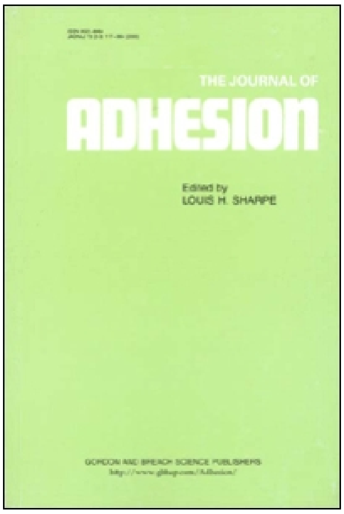

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Relationship Between Interfacial Water Layer Adhesion Loss of Silicon/Glass Fiber-Epoxy Systems: A Quantitative Study

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Water at the polymer/substrate interface is often the major cause of adhesion loss in coatings, adhesives, and fiber-reinforced polymer composites. This study critically assesses the relationship between the interfacial water layer and the adhesion loss in epoxy/siliceous substrate systems. Both untreated and silane-treated Si substrates and untreated and silane-treated E-glass fibers were used. Thickness of the interfacial water layer was measured on epoxy/Si systems by Fourier transform infrared–multiple total internal reflection (FTIR-MTIR) spectroscopy. Adhesion loss of epoxy/Si systems and epoxy/E-glass fiber composites was measured by peel adhesion and short-beam shear tests, respectively. Little water accumulation at the epoxy/Si substrate interface was observed for silane-treated Si substrates, but about 10 monolayers of water accumulated at the interface between the epoxy and the untreated Si substrate following 100 h of exposure at 24 °C. More than 70% of the initial epoxy/untreated Si system peel strength was lost within 75 h of exposure, compared with 20% loss after 600 h for the silane-treated Si samples. Shear strength loss in composites made with untreated E-glass fiber was nearly twice that of composites fabricated with silane-treated fiber after 6 months of immersion in 60 °C water. Further, the silane-treated composites remained transparent, but the untreated fiber composites became opaque after water exposure. Evidence from

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FTIR-MTIR spectroscopy, adhesion loss, and visual observation strongly indicated that a water layer at the polymer/substrate interface is mostly responsible for the adhesion loss of epoxy/untreated siliceous substrate systems and epoxy/untreated glass fiber composites and that FTIR-MTIR is a viable technique to reliably and conveniently assess the adhesion loss attributable to water sorption at the interface.

Keywords: Adhesion; Composite; Interface; Quantitative; Silane coupling agent; Silicon; Water

INTRODUCTION

Coatings, adhesives, and fiber-reinforced polymer composites are often subjected to long-term high humidity and water. In these applications, water at the polymer/substrate interface is believed to be a major cause of the adhesion loss in these materials. The detrimental effects of water and humidity on the adhesion loss are well documented for polymer-coated metals [1], adhesives [2], polymer/glass fiber composites [3,4], and asphalt pavements [5]. However, no relationship between thickness of the water layer at the polymer/substrate interface and water-induced adhesion loss has been established. The main reason for this has been the lack of a technique that can provide quantitative data on the thickness of the interfacial water layer. The development of a spectroscopic technique to quantify water concentration at the polymer/substrate interface [6–8] has made such a study possible. The objectives of this article are 1) to measure thickness of the water layer at the interface between an epoxy matrix and a Si substrate that was used without and with aminosilane surface treatment and 2) to relate thickness of the interfacial water layer to adhesion loss of epoxy/Si substrate systems and epoxy/E-glass fiber composites exposed to water. The interfacial water layer for epoxy/Si substrate systems was measured using Fourier transform infrared spectroscopy in the multiple total internal reflection mode (FTIR-MTIR), and the water-induced adhesion losses of epoxy/Si substrate systems and epoxy/E-glass fiber composites were obtained by wet peel adhesion and short-beam shear tests, respectively.

EXPERIMENTAL PROCEDURES

Materials and Specimen Preparation

The polymer matrix was composed of a stoichiometric mixture of a low-molecular-mass diglycidyl ether of bisphenol A epoxy resin (epoxide equivalent mass = 189 g) (Epon® 828, Shell Chemical

Company, Houston, TX, USA) and polyoxypropylenetriamine (amine equivalent = 81 g) curing agent (Jeffamine® T-403, Texaco Chemical Co., Houston, TX, USA). The same amine-cured epoxy matrix was used for both the interfacial water and the adhesion loss studies. For measurement of water at the polymer/substrate interface, specimens of amine-cured epoxy were applied to untreated and aminosilane-treated 50 mm × 10 mm × 3 mm, spectroscopic-grade, Si parallelogram plates (Si internal reflection elements). For water-induced adhesion loss of polymer/flat substrate systems, specimens of the same epoxy applied to untreated and aminosilane-treated 100-mm-diameter Si wafers were used. For adhesion loss study of the polymer/fiber composite, untreated and aminosilane-treated E-glass fibers were impregnated with the same epoxy matrix.

Si plates and wafers (flat substrates) were cleaned with acetone, followed by methanol, after which they were dried with hot air. The surfaces of these Si plates and wafers had a native SiO_2 (silica) layer of 2.25 nm ± 0.1 nm thick, as measured by ellipsometry. It should be noted that silica reacts readily with water vapor so that at normal working conditions its surface is covered with silanol groups (SiOH) and adsorbed water. Under ambient conditions, a silica surface generally contains about five hydroxyl (OH) groups/nm^2, independent of silica type [9]. Thus, the surface chemical structure of the Si substrates used for measuring interfacial water and adhesion loss of polymer/flat substrate systems is similar to that of a silica surface. Hereafter, the SiOH-covered Si plates and wafers are designated as Si substrates or siliceous substrates. E-glass fiber was a commercial, unsized material having a diameter of 16 μm ± 2 μm. Besides SiO_2, E-glass typically contains substantial amounts of alkaline oxides including MgO, CaO, Na_2O, and K_2O. These oxides are hygroscopic so that water adsorption on E-glass is much greater than that of a pure silica material [10]. Therefore, it is expected that water has a greater affinity toward the untreated E-glass fiber surface used for the composites than that toward the surface of the Si plates or Si wafers employed for the interfacial water and adhesion loss measurements of epoxy/flat substrate systems.

Silane-treated surfaces were prepared by immersing cleaned Si plates, Si wafers, and E-glass fibers for 30 min in an acidified (pH 4, by citric acid) water solution containing 0.1% mass fraction of aminoethylaminopropyltrimethoxysilane (Z-6020 Silane, Dow Corning, Midland, MI, USA). The treated substrates and fibers were dried for 10 min at 110°C before use. Masking tape strips of 1 mm and 10 mm in width placed along the edges of the Si plates and the Si wafers, respectively, were used to control the epoxy film thickness. After thoroughly mixing the amine curing agent and epoxy resin, followed by degassing, the mixture was applied to the substrates using a drawdown technique, similar to that described previously [7]. Epoxy-coated Si plates and wafers were then cured for 24 h at room temperature. After removing the masking tape strips, coated samples were postcured at 100°C for 2 h and stored at ambient conditions (24°C and 40% relative humidity) for 2 weeks before use. The thickness of the epoxy films on the substrate (determined at the conclusion of the experiment) was in the 130 μm to 150 μm range, as measured by a micrometer. The quality of all coated samples was good, and no visible pinholes or air bubbles were observed (with the naked eye).

Unidirectional epoxy/glass fiber composites were prepared by impregnating E-glass fibers with the same amine-cured epoxy between two transparent polyethylene (PE) sheets. Untreated and silane-treated fibers of approximately 250 mm in length were carefully laid unidirectionally onto a PE sheet. After fixing one end of the fibers onto the PE sheet (using an adhesive tape), the epoxy/amine mixture was poured liberally over the fibers. After placing the other PE sheet over the resin-soaked fibers, the resin was spread repeatedly with a glass plate in the fiber direction until a transparent mat was formed. The impregnated fibers were cut to size and placed in open-ended, aluminum molds having an inside dimension of 200 mm × 8 mm × 6.5 mm. The molds were placed in an autoclave for 3 h at 80 °C and under a pressure of 1.4 MPa, followed by postcuring at 100°C for 2 h at atmospheric pressure. After removal from the molds and conditioning in ambient environment for 2 weeks, the composite rods were polished and cut into 38-mm × 7.9-mm × 6.35-mm specimens. All composite test specimens appeared transparent, and there was no evidence of visible air voids, as observed by the naked eye. The fiber volume fraction of the composites was 24% ± 2%. This value was converted from the mass fraction value of 40% ± 2%, which was measured by thermogravimetry. The conversion was based on the relations given in Ref. [11], which link fiber volume fraction with fiber mass fraction through the densities of the composite and its constituents. The densities of the cured epoxy, E-glass fiber, and the composite were 1.13 g/cm^3, 2.54 g/cm^3, and 1.47 g/cm^3, respectively. Density of the epoxy film was obtained experimentally by the water-displacement technique, of the E-glass fiber from Ref. [12], and of the composite by the law of mixtures.

Measurement of the Water Layer at the Epoxy/Si Substrate Interface

FTIR-MTIR was used to measure the thickness of the water layer at the polymer/substrate interface. FTIR total internal reflection spectroscopy (FTIR-TIR) [13], commonly known as FTIR-ATR (FTIR–attenuated total reflection), is a powerful technique that provides qualitative as well as quantitative molecular information of surfaces and interfaces. In total 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 propagating radiation. Detection of the attenuated radiation at the exit of the substrate yields an infrared spectrum of the sample. When a polymer-coated substrate is exposed to an aqueous environment, water will eventually enter the polymer/substrate interfacial region and interact with the evanescent wave and be detected. One way to enhance the capability to detect small concentrations of water is to increase the number of internal reflections. This multiple total reflection spectroscopic technique is well suited for measurement of water at the polymer/substrate interface because 1) water interacts strongly with the infrared-generated evanescent field, *i.e.*, a very small amount of water at the polymer/substrate interface can be measured, 2) it detects water from the substrate side, thus preventing the interference of water vapor from the environment, 3) it is suitable for *in situ* study because the measurement is conducted at ambient conditions, and 4) FTIR-MTIR can be quantitative.

Thickness of the water layer at the polymer/substrate interface, l, was calculated using Eq (1) [6]:

$$l = \frac{d_{pw}}{2}\left[-\ln\frac{1-(A_t/A_\infty)}{(1-c_w)(d_{pp}/d_{pw})}\right], \qquad (1)$$

where d_{pw} and d_{pp} are the penetration depths of the evanescent wave in water and polymer, respectively; A_t is the FTIR-MTIR absorbance of water at a particular exposure time; A_∞ is the FTIR-MTIR absorbance when the water layer at the polymer/substrate interface is very thick ($l \rightarrow \infty$, *i.e.*, $l > d_{pw}$); and c_w is the mass fraction of water sorbed in the polymer film within the probing depth. It should be noted that the same value of d_{pp} (which is a function of the sample refractive index) was used for both dry and water-saturated epoxy films because the small amount of water uptake in the films ($< 2\%$ mass fraction; see Figure 3) had a negligible effect on d_{pp}. A brief discussion on the principle of total internal reflection spectroscopy for *in situ* measurement of water at the polymer/substrate interface is given in Ref. [7]. However, complete details on the derivation of Eq. (1), which was based on a two-layer model applied to the internal reflection theory, may be found in Ref. [6]. Equation (1) is still valid for the case where the water layer at the polymer/substrate interface is not continuous, *e.g.*, water clusters.

Assuming water is uniformly distributed over the entire surface area of the specimen, the amount of water at the polymer/substrate interface, W_i, is given by

$$W_i = la\rho, \tag{2}$$

where a is the area of the polymer-coated specimen in contact with water ($a = 329\,\text{mm}^2$ in this study) and ρ is the density of water at the interface, which is assumed to be the same as that of liquid water (a reasonable assumption).

Figure 1 schematically shows the specimen configuration used for *in situ* measurement of water at the polymer/substrate interface by FTIR-MTIR spectroscopy. In this setup, a water chamber was attached to each cured epoxy-coated Si plate. The specimen with the water chamber attached was placed vertically in a multiple internal reflection accessory holder, and measurement of water at the interface was carried out using an FTIR spectrometer (Magna-IR 560,

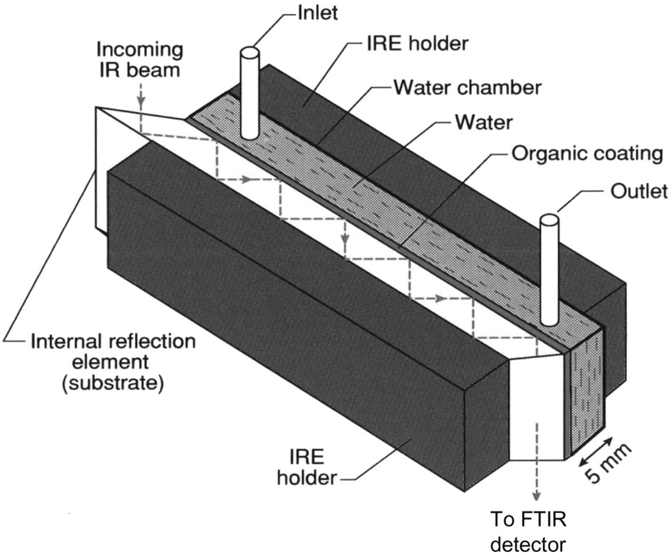


FIGURE 1 Experimental setup for measuring water at the polymer/substrate interface using Fourier transform infrared spectroscopy in the internal reflection mode.

Thermo, Madison, WI) and a variable angle multiple internal reflection accessory (Thermo, Madison, WI). After filling the chamber with distilled water at 24°C, FTIR-MTIR absorption spectra were taken automatically every 15 min without disturbance to the specimens or the spectrometer. For the specimen configuration employed in this study, the only pathway for water transport from the chamber to the epoxy/substrate interface was diffusion through the epoxy matrix. All spectra were co-additions of 128 scans taken at a resolution of $4\,\mathrm{cm}^{-1}$ using unpolarized light at 45° incident angle and purged dry air. At this incident angle, the 50-mm × 10-mm × 3-mm Si plate provided 17 reflections of the IR beam inside the substrate. Peak height was used to represent FTIR-MTIR intensity, which was expressed in absorbance (A).

Measurement of Adhesion Loss of Polymer/Si Substrate Systems and Polymer/E-Glass Fiber Composites Exposed to Water

The water-induced adhesion loss of epoxy/Si substrate systems was measured using a wet peel test. For this experiment, epoxy-coated Si wafers were completely immersed in a polyethylene container containing distilled water at 24°C. At prespecified exposure times, coated wafers were removed from the container, and each wafer was immediately incised with a razor into five 12-mm × 65-mm specimens. Each specimen was carefully peeled from the substrate, leaving a length of 35 mm of specimen unpeeled. The partially peeled coated wafer was then positioned in the 90° wet peel test apparatus, schematically displayed in Figure 2. The instrument consisted of a linear bearing slider fixed to a computer-controlled universal testing machine outfitted with a 2.0-kg load cell. All adhesion tests were conducted at room temperature and at a peel rate of 20 mm ± 0.1 mm per minute. Care was taken to ensure that the evaporation of water from the test specimens was held to a minimum by keeping liquid water on the surface of coated wafers during incision and peeling. To ensure accuracy, the testing machine was calibrated prior to each testing period using standardized load cells. All reported results were the average of 10 specimens (from two wafers). Coefficients of variation, (standard deviation/mean) × 100, of each set of specimens were always less than 5%.

Adhesion loss of the composites was followed by the interlaminar shear strength (ILSS) data, in MPa, as a function of time exposed to water at 60°C. ILSS values were determined from the peak load of the short-beam shear test (ASTM D2344):

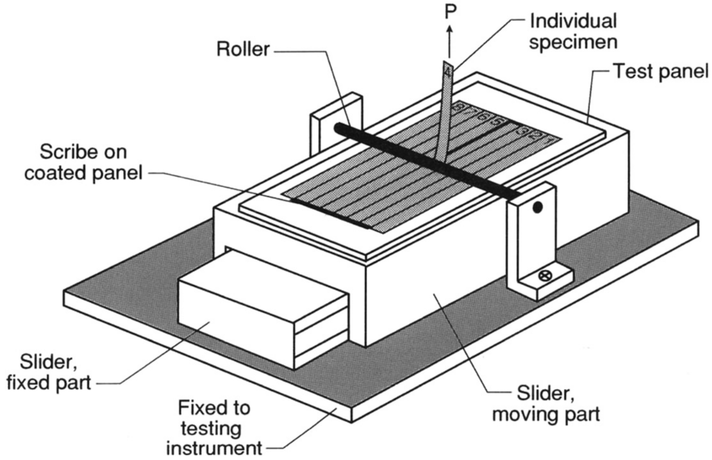


FIGURE 2 Peel adhesion test apparatus for measuring wet adhesion loss of epoxy-coated Si wafers exposed to water.

$$\mathrm{ILSS} = \frac{3F}{4bd}, \tag{3}$$

where F is the peak load (in N) and b and d are the width and thickness of the composite specimen (in mm). For this test, specimens of $38\,\mathrm{mm} \times 7.9\,\mathrm{mm} \times 6.35\,\mathrm{mm}$ immersed in distilled water at 60°C were removed from the water-filled container and tested at prespecified time intervals. The specimen was supported by a 25-mm span and tested at a displacement rate of 0.5 mm/min. Each data point is the average of four specimens.

Measurements of Other Properties

In addition to the main measurements described previously, other properties of the epoxy matrix film were measured, including water uptake, water diffusion coefficient, water solubility, total surface free energy and its polar component, surface polarity, and glass-transition temperatures before and after water saturation. The work of adhesion between the epoxy and the Si substrate before and after exposure to water was also determined.

Experiments on water uptake in the epoxy matrix film were conducted to provide the c_w value in Eq. (1) and the diffusion coefficient of water in the matrix. For this experiment, free films of approximately

150 μm thick of the same amine-cured epoxy were prepared by applying the epoxy/amine mixture to cleaned glass plates using the drawdown technique. After peeling from the substrate, the free films were cut to size, placed in a dessicator containing P_2O_5 for 48 h, weighed, and immersed in distilled water. They were taken out, blotted, and reweighed at specified time intervals. For each water uptake specimen, the film thickness was measured on three different locations using a micrometer. Water uptake is expressed as the mass fraction of the initial, dry specimens. The results were the average of six specimens.

The diffusion coefficient, D, of water in the bulk epoxy film was estimated from water uptake data using the sorption kinetics equation [14]:

$$D = \frac{0.0492}{(t/h^2)_{1/2}} \tag{4}$$

where t is the time, h is the epoxy film thickness, and $(t/h^2)_{1/2}$ is the value of (t/h^2) for which the ratio between water uptake at a particular time and that at equilibrium (*i.e.*, $M_t/M_\infty) = 1/2$; this value is obtained from the M_t/M_∞ *vs*. t/h^2 plot. D values obtained from Eq. (4) are essentially the same as those calculated using the more complex sorption kinetics diffusion equations.

The glass-transition temperatures, T_g, of the amine-cured epoxy before and after saturation with water were determined using differential scanning calorimetry (DSC) at a heating rate of 10°C/min. The solubility of water in the film was obtained as a product of equilibrium water uptake and polymer density; the latter was measured by the water displacement method. Polar and total surface free energies of the epoxy films and cleaned Si substrate were determined by the geometric-mean method [15] using contact angles of water and methylene iodide. The work of adhesion between the epoxy and SiOH-covered Si substrate in the absence and presence of water was determined by the approach described in Ref. [16] using polar and nonpolar surface free-energy values of the epoxy films and Si substrates measured in this study.

RESULTS AND DISCUSSION

Properties of Epoxy and Epoxy/Si Substrate Before and After Exposure to Water

Figure 3 displays the uptake (sorption) characteristics of water in the amine-cured epoxy free films having a thickness of 150 μm ± 7 μm at

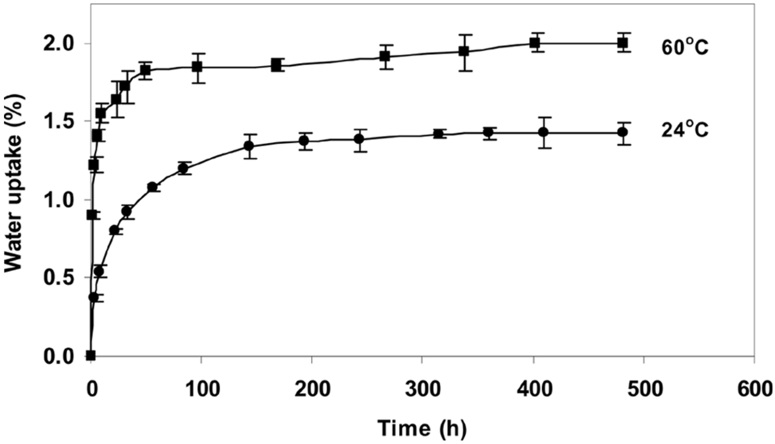


FIGURE 3 Water uptakes of epoxy free films at 24°C and 60°C (error bars indicate one standard deviation).

24°C and 60°C. Clearly, both the rate and the equilibrium (maximum) water uptake are greater at 60°C than at room temperature. Further, the sorption at 60°C reaches nearly an equilibrium value within 50 h, but it takes three times as long to reach the equilibrium at 24°C. The water uptake plots of M_t/M_∞ *vs* $\sqrt{t}$ (not shown) for exposure to both 24°C and 60°C are initially linear, indicating that the diffusion of water in this epoxy at both temperatures is Fickian. Table 1 gives the diffusion coefficient, D, of water in the films at two temperatures along with other pertinent properties. The results show a D value at 60°C that is nearly 20 times greater than that at 24°C. On the other hand, the solubility at 60°C is only 25% greater than that at room temperature.

As seen in Table 1, T_g of the epoxy matrix substantially decreases after immersion in water. Further, the effect of exposure temperature on T_g is negligible. Table 1 also provides values of the surface free-energy polar component (γ^{p}), total surface free energy (γ_{s}), and polarity (defined as $\gamma^{\mathrm{p}}/\gamma_{\mathrm{s}}$) of the epoxy matrix. Both the surface nonpolar (dispersion force) and polar components play a crucial role in the molecular interactions between a polymer and a substrate. Further, the strength of these interactions in the presence of water would determine the hydrolytic stability of a polymer/substrate interface. Table 1 shows that the work of adhesion between this amine-cured epoxy coating and the Si substrate ($\mathrm{W_{aw}}$) is positive in air but becomes negative in the presence of water.

TABLE 1 Properties of the Epoxy Matrix and Epoxy/Si Substrate Systems Before and After Exposure to Water

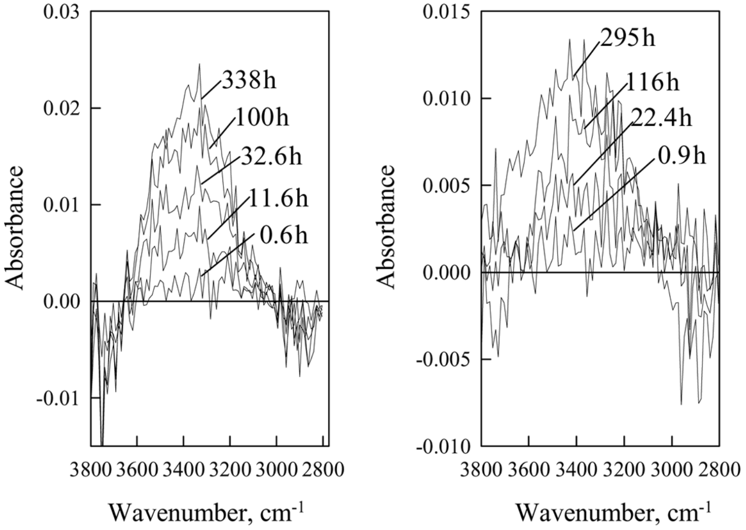
Exposure	T_g (°C)	D($\times 10^{-10}$, cm^2/s)	Solubility[a] (mg/cm^3)	W_a[b] (mJ/m^2)	γ^p (mJ/m^2)	γ_s (mJ/m^2)	Polarity (γ^p/γ_s)
Dry	80 ± 2	—	—	184	7.0	41	0.17
Water, 24°C	68 ± 3	5.3 ± 0.4	16.2 ± 2	-50	—	—	—
Water, 60°C	67 ± 3	136 ± 2	22.8 ± 2	—	—	—	—

[a] Determined using epoxy density of 1.14 g/cm^3, which was measured by the water displacement method.

[b] Calculated using $(\gamma_s - \gamma^p)$ values given in this table for the epoxy, and γ^p and $(\gamma_s - \gamma^p)$ values of 44.6 mJ/m^2 and 29.4 mJ/m^2, respectively, measured for solvent-cleaned Si wafers. All surface free-energy components were determined using the geometric mean method and contact angles of water and methylene iodide measured at ambient conditions (24°C and 40% RH). Coefficients of variation of all contact angles were $<2\%$.

Quantification of Water Layer at the Epoxy/Si Substrate Interface

Figure 4 displays FTIR-MTIR difference spectra in the 2800–3800 cm^{-1} region (water OH stretching region) of epoxy-coated untreated (Figure 4a)



(a) (b)

FIGURE 4 FTIR-MIR difference spectra of epoxy-coated untreated (a) and silane-treated (b) Si substrate exposed to 24°C water for several time intervals.

and silane-treated Si (Figure 4b) substrates exposed to water for several representative times. (Note that Figure 4a has been presented previously [8]; it is again shown here for comparison.) These spectra were obtained by subtracting the spectra taken before exposure from those collected at different exposure times. Intensity (*i.e.*, absorbance) changes observed in the difference spectra are due to the effect of water on the specimens. Bands above the zero absorbance line of a difference spectrum indicate an increase in concentration of a functional group, and bands below the zero absorbance line are due to a loss of a functional group. The relatively high noise-to-signal ratio of these spectra is due to the very low concentration of water detected in the samples, as shown by the absorbance values on the vertical axis. The bands in the 3000 cm^{-1} to 3650 cm^{-1} region of the difference spectra are due to the OH stretching mode of liquid water, as verified previously [7]. Because of the high noise-to-signal ratio, Figure 4 does not allow a detailed assignment of the OH stretching band of water. However, our FTIR-MTIR spectrum of liquid water reported previously clearly showed a broad band peaking at 3400 cm^{-1}, due to OH stretching, a prominent shoulder at 3250 cm^{-1}, due to the overtone of the OH bending near 1640 cm^{-1}, and a barely-visible shoulder near 3625 cm^{-1}, due to nonhydrogen-bonded OH stretching [6,7]. These peak positions are similar to those of liquid water spectra collected by IR spectroscopy in the transmission mode [17]. It should be noted that the amine-cured epoxy also contains the OH stretching in the same spectral region as

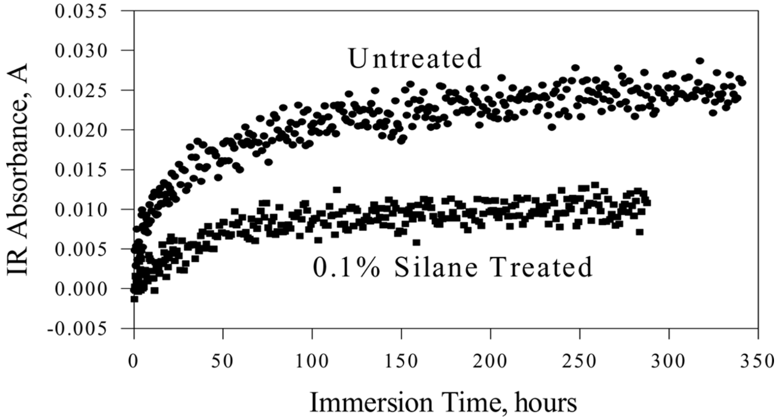


FIGURE 5 FTIR-MIR intensity changes of the water OH band with exposure time for epoxy-coated untreated and silane-treated Si plates (each dot represents a data point).

that of water. However, the FTIR-MTIR intensity change of the epoxy OH group due to water sorbed in the film is negligible because the amount of water uptake at 24°C ($\sim 1.3\%$ of the film mass; see Figure 3) in the evanescent wave penetration depth ($< 0.25\,\mu$m) is very small.

Figure 4 shows that the FTIR-MTIR intensity of the water band (in the $3000\,\text{cm}^{-1}$ to $3650\,\text{cm}^{-1}$ region) increases, while the intensity of the epoxy CH stretching bands between $2800\,\text{cm}^{-1}$and $3000\,\text{cm}^{-1}$ decreases (not highly visible in this figure because of the high noise to signal). Similar, but to much greater degrees, FTIR-MTIR intensity changes with exposure time of both the water and polymer bands have been observed for fusion-bonded epoxy coatings [18], asphalt [19], and alkyd coatings [7]. The intensity increase of the water bands, together with the intensity decrease of the polymer film bands observed in this and previous studies [6–8,18] as a function of exposure time, may be explained by the water entering the polymer/Si substrate interface. This is because as the thickness of the interfacial water layer increases, it pushes the polymer film further away from the substrate surface. Because the evanescent field decays exponentially with the probing depth in the sample, the separation of the film from the substrate surface will reduce the amount of the polymer material in the probing depth, that is, a decrease of the FTIR-MTIR intensity of the polymer bands.

Peak height (in absorbance, A) of the water OH stretching band at $3400\,\text{cm}^{-1}$ was used for quantitative analysis of water at the polymer/substrate interface. Figure 5 illustrates plots of FTIR-MTIR intensity changes of the water OH stretching for both epoxy-coated untreated and silane-treated Si systems as a function of water immersion time. Each symbol represents one data point, which were collected every 15 min, as specified in the experimental section. The scatter of data observed in the figure for each coating system is mostly due to the high noise-to-signal ratio, as indicated earlier. However, thanks to the large amount of data collected *in situ* and at short-time intervals, the data scatter does not affect the average intensity change of the water band at $3400\,\text{cm}^{-1}$. Figure 5 shows an intensity increase with exposure time up to approximately 100 h before leveling off. Further, the intensity for the water amount detected in the untreated Si samples is substantially higher than that of the silane-treated ones.

The intensity of Figure 5 represents the total amount of water detected in the epoxy-coated samples, which is the sum of water amount at the epoxy/Si substrate interface and that sorbed in the epoxy matrix within the penetration depth. To determine thickness and amount of the water layer at the epoxy/Si interface using

Eqs. (1) and (2), A_t, A_∞ , c_w, d_{pw} and d_{pc} must be known. Values of A_t are taken directly from Figure 4; A_∞ (= 0.48 absorbance) is taken from Ref. [7], which was obtained using the same experimental setup on a film-free Si substrate, *i.e.*, water was in direct contact with the Si substrate. Values of d_{pw} and d_{pc} are 0.22 μm and 0.24 μm, respectively, which were calculated from the penetration depth [Eq.] (13) using the following data given in Ref. [7]: n_1 of Si is 3.5, n_2 for water and epoxy are 1.3 and 1.50, respectively. (Note that because of its very low thickness, the SiO_2 film has little effect on the refractive index of the Si substrate.) Values of c_w at appropriate exposure times are interpolated from the 24°C result of Figure 3 for an epoxy film having a thickness of 0.24 μm, which is one penetration depth of the evanescent wave in the epoxy film at the 2.94 μm wavelength (the water OH stretching band).

Substituting all these values into Eqs. (1) and (2) enables the thickness and amount of the water layer at the interface for epoxy-coated untreated and silane-treated Si substrates to be determined. The results are given in Figure 6, in which the amount (mass) and the thickness are shown in the left and right vertical axes, respectively. Essentially, no or little water is observed at the epoxy/Si substrate interface of the silane-treated system, but a water layer of approximately 3 nm, or about 10 water monolayers (one water monolayer is approximately 0.285 nm [20]), has built up at the interface of the untreated system after 100 h of exposure. Because water tends to form

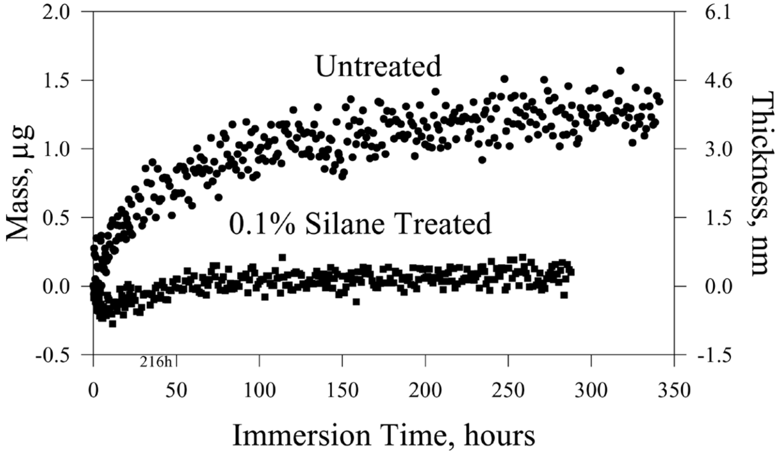


FIGURE 6 Thickness and amount of the water layer at the interface as a function of exposure time for epoxy-coated untreated and silane-treated Si plates exposed to water at 24°C (each dot represents a data point).

multiple layers on a SiO_2 surface through its SiOH groups [9], the results of Figure 6 suggest that treatment with an aminosilane agent effectively eliminates the SiOH sites for water adsorption on a silica surface. This postulation is consistent with infrared spectroscopic evidence reported previously, showing clearly the conversion of SiOH groups into Si-O-Si bonds after silanization of SiO_2 [21]. The highly polarized Si-OH group readily forms strong hydrogen bonds with H_2O, but the Si-O-Si group, because of its very low dipole moment, interacts weakly with water molecules. The negative absorbance between 0 and 20 h of exposure observed in Figure 7 is probably due to a relaxation/swelling stress of the film upon immersion in water. This change can cause debonding in some weakly bonded areas of the interface. Because the evanescent field decays exponentially with the probing depth in the sample, such debonding will decrease the amount of the polymer material within the probing depth, *i.e.*, a decrease of the FTIR-MTIR intensity of the epoxy bands. Because epoxy and water OH groups absorb infrared radiation in the same region, if no or a very little amount of water was present at the interface (due to short exposure time), the decrease of the epoxy OH intensity will result in a negative value in the difference spectrum.

For commercial polymeric coatings and asphalts, the thickness of the polymer/substrate interfacial water layer has been observed in the hundreds of nanometers to micrometer range [7,8,19]. The thick

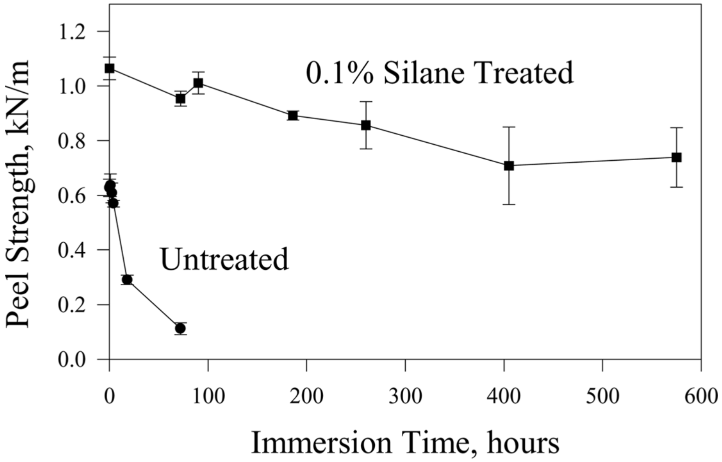


FIGURE 7 Peel adhesion loss with exposure time for epoxy-coated untreated and silane-treated Si wafers exposed to water at 24°C (error bars indicate one standard deviation).

interfacial water layer has been attributed to water-sensitive contaminants at the interface, including hydrophilic unreacted and partially reacted resins and curing agents, additives, and impurities [7,19]. These hydrophilic materials are present at the interface during the film formation or leach out from the films during exposure to water.

One concern is that the OH stretching band of water is broad and may consist of many different species that have different molar absorptivities. In such a case, the use of this band for quantitative analysis of water may produce substantial errors. There are several pieces of information to justify that the use of this band is valid for quantitative study of liquid water at the polymer/substrate interface. First, an in-depth review [20] of water structure and its vibrational characteristics has concluded that, at normal temperature, liquid water does not contain a number of distinctly different molecular species. Instead, it consists of mostly hydrogen-bonded molecules, as indicated by the smooth infrared OH stretching band contours that pass through a maximum. These features are the basis of the continuum model of water structure. Our FTIR-MTIR spectra of water at different D_2O concentrations [8] clearly showed that, in the absence of the combination band at $3250\,\mathrm{cm}^{-1}$, the OH stretching band is symmetrical and smooth and has a Gaussian shape, in good agreement with the continuum model. Second, the molar absortivity of the OH stretching band between $3350\,\mathrm{cm}^{-1}$ and $3450\,\mathrm{cm}^{-1}$ has been reported to be essentially unchanged [22]. Lastly, the periods of vibration (10^{-13} to 10^{-14} s) for both intermolecular and intramolecular modes of water are short as compared with the average time (10^{-11} to 10^{-12} s) between diffusional motions of water molecules (time for breaking and forming hydrogen bonds) [17,20]. As a result, no change in the number of hydrogen bonds would occur during the period of interaction between water and infrared radiation. Therefore, it is expected that vibrational spectroscopies can provide reliable information on the nature and variety of hydrogen bonding interactions between water molecules. For these reasons, the use of the OH stretching peak height at $3400\,\mathrm{cm}^{-1}$ is valid and should produce little error in the analysis of water at the polymer/substrate interface.

The presence of a water layer at the interface of the epoxy/Si substrate system shown in Figure 6 is consistent with the negative works of adhesion in water (W_{aw}) shown in Table 1 and reported previously for an epoxy adhesive/silica substrate [23]. A negative W_{aw} value indicates that the epoxy/SiOH bonds are not stable in the presence of water and that water will displace these bonds and form a water layer at the epoxy/Si substrate interface when an epoxy-coated Si substrate systems or polymer/glass fiber composites are exposed to water or high relative humidities. Negative W_{aw} values have also been reported for other polymer/substrate systems such as epoxy adhesive/Fe_2O_3, epoxy adhesive/Al_2O_3 [23], and PMMA/Al_2O_3 and PMMA/Fe_2O_3 [24], implying that polymer/untreated substrate (or more accurately polymer/hydroxylated oxide) bonds are weak and cannot resist the affinity of water toward the substrate surface. The reason for the weak polymer/substrate bonds is that most common metals found in inorganic oxides are considerably more electropositive than the carbon atoms in polymers or organic compounds [25]. As a result, the electron density of the oxygen atom on the oxides is markedly higher than that of the oxygen atom on water or in most organic molecules. Therefore, covalently bonded interfaces rarely exist in polymer/unmodified substrate systems. Therefore, if high-energy inorganic surfaces are not chemically modified, a layer of water is likely to form at the interface when a polymer/substrate system is exposed to water or high relative humidities. The accumulation of many monolayers of water at the interface will decrease the adhesion of polymer/substrate systems. For thin polymer films ($< 10\,\mu m$) or thick films containing pores or defects, the transport of water to the interface is relatively rapid, and the adhesion loss can start shortly after exposure. However, for thick, intact, or multicoat films, it may take a long time before any evidence of an adhesion loss is observed.

The presence of very little water at the interface of the epoxy/silane-treated system (Figure 6, lower curve) suggests that the bond strengths between the silane-treated Si substrate and the epoxy are stronger than those between the untreated surface and water. Therefore, water molecules could not displace the interfacial bonds of the treated samples and thus are not able to enter the interface. This result, which has been confirmed by duplicate specimens, is consistent with the interfacial reinforcement mechanism that has been used to explain the enhanced hydrolytic stability of epoxy composites made with silane-treated E-glass fibers [26]. It should be mentioned that water is a weakly adsorbed species, in that the magnitude of water-oxide and water-silanol (SiOH) bonds are in the 25–65 kJ/mol range [27,28] and thus incapable of replacing stronger chemical bonds between the silane and the siliceous surface or between the silane and the epoxy matrix. Further, water probably enters the epoxy/Si substrate interface by breaking the water-SiOH bonds and builds up the water layer on the SiOH-terminated surface. This occurs because the hydrogen bonds between the first water layer and the SiOH groups on a silica surface are substantially weaker (about 25 kJ/mol) mol) than the bonds between the first and second layer of water ($>$40 kJ/mol) [28].

Peel adhesion losses as a function of time exposed to 24°C water for epoxy-coated untreated and silane-treated Si wafers are presented in Figure 7. The epoxy/untreated systems lose most of their peel strength within 75 h of exposure, whereas the epoxy/silane-treated specimens retain 80% of their adhesion even after 600 h of immersion in water. (It should be noted that the 0.1 kN/m residual peel strength observed for the epoxy/untreated system in Figure 7 is from the apparatus friction.) The peel adhesion loss for the silane-treated samples (Figure 7, upper curve) is probably due to factors such as hydrolysis of the silane/glass bonds [26] and plasticization and swelling stress of the matrix.

An examination of the adhesion loss (Figure 7, lower curve) and the water concentration increase at the interface (Figure 6, upper curve) of the untreated systems reveals that the changes of these two quantities with water-exposure time are closely correlated, as shown in Figure 8. That is, as the thickness (or mass) of the water layer increases from 0 to 3 nm, or from 0 to 1 μg in mass, the peel strength decreases from approximately 0.6 kN/m to essentially 0. Figure 8 was generated using data from the same exposure time for both the interfacial water measurement (Figure 6, upper curve) and the adhesion-loss measurement (Figure 7, lower curve) of nonsilane Si

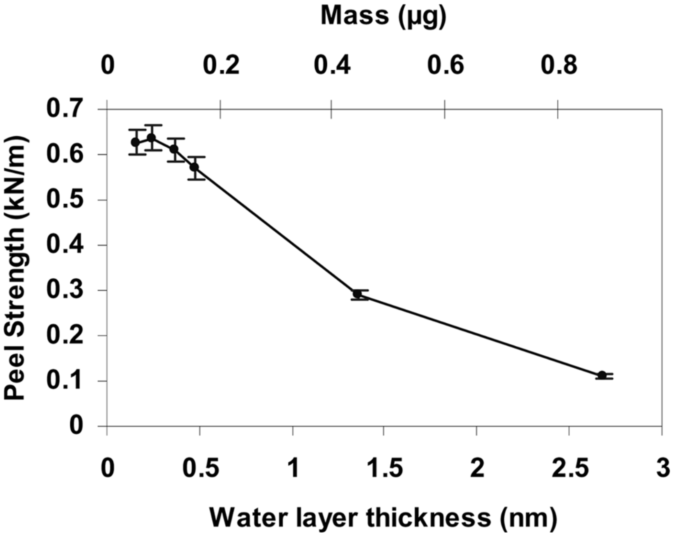


FIGURE 8 Relationship between interfacial water layer thickness or amount and adhesion loss for an amine-cured epoxy-coated Si substrate exposed to water at 24°C.

substrate samples. Similar relationships between water thickness layer and peel adhesion loss have been also observed for several asphalts on untreated siliceous substrates [29] and a powder epoxy/untreated steel system [18]. These results provide the first quantitative experimental evidence to show that the gradual buildup of multiple monolayers of water at the interface is mostly responsible for the adhesion loss of an epoxy/untreated Si substrate system. Further, the results of Figures 6 to 8 again illustrate the great affinity of water toward untreated siliceous surfaces and that these surfaces must be modified to improve the adhesive durability of polymer/siliceous substrate systems exposed to aqueous environments.

Figure 9 depicts ILSS changes with exposure time immersed in distilled water at 60°C for epoxy composites prepared with untreated and aminosilane-treated E-glass fibers. Untreated and silane-treated composites lose nearly 65% and 30%, respectively, of their initial shear strengths after 6-months of immersion. Besides the great affinity of unmodified SiO_2 for water, E-glass fiber in the composite also undergoes corrosion during water exposure [4], generating alkaline ions at the resin/fiber interface. These water-soluble ions likely create an osmotic pressure that greatly increases the delamination gap, as observed by optical anisotropy [30]; that is, a substantial increase in the thickness of the interfacial water layer. Because the two composites used in our study differ only in fiber surface treatment, the difference in the ILSS loss between untreated and silane-treated composites

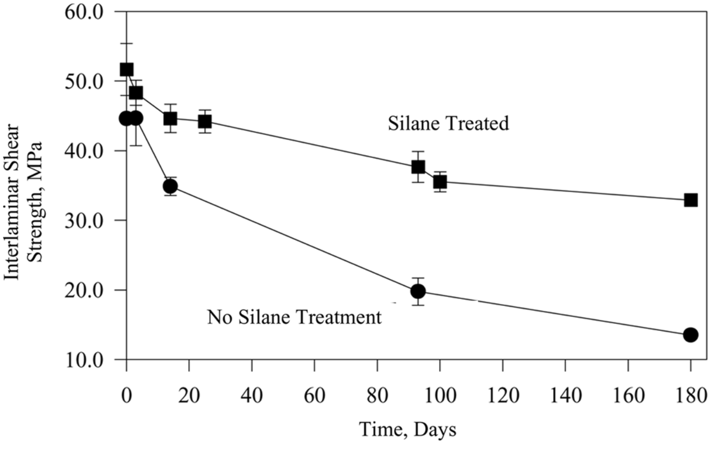


FIGURE 9 ILSS loss with exposure time in 60°C water for untreated and silane-treated E-glass fiber/epoxy composites.

shown in Figure 9 is attributed solely to the presence of a water layer at the epoxy/fiber interface. This assertion is supported by the results given in Figure 6, which show a water layer about 3 nm thick at the interface of the epoxy/untreated Si substrate system after 75 h exposure, but little evidence of water at the interface of the silane-treated samples. This conclusion is also consistent with numerous previous reports that attributed the interfacial shear strength loss of polymer E-glass and graphite composites exposed to water as due to cumulative degradation of the interfacial bonds or presence of a water layer at the fiber/matrix interface [30–34].

One more aspect that needs to be emphasized is that the exposure temperature used in this study was close to the T_g of the water-saturated epoxy matrix. Further, amine-cured epoxies are known to be heterogeneous materials, consisting of hard and soft domains [35,36]. The heterogeneous microstructure of this epoxy coating is confirmed by the shape of its loss tangent curve obtained by dynamic mechanical analysis (not shown), which showed the main, broad peak near 80°C and a small peak around 56°C. Such behavior in a loss tangent curve generally indicates a phase-separation structure [37]. Therefore, T_g of the soft domains in this epoxy film was likely to be less than the 60°C exposure temperature. In such a case, both the rate of water transport from the environment to the interface and the decrease in the mechanical strength of the matrix are greatly enhanced. The former effect, *i.e.*, enhanced water transport above T_g of the soft domains, may explain the 20-fold increase in the water diffusion coefficient at 60°C as compared with that at 24°C, as shown in Table 1. On the other hand, the decrease in the mechanical properties above T_g may partially account for the shear strength loss of epoxy/silane-treated E-glass fiber composites (Figure 9, upper curve).

A strong relationship between interfacial water layer thickness and shear strength loss of polymer/E-glass fiber composites is further corroborated by the photograph shown in Figure 10. This picture was taken from the following experiment. An open-ended glass tube was bonded to one end of the untreated or silane-treated composite specimen used for the ILSS measurement. After adding water to the tubes, the specimens (with the attached glass tubes) were placed vertically in an oven maintained at 60°C. The photograph of Figure 10 was taken after the glass tube–attached specimens were in the oven for 72 h. As seen in this photograph, the end section (in contact with water) of the silane-treated specimen (Figure 10a) is still transparent, whereas that of the untreated specimen (Figure 10b) becomes opaque. Opacity is due to clusters of water molecules present in the untreated composite specimens. Because the two composites differed only in fiber

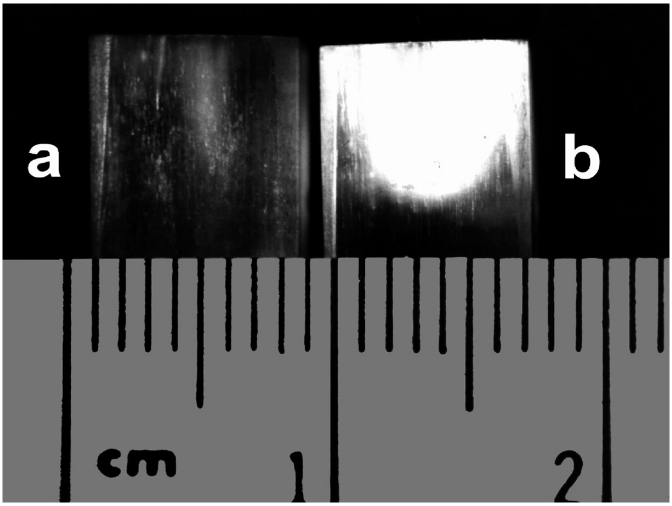


FIGURE 10 Appearance of silane-treated (a) and untreated (b) E-glass fiber/epoxy composites after ponding the ends of the composite specimens in liquid water at 60°C for 72 h, showing clearly that the untreated glass fiber composites become opaque whereas the silane-treated composites remain transparent after exposure.

surface treatment, water present in the untreated specimens must be at the epoxy/fiber interface, consistent with the data shown in Figure 6. Together with the results for epoxy/Si substrate systems (Figure 6), Figures 9 and 10 strongly indicate that a water layer at the polymer/fiber interface contributes substantially to the shear strength loss of epoxy/untreated E-glass fiber composites. Other factors, including internal stress resulting from swelling of the matrix, matrix plasticization, and mechanical loss of the fiber as a result of corrosion, may also contribute to the loss of the shear strength but to a smaller extent. This conclusion is consistent with previous reports that the bonding strength loss was greatest with E-glass fiber (where it leached water-soluble ions), much less with fumed silica (which contained the least amount of hydroscopic impurities), and greatly reduced with silane-treated fibers [30,38]. The results of Figures 9 and 10 again confirm that the epoxy/untreated glass fiber bonds are weak and cannot resist displacement by water when the composites are exposed to aqueous environments. It can be concluded from this study that water must be prevented from entering the interface between the polymer and the siliceous substrate or fiber, either through substrate and fiber surface treatment or other methods, if polymer/substrate systems and polymer/glass fiber composites are to be used in aqueous environments. The results of this study also demonstrate that FTIR-MTIR is a viable technique to reliably and conveniently assess the water resistance of polymer/Si substrate systems and polymer/glass fiber composites.

SUMMARY AND CONCLUSIONS

Water accumulation at the polymer/substrate interface is a major cause of adhesion loss in coatings, adhesives, and fiber-reinforced polymer composites. The relationship between thickness of the polymer/substrate interfacial water layer and adhesion loss of epoxy/Si substrate systems and epoxy/E-glass fiber composites has been critically assessed. Both untreated and silane-treated Si substrates and untreated and silane-treated E-glass fibers were used. The thickness of the interfacial water layer was measured by FTIR-MTIR spectroscopy, and adhesion losses of epoxy/Si substrate systems and epoxy/E-glass fiber composites exposed to water were measured by peel adhesion and short-beam shear tests, respectively. Based on data of water at the interface and adhesion losses of both epoxy/Si substrate systems and epoxy/E-glass fiber composites, the following conclusions are made.

1. Essentially little or no water is observed at the interface of the epoxy/silane-treated Si substrate systems, but many monolayers of water have accumulated at the interface of the epoxy/untreated Si systems exposed to ambient temperature water.
2. Epoxy/untreated Si substrate systems lose most of their peel strength after a short exposure, but the epoxy/silane-treated samples retain most of their adhesion even after prolonged exposure to water.
3. ILSS loss of epoxy/untreated E-glass fiber composites is nearly twice that of the composites made with silane-treated fibers after 6 months of exposure in water at 60°C. Further, silane-treated composites remain transparent, but the untreated composites become opaque after water exposure.
4. Data from the water-induced adhesion loss, spectroscopic analysis, and visual observation provides strong evidence that water at the polymer/substrate interface is mainly responsible for the water-induced adhesion loss in epoxy/untreated Si substrate systems and epoxy/untreated E-glass fiber composites. Matrix plasticization and swelling stress for the flat substrate systems, and

corrosion of glass fiber for the composites, may also contribute, but to a small extent, to the adhesion losses of these systems and composites.

5. FTIR-MTIR is a viable technique for assessing the water resistance of polymer/substrate systems and polymer/glass fiber composites used in aqueous environments.

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