



**DURABILITY OF FIBRE REINFORCED POLYMER (FRP)
COMPOSITES FOR CONSTRUCTION**

***DURABILITÉ DES COMPOSITES EN POLYMERES
RENFORCÉS DE FIBRES (PRF) POUR LA CONSTRUCTION***

**WATER AT THE POLYMER/SUBSTRATE INTERFACE AND ITS ROLE IN
THE DURABILITY OF POLYMER/GLASS FIBER COMPOSITES**

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ABSTRACT

Fiber-reinforced polymer composites are increasingly used in offshore and civil engineering structures. In these applications, composite materials are often exposed to aqueous environments. Water can reduce polymer composite durability by affecting the matrix, the fiber, and the fiber/matrix interface. This study investigated the role of the polymer/substrate interfacial water layer on the shear strength of polymer/glass fiber composites. The thickness of the interfacial water layer was measured by Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy of an epoxy applied to a model siliceous substrate. The shear strength of the composite was determined from the short-beam test of unidirectional composites made of E-glass fiber and the same epoxy matrix. Both untreated and silane-treated siliceous substrates and E-glass fibers were used. Little water was observed at the interface of the silane-treated specimens, but about 10 monolayers of water accumulated at the epoxy/substrate interface of the untreated samples after exposure to water. Shear strength loss of the untreated composite was twice that of the silane-treated material after a 3-month immersion in 60 °C water. Further, the treated specimens remained transparent but the untreated specimens became opaque after water exposure. Evidence from mechanical and spectroscopic analyses and visual observation indicated that water at the polymer/fiber interface was responsible for the difference in the loss of the shear strength of the untreated and surface-treated composites. Data on solubilities and diffusion coefficients of water in the epoxy for two exposure temperatures and changes of epoxy glass transition temperature and work of adhesion of epoxy/silica due to water are presented.

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INTRODUCTION

There is a growing interest in extending the use of fiber-reinforced polymer (FRP) composites to offshore and civil engineering structures. In these applications, FRP are often subjected to aqueous environments, such as high relative humidities, water, sea water, wet concrete, and rain. Because of their low cost, glass fibers are preferred in these applications. However, polymer/glass fiber composites are sensitive to moisture. Water can reduce the performance of these composites by affecting the matrix, the fiber, or the glass fiber/matrix interface. There has been extensive research on the effects of water on the mechanical properties of polymer matrices and E-glass fibers, as reviewed by Schutte (1994). However, the effects of the water layer at the polymer/substrate interface on the shear strength of polymeric composites have not been examined. This study investigated the role of the polymer/substrate interfacial water layer on the loss of the shear strength of polymer/glass fiber composites. The thickness of the water layer at the polymer/substrate interface was measured using Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy of an epoxy applied to a model siliceous substrate. The shear strength of the composite was assessed from the short-beam, three-point bending test of a unidirectional epoxy/E-glass fiber composite.

EXPERIMENTAL SECTION

Materials and Specimen Preparations

For measuring water at the interface, specimens of epoxy applied to untreated and silane-treated, 50 mm x 10 mm x 3 mm spectroscopic grade, silicon (Si) parallelogram plates were fabricated. Shear strength loss of the composite was determined from specimens prepared using unsized, untreated and silane-treated, 16 ± 2 μm diameter E-glass fibers impregnated with the same epoxy resin.

The epoxy matrix 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. The Si plates were cleaned with acetone followed by methanol and dried with hot air before use. The surfaces of these Si plates had a native SiO_2 layer of $2.5 \text{ nm} \pm 0.1 \text{ nm}$ thick, as measured by ellipsometry. It should be noted that SiO_2 reacts readily with water so that, at ordinary temperature, it is covered with silanol groups and adsorbed water (Iler, 1979). Thus, the surface chemical structure of the substrates used for measuring water at the interface is similar to that of a silica surface. The hydroxylated SiO_2 -covered Si plates are designated as the model siliceous substrates. E-glass fiber was a commercial, unsized material. Besides SiO_2 , E-glass typically contains substantial amounts of alkaline (MgO and CaO) and alkaline earth (Na_2O and K_2O) oxides. These oxides are hygroscopic so that water adsorption on E-glass is much greater than that on silica (Bascom, 1970). For that reason, 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 model siliceous substrates employed for the measurement of water at the interface.

Silane-treated surfaces were prepared by immersing cleaned model siliceous substrates and E-glass fibers for 30 minutes in an acidified (pH=4) water solution containing 0.1% mass fraction of aminoethylaminopropyltrimethoxysilane. The treated materials were dried for 10 minutes at 110 °C before use. After mixing thoroughly the two components and degassing, the epoxy was applied to the substrates using the drawdown technique, similar to that described previously (Nguyen et al., 1994). Epoxy-coated substrates were cured at 80 °C for three hours, post cured at 100 °C for two hours, and stored at ambient conditions (24 °C and 45 % relative humidity) for two weeks before use. The thickness of the epoxy films on the model substrates (determined at the conclusion of the experiment) was in the 130-150 μm range. The quality of all coated specimens was good, and no visible pinholes or air bubbles were observed with the naked eye on the sample surfaces.

Unidirectional epoxy/glass fiber 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 of approximately 250 mm in length were carefully laid unidirectionally on one PE sheet. After fixing one end of the fibers onto the PE sheet (using 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 repeatedly, with a glass plate placed on the PE sheet, along the fiber direction 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 200 mm x 8 mm x 6.5 mm. The molds were placed in an autoclave for three hours at 80 °C and under a pressure of 1.4 MPa, followed by post curing at 100 °C for 2 h at atmospheric pressure. After removing from the molds and conditioning in an ambient environment for two weeks, the composite rods were polished and cut to a specimen size of 38 mm x 7.9 mm x 6.35 mm for exposures and testings. All composite test specimens appeared transparent and there was no evidence of visible air voids, as observed by the naked eye. The fiber fraction of the composites was 40 % (as determined by thermogravimetry).

Measurement of the Water Layer at the Polymer/Substrate Interface

Figure 1 schematically displays the specimen configuration used for the measurement of water at the polymer/substrate interface using Fourier transform infrared-multiple internal reflection (FTIR-MIR) 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 an internal reflection accessory holder, and measurement of water at the interface was carried out using an FTIR spectrometer with a variable angle internal reflection 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 film thickness. All spectra were the co-additions of 32 scans and taken at a resolution of 4 cm^{-1} . Unpolarized light at 45° incident angle and purged dry air were used.

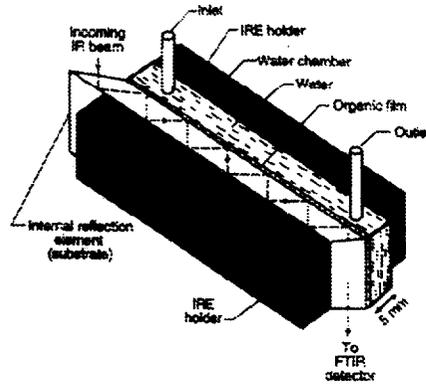


Figure 1. Experimental setup for measuring water at the polymer/substrate interface using Fourier transform infrared spectroscopy in the internal reflection mode.

The thickness of the water layer, l , at the polymer/substrate interface was determined using the following expression (Nguyen, 1994):

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

where A is the FTIR-MIR absorbance; A_w is the maximum infrared absorbance of water on a polymer-free substrate; c_w is the mass fraction of water sorbed in the polymer film within the FTIR-MIR probing depth; d_{pw} and d_{pc} are the penetration depths of the evanescent wave in water and polymer, respectively. They may be calculated from (Harrick, 1979):

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

where λ is the wavelength of the infrared radiation in vacuum; n_1 and n_2 are the refractive indices of the substrate and sample, respectively; and θ is the angle of incidence.

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

$$Q_i = l \sigma \rho \quad [3]$$

where a is the area in contact with water ($a = 329 \text{ mm}^2$ in this study) and ρ is the density of water at the polymer/substrate interface. It should be noted that Eq. 1, which was derived from the internal reflection theory using a two-layer model, is still valid for the case where the water layer at the polymer/substrate interface is not continuous, e.g., discrete droplets.

Water Uptake in Epoxy

Water uptake, measured gravimetrically, was obtained to provide the c_w value in Eq. 1 and the diffusion coefficient of water in the epoxy matrix. Free films were prepared by applying the epoxy resin to soda glass plates using the draw down technique. (The cured films were peeled off readily from the glass substrate.) Films were cut to size, weighed, and immersed in distilled water. They were taken out, blotted, and reweighed at specified time intervals. The thickness of each free film was measured at three locations using a micrometer. Water uptake is expressed as the fraction of the mass of the initial, dry specimens. The results were the average of six specimens. The bulk diffusion coefficient, D , of water in epoxy was calculated from the water uptake data using the sorption kinetics approach of Crank and Park (1968):

$$D = \frac{0.04919}{(\tau/t^2)_{1/2}}$$

where τ is time, t is the polymer film thickness, and $(\tau/t^2)_{1/2}$ is the value of τ/t^2 for which the ratio between water uptake at a particular time (M_t) and that at equilibrium (M_∞) = $1/2$; this value is obtained from the M_t/M_∞ vs τ/t^2 plot.

Measurement of Shear Strength Loss of Composite

Shear strength loss of the composites was provided 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, three-point bending test (ASTM D2344):

$$\text{ILSS} = 3F/4bd$$

where F is the peak load (in N) and b and d are the width and thickness of the specimen (in mm), respectively. Experimentally, specimens of $38 \text{ mm} \times 7.9 \text{ mm} \times 6.35 \text{ mm}$ immersed in distilled water at 60°C were removed from the water-filled 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 testing machine was calibrated at each testing period. The results were the average of three or four specimens.

Other Measurements

In addition to the above experiments, the following matrix and polymer/fiber properties pertinent to this study were measured. The glass transition temperatures of the epoxy before and after saturation with water were determined by differential scanning calorimetry (DSC); solubility of water in epoxy, which is a product of equilibrium water uptake and polymer density, the latter was measured by water displacement method; polar and total surface free energies of the epoxy films by the geometric-mean approach (Owens and Wendt, 1968) using water and methylene iodide as the liquids to provide contact angles; and work of adhesion between the epoxy and glass fiber in water was determined by the approach of Gledhill and Kinloch (1974) using values of surface free energy of silica given by Shafin and Zisman (1967) and the epoxy used in this study.

RESULTS AND DISCUSSION

Characteristics of Epoxy and Epoxy/Glass Fiber in Water

Figure 2 presents the uptake characteristics of water in epoxy films having a thickness of $300 \mu\text{m} \pm 12 \mu\text{m}$ at 24°C and 60°C . The rate of uptake was greater at 60°C than at room temperature. The uptake at 60°C nearly reached equilibrium within 50 h, but it took three times longer to reach maximum uptake at room temperature. The reduced sorption curves (M_t/M_∞ vs $\sqrt{t/l}$) (not shown) for both 24°C and 60°C exposures were linear up to approximately $M_t/M_\infty = 0.8$, indicating that the diffusion of water in the films at both temperatures followed a Fickian process. The diffusion coefficients, D , of water in the films at two temperatures along with other properties are given in Table 1. The diffusion at 60°C is nearly 20 times greater than that at room temperature. On the other hand, the solubility at 60°C is only 25 % greater than that at room temperature.

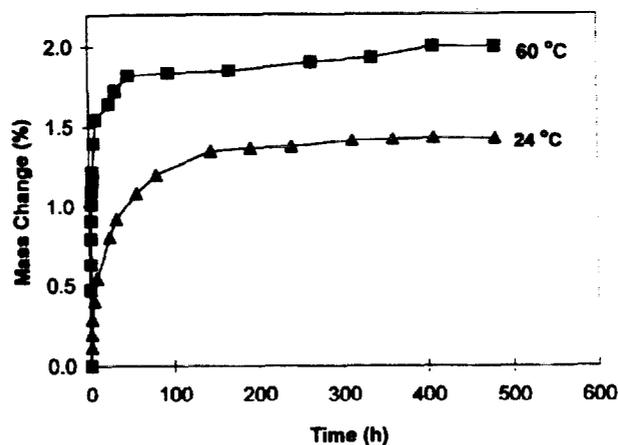


Figure 2. Water sorption characteristics of epoxy free films at 24°C and 60°C .

Table 1: Properties of epoxy and epoxy/glass fiber systems in dry and in water

Exposure	Density	T_g	D	Solubility	W_a	γ^p	γ_s	Polarity
	g/cm ³	°C	$\times 10^{-10}$, cm ² /s	mg/cm ³	mJ/m ²	mJ/m ²	mJ/m ²	γ^p/γ_s
Dry	1.14	80	—	—	184	7.0	41	0.17
water, 22 °C		68	5.3	16.2	-53	—	—	—
water, 60 °C		67	136	22.8	—	—	—	—

As seen in Table 1, immersion in water substantially reduced the T_g of the epoxy matrix. Further, there appears little difference between T_g 's of specimens exposed at 22 °C and 60 °C. It should be noted that the T_g values during exposure, instead of those in the dry state, should be used for relating with other phenomena in polymers. This is because many polymer properties (e.g., mechanical, transport, etc.) change substantially when moving from below to above the T_g . Table 1 also gives values of the polar component (γ^p), total surface free energy (γ_s), and polarity (γ^p/γ_s) of the epoxy. Since the interactions between a polymer and a fiber are mostly governed by the surface polar components, the strength of these interactions would determine the hydrolytic stability of the polymer/fiber interface. Table 1 shows a negative value for the work of adhesion in water (W_{aw}), indicating that the epoxy/untreated glass fiber bonds are not stable in the presence of water, and that water would displace these bonds and form a layer at the polymer/fiber interface when polymer/glass fiber composites are exposed to water and high relative humidities. The result implies that epoxy/untreated silica bonds are weak and can not resist the affinity of water toward the silica, reinforcing the need to modify the polymer/glass fiber interface (interphase) to improve the durability of this type of composites in moist environments.

Quantification of the Water Layer at the Polymer/Substrate Interface

Figure 3 displays FTIR-MIR difference spectra in the 2800-3800 cm⁻¹ region (water OH stretching) of epoxy-coated untreated and silane-treated model substrates exposed to water for several representative times. These spectra were obtained by subtracting the spectra taken before exposure from those collected at different exposure times. The intensity changes observed in the difference spectra are due to the effect of water on the specimens. Bands above the base line of a difference spectrum indicate an increase of a functional group, and bands below the base line are due to a loss of the material. The high noise-to-signal ratio of these spectra is due to the low concentration of water detected in the samples. The bands in the 3000-3650 cm⁻¹ region are due to the OH stretching mode of water, as

verified previously (Nguyen, 1991). The band centers near 3400 cm^{-1} was chosen for the analysis, and its intensity changes as a function of exposure time in water are presented in Figure 4. 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 were due to water entering the polymer/substrate interfacial region and interacting with the evanescent wave. It can be seen that the intensity of water detected in the untreated specimen is higher than that of the silane-treated one.

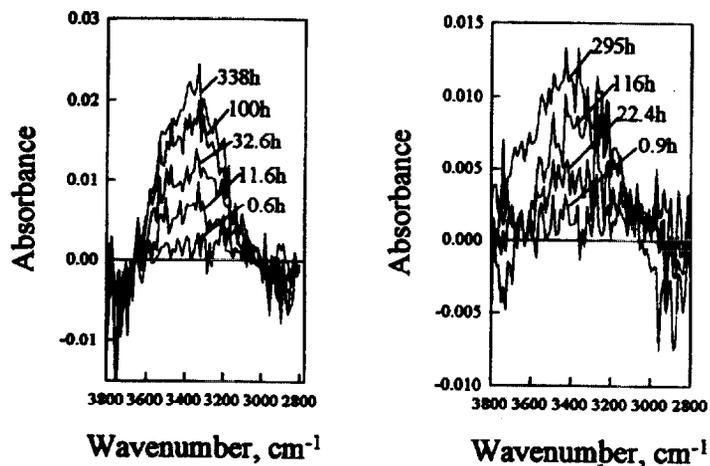


Figure 3. FTIR-MIR difference spectra of epoxy-coated untreated (a) and silane-treated (b) model siliceous plates exposed to 24°C water for several time intervals.

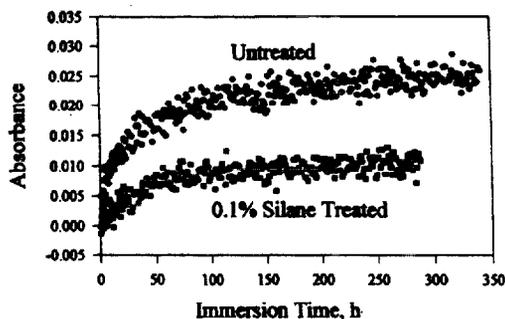


Figure 4. FTIR intensity change with exposure time of the water band for epoxy-coated, untreated and silane-treated model substrates (each dot represents a data point).

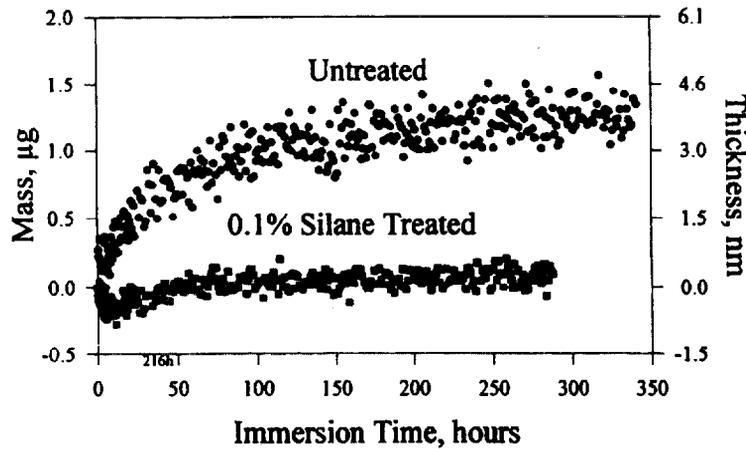


Figure 5. Thickness of the interfacial water layer of epoxy-coated, untreated and silane-treated model substrates exposed to water (each dot represents a data point).

In order to determine the thickness and amount of water at the polymer/substrate interface using Eqs. 1 and 3, A , A_w , c_w , d_{pw} and d_{pc} must be known. Values of A are taken directly from Fig. 4; A_w is taken from results of Nguyen et al. (1994) for water on a film-free Si substrate. Values of d_{pw} and d_{pc} are $0.22 \mu\text{m}$ and $0.24 \mu\text{m}$, respectively, which were calculated from Eq. 2 using the following data given in Nguyen et al. (1994): n_1 of Si is 3.5, n_2 for water and polymer are 1.3 and 1.5, respectively. And the c_w value at appropriate time is interpolated from the 22°C result of Figure 2. Substituting these values in Eqs. 1 and 3, the thickness and amount of the water layer at the interface for epoxy-coated untreated and silane-treated SiO_2 -Si substrates were determined; the results are given in Figure 5. Essentially, no or little water entered the interface of the silane-treated specimens, but about 10 monolayers (one monolayer of water is about 0.3 nm) has built up at the interface of the untreated samples after 100 h exposure. The presence of a water layer at the epoxy/model substrate interface is consistent with the negative value of the work of adhesion. On the other hand, the results for the silane-treated specimens suggest that the bond strengths between the treated model siliceous surface and the epoxy resin were stronger than those between the untreated surface and water. Therefore, water molecules could not displace the bonds of the treated samples and, thus, no or little water entered their interface. This result, which has been confirmed by a duplicate specimen, is consistent with the interfacial reinforcement mechanism explaining for the enhanced hydrolytic stability of composites made with silane-treated glass fibers (Koenig and Emadipour, 1985). It is noted that water is a weakly-sorbed species: the magnitude of water-oxide bonds are in the $40\text{--}65 \text{ kJ/mol}$ range (Thiel and Madey, 1987), and thus incapable of replacing stronger chemical bonds between the silane and the siliceous surface or between the silane and the epoxy resin.

Figure 6 presents ILSS results of composites prepared with untreated and silane-treated E-glass fibers immersed in distilled water at 60°C . Untreated and treated composites

lost nearly 70% and 38%, respectively, of their initial shear strengths after a three-month immersion. The loss of ILSS of the treated composite was probably due to a combination of factors including matrix plasticization, swelling stress, and some water entering the epoxy/fiber interface. It should be emphasized that, except for fiber surface pretreatment, the two composites were prepared under similar conditions. Thus, the difference in the shear strength loss between these two composites is attributed to a difference in the amount of water at the polymer/fiber interface. This assertion is supported by the results of the interfacial water layer given in Figure 5, which shows a greater amount of water at the interface of the untreated sample than that of the treated system. The correlation between the interfacial water layer and shear strength loss of composites is also in agreement with results on bonding strength of epoxy and asphalt coatings on flat substrates, which showed a general relationship between the interfacial water layer and the adhesion loss (Nguyen et al., 1995).

A relationship between the interfacial water layer and the shear strength loss of polymer/glass fiber composites is further corroborated by the photograph shown in Figure 7. This picture was taken from the following experiment. A glass tube was glued to one end of untreated and silane-treated composite specimens 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 7 was taken after 72 h in the oven. As seen in this photograph, the end section (in contact with water) of the untreated specimen became opaque and that of the silane-treated sample was still transparent. The opacity was due to water entering the untreated specimen. Since the two composites differed only in fiber surface treatment, water must have entered the untreated specimens along the polymer/fiber interface.

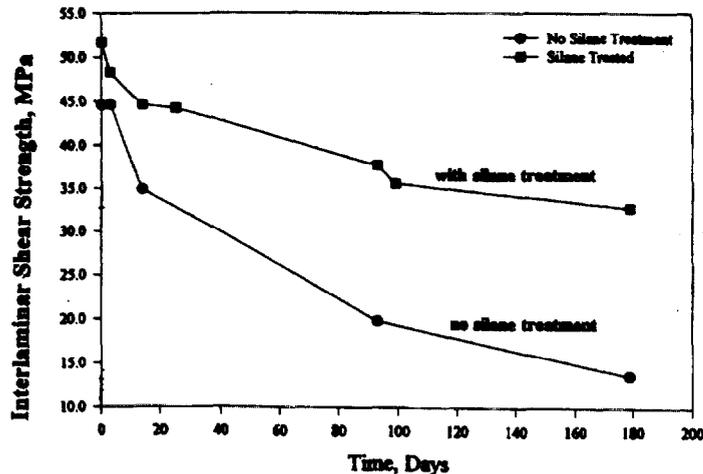


Figure 6. ILSS loss as a function of time in 60 °C water of untreated and silane-treated epoxy/E-glass fiber composites.

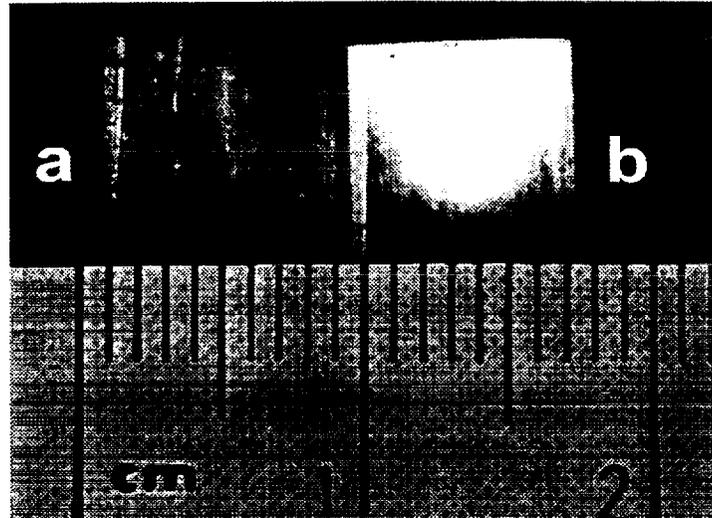


Figure 7: Appearance of silane-treated (a) and untreated (b) epoxy/E-glass fiber composites after ponding liquid water at 60 °C on the ends of the specimens.

The results of Figures 5, 6, and 7 strongly indicate that the water layer at the polymer/fiber interface contributes substantially to the shear strength loss of epoxy/E-glass fiber composites. They also imply that the epoxy/untreated glass fiber bonds are weak and can not resist the displacement by water when the composites are exposed to aqueous environments. The results reinforce the need to prevent water from entering the interface between the polymer and glass fiber, either through fiber surface treatment or other methods, if polymer/glass fiber composites are to be used in civil engineering and offshore structures.

SUMMARY AND CONCLUSIONS

Fiber-reinforced polymer composites are increasingly used in offshore and civil engineering structures. In these applications, composite materials are often exposed to aqueous environments. Water can reduce polymer composite durability by affecting the matrix, the fiber, and the fiber/matrix interface. This study investigated the role of the polymer/substrate interfacial water layer on the shear strength loss of polymer/E-glass fiber composites. The thickness of the interfacial water layer of an epoxy applied to a model siliceous substrate was measured by Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy. The shear strength of the composite was obtained from the short-beam, three-point bending test of specimens made of E-glass fiber and the same epoxy matrix. Shear strength and spectroscopic results and visual observation indicated that water

accumulated at the polymer/fiber interface contributes substantially to the shear strength loss of epoxy/E-glass fiber composites. Further, epoxy/untreated glass fiber bonds are weak and cannot resist the displacement by water when the composites are exposed to aqueous environment. The results reinforce the need to prevent water from entering the polymer/fiber interface, either through fiber surface treatments or other methods, if E-glass fiber-reinforced polymer composites are to be used in civil engineering and offshore structures.

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REFERENCES

- W.D. Bascom, *J. Adhesion*, 2, 168 (1970).
J. Crank and G.S. Park, in *Diffusion in Polymers*, J. Crank and G.S. Park, Eds., Academic Press, N.Y., 1968, p.16.
R.A. Gledhill and A.J. Kinloch, *J. Adhesion*, 6, 315 (1974).
N.J. Harrick, *Internal Reflection Spectroscopy*, Harrick Sci., Ossining, N.Y., 1979, p. 30
R.K. Iler, the Chemistry of Silica, John Wiley, N.Y., 1979, Chapter 6.
J.L. Koenig and H. Emadipour, *Polymer Composites*, 6, 142 (1985).
T. Nguyen, W.E. Byrd, and C. Lin, *J. Adhesion Sci. Technol.*, 5, 697 (1991).
T. Nguyen, D. Bentz, and W.E. Byrd, *J. Coatings Technol.*, 66, no. 834, 39 (1994).
T. Nguyen, D. Alsheh, D. Bentz, and W.E. Byrd, *Proc. Adhesion Society Conference*, February, 1995, p. 252.
D.K. Owens and R.C. Wendt, *J. Appl. Polym. Sci.*, 13, 1740 (1969).
C.L. Schutte, *Materials Sci. Eng.*, R13, 265 (1994).
E.G. Shafin and W.A. Zisman, *J. Amer. Ceram. Soc.*, 50, 478 (1967).
P.A. Thiel and T.E. Madey, *Surface Sci. Rep.*, 7, 211 (1987).