

INTERFACIAL WATER AND ADHESION LOSS OF POLYMER COATINGS ON A SILICEOUS SUBSTRATE

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ABSTRACT

Water is often the main cause of adhesion loss of a polymer coating/substrate system. The buildup of the interfacial water layer and the loss of adhesion of polymer-coated siliceous substrates exposed to liquid water has been investigated. The thickness of the interfacial water layer was measured on epoxy-coated SiO_2 -Si prisms using FTIR-multiple internal reflection (FTIR-MIR) spectroscopy. Adhesion loss on flat siliceous substrates was determined by a wet peel test on epoxy-coated SiO_2 -Si wafers and adhesion loss of composites was obtained by measuring the interlaminar shear strengths of epoxy/E-glass fiber composites. Both untreated and 0.1% silane-treated substrates were used. Little water was observed at the interface of the silane-treated samples but about 10 monolayers of water have accumulated at the interface of the untreated samples after 100 h of exposure to 24 °C water. Untreated, flat substrates lost most of their bonding strengths within 75 h of exposure but silane-treated specimens retained 80% of their adhesion after 600 h of exposure to 24 °C water. Adhesion loss of untreated composites immersed in 60 °C water was greater than that of treated samples; however, the rate of loss of both silane-treated and untreated composites was much lower than that of flat substrates. Adhesion loss was found to follow the same trend as interfacial water buildup.

INTRODUCTION

The detrimental effects of water and water vapor on the adhesion of polymer-coated metals¹, adhesive bondings², polymer/fiber composites³ and asphalt pavements⁴ are well documented. However, there has not been a study that examined the relationship between the water layer at a polymer coating/substrate interface and the adhesion loss. The main reason for this is the lack of quantitative information on the interfacial water layer. A recent development of a technique to quantify the water layer at the polymer coating/substrate interface⁵ has made it possible to study the linkage between these two phenomena. In the present study, the thickness of the interfacial water layer and the loss of adhesion of polymer coating/siliceous substrate systems as a function of time of exposure to water has been investigated. The interfacial water layer was measured on specimens of coatings applied on flat substrates, while adhesion loss was determined on both flat substrates and unidirectional polymer/E-glass fiber composites.

EXPERIMENTAL SECTION

Materials and Specimen Preparations

For measuring water at the polymer coating/siliceous substrate interface, specimens of an epoxy coating applied on untreated and silane-treated, 50x10x3 mm spectroscopic grade, Si parallelogram prisms were prepared. For adhesion loss measurements on flat siliceous substrates,

specimens of coatings on untreated and silane-treated, 100-mm diameter Si wafers were used. Adhesion loss of the composites was determined from unsized, untreated and silane-treated 16 ± 2 μm diameter E-glass fibers impregnated with an epoxy resin.

The polymer coating was a stoichiometric mixture of a low molecular weight, diglycidyl ether of bisphenol A (epoxide equivalent weight = 189 g) and a polyethertriamine (amine equivalent = 83 g) curing agent. This epoxy coating was used for both flat substrates and composites. Si prisms and wafers were cleaned with acetone followed by methanol and dried with hot air before use. The surfaces of these substrates had a native SiO_2 layer of about 2.5 nm thick, as determined by an ellipsometer. Under ambient conditions (24 °C and 45% relative humidity), they should be covered with silanol groups (SiOH) and adsorb water⁶. The hydroxylated, SiO_2 -covered Si (SiO_2 -Si) prisms and wafers, and E-glass fibers are designated as the siliceous substrates in this study. Silane-treated surfaces were prepared by immersing cleaned Si prisms, Si wafers, and E-glass fibers for 30 minutes in an acidified (pH=4) water solution containing 0.1% aminoethylaminopropyltrimethoxysilane. The treated substrates were dried for 10 minutes at 110 °C before use. After mixing thoroughly the two components and letting them stand for 30 minutes at ambient conditions, the coating was applied on the prisms and wafers using the drawdown technique, similar to that described in Reference 5. All coated samples were cured at 80 °C for four hours followed by two weeks at ambient conditions. The thicknesses of the coatings on the prisms and wafers (determined at the conclusion of the experiment) were in the 130-150 μm range. The quality of all coated specimens was good and no visible pinholes or air bubbles were observed (with a naked eye) on the sample surfaces. Tg of the cured epoxy films was 83 °C (by differential scanning calorimetry, DSC).

Unidirectional composites were prepared by impregnating E-glass fibers with the same epoxy in between two transparent polyethylene (PE) sheets. Unsized, untreated and silane-treated fibers approximately 250 mm long were carefully laid unidirectionally on one PE sheet. After fixing one end of the fibers onto the PE sheet (by an adhesive tape), the epoxy was poured liberally on the fixed end of the fibers. After placing the other PE sheet over the resin-soaked fibers, the resin was spread by a glass plate placed on the PE sheet. The resin was spread along the fiber direction repeatedly until the fibers and the resin formed a transparent mat. The impregnated fibers were cut to size and placed in open-ended, aluminum molds having an inside dimension of 200x8x6.5 mm. The molds were placed in an autoclave for three hours at 80 °C and under a pressure of 1.4 MPa above atmospheric pressure, followed by post curing at 100 °C for 12 h. After removing the composites from the molds and conditioning them at ambient conditions for two weeks, they were polished and cut to a specimen size of 38x7.9x6.35 mm for exposures and testings. All specimens were transparent and there was no evidence of visible air voids, as observed by the naked eye. The fiber fraction of the composites was 40% (determined by thermogravimetric analysis) and Tg of the epoxy in the composites was 84 °C (by DSC).

Measurement of Water at the Polymer Coating/Siliceous Substrate Interface

Specimen configuration and Fourier transform infrared-multiple internal reflection (FTIR-MIR) procedure used for the measurement of water at the polymer coating/siliceous substrate interface are similar to those described in Reference 5. Briefly, a water chamber was attached to each cured, coated prism. The specimen with the water chamber attached was placed vertically in an attenuated total reflection (ATR) accessory holder and measurement of water at the interface was carried out using an FTIR spectrometer with a variable ATR accessory. After filling the chamber with distilled water at 24 °C, FTIR-MIR spectra were taken automatically every 15 minutes without disturbance to the specimens or the spectrometer. For the specimen

configuration employed in this study, the only pathway for water migration from the environment to the interface is through the coating film thickness. All spectra were the co-additions of 32 scans and taken at a resolution of 4 cm⁻¹. Unpolarized light at a 45° incident angle and purged dry air were used.

The thickness of the water layer, l , at the polymer coating/siliceous substrate interface was determined using the following expression⁵:

$$l = \frac{d_{pw}}{2} \left[-\ln \frac{1 - \frac{A}{A_{\infty}}}{1 - c_w \frac{d_{pc}}{d_{pw}}} \right] \quad (1)$$

where A is the FTIR-MIR absorbance; A_{∞} is the maximum infrared absorbance of water (provided by FTIR-MIR analysis of water on a coating-free siliceous substrate); c_w is the fraction of water sorbed in the coating within the FTIR-MIR probing depth (extrapolated from water uptake in coating); d_{pw} and d_{pc} are the penetration depths of the evanescent wave (calculated from internal reflection theory) in water and coating, respectively. For a Si substrate, d_{pw} is 0.22 μm and d_{pc} is 0.24 μm. Equation 1 is still valid for the case where the water layer at the coating/substrate interface is not continuous, e.g., discrete droplets.

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

$$Q_i = l a \rho \quad (2)$$

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

Measurement of Adhesion Loss

The adhesion loss of epoxy-coated SiO₂-Si wafers as a function of exposure to water at 24 °C was measured using an improved version of a wet, 90° peel adhesion tester described in Reference 7. The apparatus consists of a linear bearing slider fixed to a computer controlled universal testing machine fitted with a 2.0 kg load cell. The improvement arose from lighter materials used and a low-friction moving slider. This resulted in a friction reduction from 200 g to 120 g. At each pre-specified exposure time, epoxy-coated wafers were removed from the test chamber and each wafer was immediately incised with a razor into five 12x65-mm specimens. Each specimen was carefully peeled from the substrate, leaving a 35-mm length of the specimen unpeeled. The wafers were then positioned in the test apparatus and peeled at a rate of 20 mm/min. All peel tests were conducted at room temperature and took approximately 30 minutes for each wafer from the moment it was taken out from the test solution. Ten specimens on two wafers were tested and the results averaged.

Adhesion loss of the composites was determined from the interlaminar shear strengths (ILSS), which is a measure of the adhesion between the resin and the fiber. ILSS values were calculated from the peak load of the short-beam, three-point bending test (ASTM D2344):

$$ILSS = 3F/4bd \quad (3)$$

where F is the peak load in kN, and b and d are the width and thickness of the specimen in m. Specimens of $38 \times 7.9 \times 6.35$ mm immersed in distilled water at 60°C were removed from the container and tested at pre-specified time intervals. The specimen was supported by a 25-mm span and tested at a displacement rate of 0.5 mm/min. To ensure accuracy, the calibration of testing machine was verified at each testing period. Except for two cases where only two specimens were used, the results were the average of three or four specimens.

RESULTS AND DISCUSSION

In order to provide quantitative information on water at the coating/substrate interface, FTIR-MIR difference spectra were acquired. This was done by subtracting spectra taken before exposure from those collected at different exposure times. Figures 1a and 1b display difference spectra in the $2800\text{--}3800\text{ cm}^{-1}$ region (water OH stretching) of epoxy-coated untreated and 0.1 % silane-treated $\text{SiO}_2\text{-Si}$ primers exposed to water for several representative times. The high signal-to-noise ratio of these spectra is due to the low concentration of detected water in these samples. The bands in the $3000\text{--}3650\text{ cm}^{-1}$ region are due to OH stretching mode of water, as verified previously⁸. The band peaking near 3400 cm^{-1} was chosen for the analysis, and its intensity changes as a function of exposure time are presented in Figure 2 for untreated and silane-treated specimens. The intensity of the water bands of both untreated and silane-treated samples increased with exposure time up to approximately 100 h then leveled off. These changes are the result of water entering the coating/substrate interfacial region and interacting with the evanescent wave⁸. Further, it can also be seen that the intensity of water detected for the untreated specimen is higher than that for the silane-treated one.

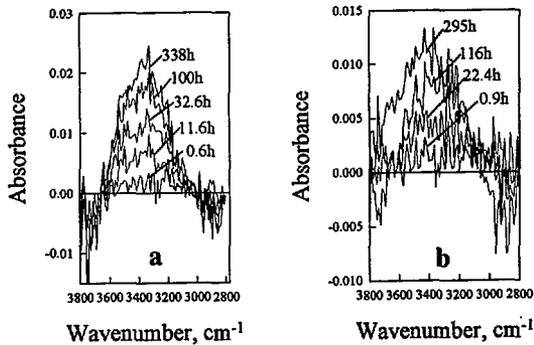


Figure 1. FTIR-MIR difference spectra of epoxy-coated untreated (a) and 0.1% silane-treated (b) $\text{SiO}_2\text{-Si}$ primers exposed to 24°C water for several time intervals.

Substituting FTIR-MIR absorbance data (A) given in Figure 2, and c_w , A_∞ , d_{pc} and d_{pw} values, which are taken from Reference 5, into Equations 1 and 2, thickness and amount of the water layer at the interface for epoxy coated untreated and 0.1% silane-treated $\text{SiO}_2\text{-Si}$ substrate are determined. The results are given in Figure 3, which shows that essentially no or little water had entered the interface of the silane-treated specimens, but about 10 monolayers (one monolayer of water is about 0.3 nm) had built up at the interface of the untreated samples after 100 h exposure. The results on water at the interface for the silane-treated specimens suggest that the bond strengths between the treated surface and epoxy resin were stronger than those between the treated surface and water. Therefore, water molecules could not displace these bonds and thus

no or little water entered the interface. This result, which has been confirmed by a duplicate specimen, is supported by the adhesion loss data given in Figure 4. It is also consistent with the chemical bonding theory, which has been proposed as an explanation for the interfacial reinforcement mechanism and enhanced hydrolytic stability of composites made with silane-treated fibers⁹. It is noted that water is a weakly-sorbed species: the magnitude of water-oxide bonds are in the 40-65 kJ/mol range¹⁰ and thus incapable of replacing stronger chemical bonds between the silane and the siliceous surface or between the silane and the epoxy resin.

It is important to point out here that the results of Figure 3 provide the first evidence that Equation 1 is valid for calculating water at the polymer/substrate interface. This equation, which was derived from the internal reflection theory, was based on a two-layer model consisting of the water layer at the interface and water sorbed in the coating film within the FTIR-MIR probing depth. If no water was at the interface, the total water detected (e.g. FTIR-MIR absorbance given in Figure 2) is due to only water in the polymer layer near the interface. This is the case for the coated, silane-treated specimens. These specimens had a hydrolytically stable interface, as evidenced by the small reduction in the adhesion after prolonged exposure (Figure 4) and corroborated by the well-established mechanism of silane coupling agents on glass fibers. Such an interface should allow little or no water entering this region. This is consistent with the results calculated from Equation 1 (Figure 3).

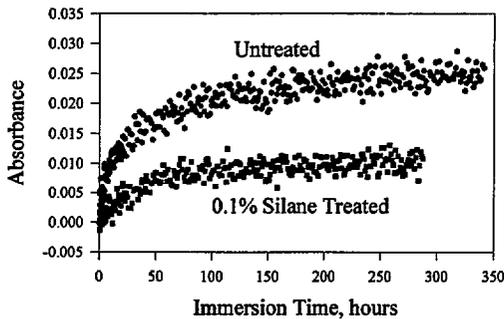


Figure 2. Intensity change of water band with time exposed to 24°C water for epoxy coated, untreated and 0.1% silane-treated SiO₂-Si prisms (each dot represents a data point).

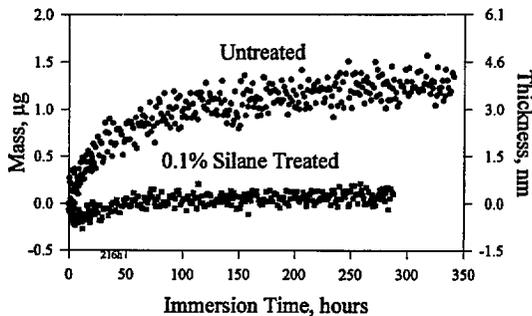


Figure 3. Thickness and amount of the interfacial water layer of epoxy-coated untreated and 0.1% silane-treated SiO₂-Si prisms exposed to 24°C water (each dot represents a data point).

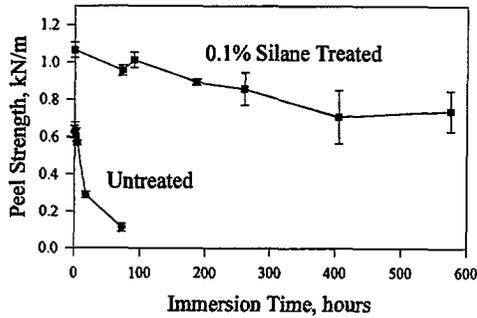


Figure 4. Peel adhesion of epoxy-coated untreated and 0.1% silane-treated $\text{SiO}_2\text{-Si}$ wafers exposed to 24 °C water (bars on curves indicate one standard deviation).

Figure 4 presents adhesion changes as a function of time exposed to 24 °C water for epoxy-coated untreated and 0.1% silane-treated $\text{SiO}_2\text{-Si}$ wafers. Untreated specimens lost most of their adhesion within 75 h of exposure, while silane-treated samples retained 80% of their adhesion even after 600 h immersion. These results, which are in good agreement with interfacial water data given in Figure 3, provide the first experimental evidence to show that the gradual buildup of a water layer at the interface is the main cause of adhesion loss of polymer coatings on an untreated siliceous substrate. The results of Figures 3 and 4 again illustrate the great affinity of untreated siliceous surfaces for water and that these surfaces must be modified to improve the durability of a polymer/siliceous substrate system.

Figure 5 displays ILSS data of composites prepared with untreated and silane-treated E-glass fibers immersed in distilled water at 60 °C for different times. Although at a lesser extent, the results follow the same trend with the adhesion loss of flat $\text{SiO}_2\text{-Si}$ substrates; that is, composites of untreated fibers lost more of their shear strengths and at a faster rate than the composites of treated fibers did. Untreated and treated composites lost 55 and 23%, respectively, of their original shear strengths after three-month immersion. This compares with 83% adhesion loss after 75 h and 25% loss after 600 h exposed to water at 24 °C for untreated and treated flat substrates, respectively. The results also show that the larger amounts of water at the polymer/substrate interface corresponded to the greater ILSS losses of the composites, suggesting that water at the resin/fiber interface may also play a role in the adhesion loss of composites.

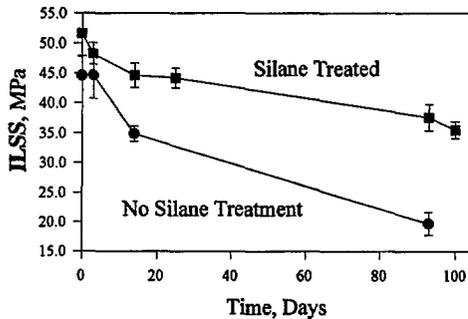


Figure 5. ILSS as a function of time in 60 °C water of untreated and 0.1% silane-treated epoxy/E-glass fiber composites (bars on curves indicate one standard deviation).

The results of this study and other data for solvent-free organic coatings on siliceous substrates¹¹ indicate that larger amounts of water at the coating/substrate interface generally correspond with greater loss of adhesion. Additional data are needed to determine more precisely the range of the interfacial water layer corresponding with the range of the adhesion loss. If a relationship between adhesion loss and interfacial water layer exists, FTIR-MIR technique could be useful for estimating the adhesion loss at the molecular level and for predicting the durability of polymer/siliceous substrate systems.

SUMMARY AND CONCLUSIONS

Water is often the main cause of adhesion loss of a polymer coating/substrate system. This study investigated the accumulation of water at the interface, and adhesion loss of epoxy coatings on flat siliceous substrates and of epoxy/E-glass fiber composites. Both untreated and 0.1 % silane-treated flat substrates and fibers were included. Silane treatment effectively prevented water from entering the interface but a water layer of about 3 nm thick has built up at the interface of the untreated SiO₂-Si specimens after 100 h exposure to 24 °C water. Untreated, flat substrates lost most of their bonding strengths within 75 h exposure but silane-treated specimens retained 80% of their adhesion after 600 h exposure. Adhesion loss of untreated composites immersed in 60°C water was greater than that of treated samples; however, the rate of loss of both silane-treated and untreated composites was much lower than that of flat substrates. Adhesion loss of both flat siliceous substrates and composites was found to follow the same trend with interfacial water buildup. If further analysis confirms that a relationship between the adhesion loss and the interfacial water layer exists, the FTIR-MIR technique could be useful for estimating the adhesion loss at the molecular level and for predicting the durability of polymer coating/siliceous substrate systems.

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