were substantially higher than those for the polyurethane coatings.

Water can reach the interface from the outside by a number of pathways: by diffusing through the matrix asphalt and by migrating through pinholes, pores, defects, and local inhomogeneities in the asphalt films. Based on the evidences of 1) a high concentration of water present at the interface after a short exposure time and 2) a much thinner water layer for thicker asphalt films, we propose that water transport from the outside to the interface is through water-soluble, hydrophilic regions in an asphalt film. The hydrophilic regions are areas occupied by the highly polar groups of the asphalt molecules or by the water-soluble impurities (*e.g.*, ions and salts) in the asphalt film. It is likely that each water-soluble impurity particle is associated with a polar site in the asphalt. Thus, a hydrophilic region in an asphalt film probably consists of polar groups of the asphalt molecules and water-soluble impurities. This postulation is based on extensive data on the inhomogeneous nature of polymers and on the relationship between polymer heterogeneity and its protective and hydrolysis resistance properties [61, 62]. Organic polymers are known to consist of high-density, high-molecular mass segments separated by narrow boundaries of hydrophylic low-density, low-molecular mass materials. The transport of water through polymer films has been experimentally observed to be not uniform throughout the film surface, but along the boundaries around the high-density, high-molecular mass segments [63]. The sorption of water in the low-density, low-molecular mass areas has been found to be typical for a hydrophilic, ion-exchange membrane, which usually sorbs 45 to 75% water (based on mass) [64]. This means that these areas (*i.e.*, the hydrophilic, low-density, low-molecular mass regions) take up a substantial amount of water and have a much lower ionic resistance than the rest of the film. The corrosion of metals under these polymer coatings has been observed at the locations directly corresponding to the hydrophilic regions [64, 65].

We believe that water first dissolves the hydrophilic regions (an emulsification process) and opens up a tortuous pathway system in the asphalt matrix, allowing water containing ions (from asphalt and environment) to reach the interface. Thus, the water transport through an asphalt layer is not a uniform diffusion through the homogeneous asphalt matrix but rather a transport process mediated by the pores, which are opened up by the dissolution by water in the areas occupied by the hydrophilic materials. A similar mechanism has been proposed for the transport of ions through polymer coatings to reach the film/metal interface [61], and a mathematical model for such transport in polymer coatings has been developed [66]. It is noted that emulsification of asphalts is commonly observed and that the emulsified products can dissolve polar as well as nonpolar components of the asphalts. For thick and low-water-soluble impurity asphalt film, the pores may not be continuous from the exterior surface to the interface. In such cases, prolonged or repeated exposure is required for water to reach to the interface. Because the chance for the overlapping of two or more water-soluble regions is small, thicker or multiple-layer asphalt film is more effective than a single coat of the same thickness.

The transport of water increases if there is an osmotic force between the outside environment and the interface, or when the interface also contains hydrophilic contaminants. Once entering the interface, water can transport along the film/substrate interface. Using model polymers of different thicknesses applied to substrates having different levels of adhesion, Linossier *et al.* [29, 30] have demonstrated that for untreated substrate surfaces where the adhesion is poor, the transport of water along the interface is the dominant process responsible for the water layer buildup at the polymer/substrate interface. Nanoscale defects or pores in the polymers provide the channels for rapid water movement to the interface. They also showed that when the polymer/substrate adhesion is very good, for example, after plasma treatment of the substrate, the transport of water from the environment to the interface follows a classic diffusion process through the film matrix, which can be predicted by the diffusion theory.

In summary, water-soluble materials, migrating from the environment as well as from the asphalt film and those present at the interface (from both asphalt and aggregate) constitute a water-sensitive layer at the asphalt/aggregate interface. This water-sensitive layer is the main reason for the formation of a water layer many monolayers thick at the interface, responsible for the stripping of asphalt from a siliceous aggregate. Modifying siliceous surfaces with a very thin layer of a base, such as an amine, will render the surface basic; this surface would form strong bonds with the acidic asphalts and thus can resist the water displacement. However, since low-molecular-mass amines are highly hygroscopic, an excess of these materials at the asphalt/aggregate interface may induce an osmotic pressure. This would likely increase the transport rate of water from outside to the interface and result in an increase of water accumulation at the asphalt/aggregate interface. Thus, if antistripping agents based on amines are not applied on the aggregates properly (*e.g.*, in excess of a monolayer), they may enhance stripping rather reducing it.

CONCLUSIONS

A sensitive, spectroscopic technique for measuring water *in situ* at the asphalt/siliceous aggregate has been developed. The technique can detect and provide quantitative information on the water layer at the asphalt/siliceous aggregate interface. This information, which relates to the adhesion loss of asphalt/siliceous aggregate mixture, is useful for predicting the water susceptibility of asphalt/siliceous aggregate mixtures. The technique is convenient for studying the effects of the aggregate and asphalt types, aggregate contamination, and antistripping agents on the water susceptibility of asphalt/siliceous aggregate mixtures. It is also unique in providing data on the transport of water through an asphalt layer of any thickness attached to an aggregate.

A water layer many monolayers thick at the asphalt/aggregate interface is mainly responsible for the displacement (stripping) of asphalt from a siliceous aggregate when asphalt/aggregate mixtures are exposed to water or high relative humidities. This thick interfacial water layer is formed because of the presence of a water-sensitive layer at the asphalt/aggregate interface. Hygroscopic materials present at the interface (from both asphalt and aggregate) and water-soluble materials that have migrated from the asphalt film during exposure constitute this interfacial water-sensitive layer. Water migration from the environment to the interface is not a uniform diffusion through the asphalt matrix but rather a transport process mediated by the pores, which are opened up by the dissolution by water in the areas occupied by the hydrophilic materials. Once entering the interface, water transport along the film/substrate interface is responsible for the rapid formation of the many-monolayer interfacial water layer. A base-modified siliceous surface is desirable to form strong bonds with the acidic asphalts, which can retard the water displacement process.

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