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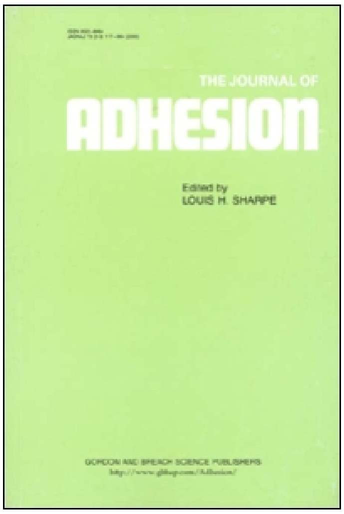

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Water at the Interface

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ABSTRACT

The subject of moisture-induced failure in glass-resin composite materials is reviewed. Emphasis is given to the fundamental surface chemistry and fracture mechanics involved. These disciplines offer substantial information about water adsorption on polar solids, including glass, and about the fracture of solids. However, this information is shown to be inadequate in describing the mechanisms involved in the failure of glass-resin materials. Some insight into these mechanisms is possible from various studies of the moisture-induced failure of bulk glass and adhesive/adherend systems. Also, some light is shed on moisture-induced failure by considering the empirical methods used to improve composite wet-strength, especially the use of silane adhesion promoters. Recent research on the silanes suggests that their action may involve a modification of the resin in the vicinity of the glass/resin interface.

INTRODUCTION

IN MANY RESPECTS our fundamental understanding of how water degrades material strength lags far behind the development of new materials. This fact is especially evident for the reinforced resin composites which have great technical potential except for their poor reliability in wet environments. Some improvement in composite wet-strength can be realized through the use of adhesion promoters, by changes in material composition or by improvements in fabrication methods. However, these are essentially empirical solutions and are not based on any real knowledge of the stress corrosion mechanisms.

Stress-corrosion, or more generally moisture-induced material failure of composites, is a problem in both surface chemistry and fracture mechanics. This review will touch on both aspects by considering first water adsorption on polar solids and then the elementary features of fracture mechanics. Ideally, we would like to bring these two areas of knowledge together to form a detailed picture of the mechanisms of stress-corrosion. This is not possible at our present state of knowledge. The best that can be done is to select for discussion a few studies of stress-corrosion that shed some light on the atomic and molecular events involved in moisture-induced failure. In addition to examining the problem from the fundamental side, we will also consider the empirical methods used to improve wet strength for what these methods teach about the degradive action of water.

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To keep this review to a reasonable length, it will be restricted to topics pertinent to glass and glass-resin composites. Certainly the general concepts presented are also applicable to carbon and metal reinforcements, but there are specific differences in the way water attacks these materials compared to its attack on glass and these differences will be mentioned briefly.

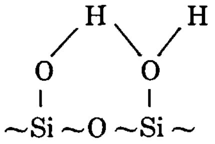
WATER ADSORPTION

Inorganic Oxides

Water is adsorbed on the surface of nonhydroscopic oxides (SiO_2, Fe_2O_3, and Al_2O_3) as hydroxyl groups (~M-OH) and as molecular water held by H-bonding to the surface hydroxyls. There may be some adsorption of molecular water on nonhydroxyl sites due to weak dispersion force interactions. Despite these features of similarity, the hydrated oxides differ greatly in their surface chemical behavior and these differences are largely due to the M-O bonds having different degrees of ionic-covalent character.

Extensive studies have been made of water adsorption on amorphous, nonporous silica powders and one of the most informative methods of investigation is infrared spectroscopy[1,2]. This is not to imply that other investigative methods are less valuable. The merit of the spectroscopy results is that they give direct information about the molecular state of adsorbed water and the results provide an easy vehicle for discussion. We will restrict ourselves to the nonporous silicas in order to avoid the complexities of capillary condensation. This phenomena is probably not pertinent to most of the filament or fiber reinforcements which have little surface porosity.

The amorphous, nonporous silicas are formed by the gas phase hydrolysis of silicon tetrachloride which leaves no detectable internal water. Consequently, infrared adsorption in the 4000-3000 cm^{-1} region can be attributed to the O-H stretching vibration of adsorbed water. The silica is examined spectroscopically either as thin, transparent wafers formed by compressing the powder or as a suspension in carbon tetrachloride (the suspension is transparent because the solid and liquid have nearly the same refractive index). Most of the physically and chemically adsorbed water can be removed by heating to ~800°C in vacuum (10^{-4} mm Hg) for a few hours. After this treatment, the infrared spectra shows only a low intensity, narrow band at 3750 cm^{-1}. This band is in the region of the stretching vibration for non-H bonded ("isolated") hydroxyl groups and is attributed to residual surface silanols (~Si-OH). Rehydration of the silica by water vapor at ambient temperatures produces an increase in intensity of the 3750 cm^{-1} band and the appearance of a new band at about 3650 cm^{-1} (Figure 1). These spectral developments correspond to the formation of more isolated surface silanols and silanols close enough to hydrogen bond;



The time required for rehydration depends on the amount of stress in the siloxane bonds (~ Si-O-Si ~) in the surface. A well annealed material may require many days contact with water or water vapor before showing significant rehydration[3].

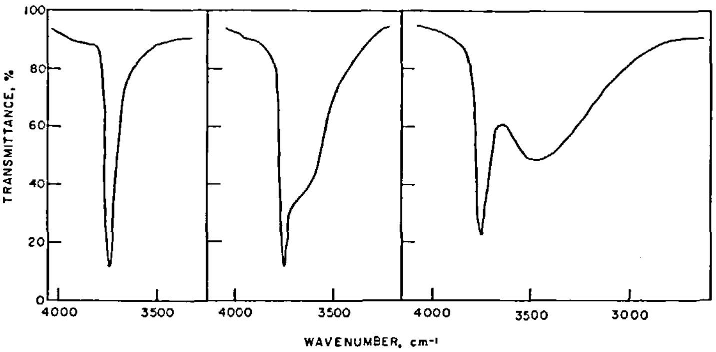


Figure 1. The infrared spectra of amorphous silica powder. The band assignments are; 3750-isolated surface hydroxyls, 3650-adjacent H-bonded surface hydroxyls, 3450-adsorbed molecular water.

Table 1

Frequency, cm^{-1}	*Assignment*	*Reference*
	SiO_2	
3750	Isolated Si-OH	1,2
3650	H-bonded Si-OH	1,2
	Al_2O_3	
3800	Al-OH, 4 Adjacent O^{--}	6,1,2
3780	Al-OH, 3 Adjacent O^{--}	6,1,2
3744	Al-OH, 2 Adjacent O^{--}	6,1,2
3733	Al-OH, 1 Adjacent O^{--}	6,1,2
3700	Al-OH, 0 Adjacent O^{--}	6,1,2
	TiO_2	
3740	Isolated Ti-OH	7
3690 3660	H-bonded Ti-OH	7
	Fe_2O_3	
3600	Fe-OH	8

Molecular water appears in the infrared spectra as a band at 3450 cm^{-1} (and also at 1600 cm^{-1}). Its appearance is accompanied by a decrease in the silanol band at 3750 cm^{-1} (Figure 1), thus indicating that the molecular water adsorbs by H-bonding to surface hydroxyls. Clusters of water molecules develop over the surface and at this stage the adsorbed film is considered to be "mobile". This mobility refers to the continual diffusion of water molecules from one cluster to another[4]. In addition, proton exchange occurs between the adsorbed molecular water and the surface hydroxyls and there is good reason to believe that protons (or hydronium ions) as well as molecular water are in diffusional motion over the surface. Fripiat[5] has estimated from conductivity measurements that at a monolayer coverage of water on silica the H^+/H_2O ratio is 10^{-2} compared to 10^{-8} for pure water.

There is spectroscopic evidence for surface hydroxyls and molecular water on other oxide surfaces. In Table 1, the infrared bands and their assignments are listed for Fe_2O_3, TiO_2 and Al_2O_3. Note that multiple bands are observed for isolated hydroxyls on alumina. This is a consequence of the crystalline nature of the aluminum oxide. According to Peri[6] the lattice structure of the surface allows five different hydroxyl sites, each differing in the number of adjacent oxide ions (Figure 2).

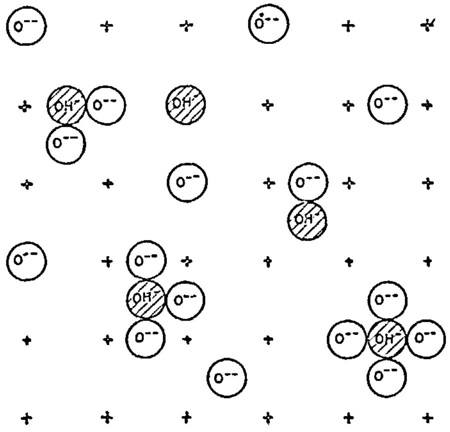


Figure 2. Schematic configuration of surface hydroxyls on Al_2O_3 showing five sites differing in the number of adjacent oxide ions. Positive sites are Al^{+3} in lower layer (reference 6).

The acid-base properties of oxide surfaces depend upon the ionic character of the metal-oxygen band. This distinction is evident when we consider the oxide/bulk water interface and the zero point of charge (zpc). The zpc is the pH of the aqueous solution at which the oxide surface is uncharged and thus represents the proton or hydroxyl ion concentration required to suppress ionization of the surface hydroxyl group. Healy and Fuerstenau[9] established a relation between the zpc and the heat of immersion in water (Figure 3) for six inorganic oxides. Note the low zpc for silica which is consistent with the

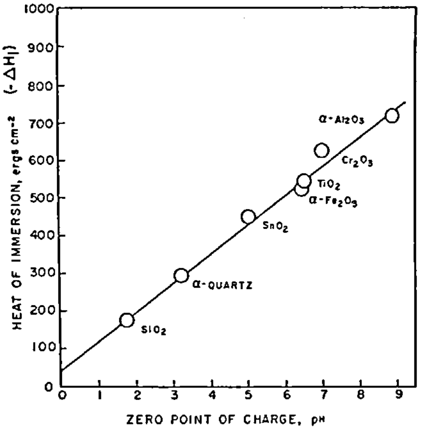


Figure 3. Interrelation of the heats of immersion in water and the zero points of charge for nonhydroscopic oxides (reference 9).

acid character of this oxide already discussed. The heat of immersion values in Figure 3 are for oxides dried at only 200°C which would remove only physically adsorbed water and leave the surface densely populated with $-OH$ groups. Thus, the heat of immersion (ΔH_i) values reflect the interaction of water with heavily hydroxylated surfaces. The data in Figure 3 can be fitted by the equation,

$$-\Delta H_i = 4.606\,RT\,(pH)_{zpc} + (\Delta H_c). \qquad (1)$$

The quantity ΔH_c is a constant for the oxide-water series and represents energy changes due to solid-liquid interactions not related to hydroxyl ionization. The value of ΔH_c is about 40 ergs/cm^2 and represents a rather small part of the total heat of immersion. Thus the heat of immersion for the various oxides is largely a function of the solid-liquid electrostatic interactions. This interaction is greatest when the M-O bond is highly ionic (Al_2O_3) and least when M-O is essentially covalent (SiO_2).

The heat of immersion and the zpc are average properties of a surface and do not reflect the heterogeneous character of the surface groups. For example, we can speak of aluminum oxide as having a basic surface character. However, it is well to keep in mind that certain sites will liberate hydroxyl ions more readily than others and these "high energy" sites may dominate surface behavior in certain situations.

Silicate Glasses

The surface chemistry of glass departs considerably from that of the inorganic oxides. All silicate glasses are mixtures of metal oxides dispersed in a silica network. The nonsilica components exist as microheterogeneities with dimensions estimated to be from 15A to 200A[10,11]. They constitute up to 50% of the glass composition and occupy about the same percentage of the glass surface. Even in the more water resistant glass formulations such as E-glass (16% CaO, 14.5% Al_2O_3, 9.5% B_2O_3, 5% MgO and 55% SiO_2), a significant proportion of the nonsilica content is alkali or alkaline earth oxides. These oxides are hydroscopic so that water adsorption on glass is characterized by the hydration of these oxide microheterogeneities. Pike and Hubbard[12] observed that glass powders adsorbed considerably more water than did a silica powder of comparable surface area. The soda-lime glasses were the most hydroscopic, but even an E-glass powder adsorbed twice as much water as the silica. Deitz has investigated water adsorption on continuous E-glass filament at low water vapor pressures (~ 2 mm) and at temperatures near 100° C[13]. The filaments were well protected from atmospheric contamination during the entire experiment. Deitz found that, (a) E-glass filaments adsorb more water per unit area at 100° C than does porous silica at 30° C, (b) the initial water adsorption was very rapid and probably represents the hydration of hydroscopic inclusions and (c) subsequent adsorption was very slow but continuous at least for the 48 hours of the experiment.

Not only does glass adsorb relatively thick water films but this water is strongly alkaline. Fraser, Patrick and Smith[14] observed a visible film of water formed from subsaturation vapor pressures on the inside of freshly blown glass bulbs. The condensate could be titrated with acid solution. Deitz[15] observed that when wads of E-glass, Pyrex and sodalime glass filaments are wet with small amounts of water, this water tests alkaline with phenolphthalein. Washing the wads with water and then testing for alkalinity gave a negative test. Fraser, et al. found that washing out their glass bulbs left a surface that would not adsorb a visible film of water.

According to Fripiat *et al.*[5], the adsorbed water film on powdered glass is immobile up to a monolayer coverage. The conductivity is low and they believe that the charge carrier is protionic. Evidently, at these low coverages the water is strongly held by the metal cation and that there is less surface diffusional motion than on silica powder having the same amount of adsorbed water. At coverages greater than a monolayer, the surface conductivity of glass increases considerably and charge transfer involves the cation. Studies of glass filaments[16] indicate a high surface conductivity for the pristine filaments but if they are washed with water before testing, the conductivity dropped to a level comparable to that of silica filaments.

Multilayer Adsorption

Some years ago, Bowden and Throssell[17] studied water adsorption on foils of platinum, gold, silver and aluminum. Their intent was to investigate claims[18] that, at partial pressures just below saturation, polar solids adsorb water films tens of molecular layers thick. The adsorption of such thick films implies that the attractive force of the surface is relayed through successive layers of water. In fact, the heavy adsorption of water has been cited as evidence for long range surface forces[19]. Bowden and Throssell discovered that the apparent heavy adsorption of water was due to contamination of the metal surfaces by hydroscopic ions. They could thermally desorb these ions by heating the foil to red heat after which the water adsorption corresponded to no more than two monolayers even up to partial pressures close to saturation. The adsorption of many molecular layers could be reestablished by rinsing the foils with tap water. Most of their adsorption studies were carried out by direct weighing on a microbalance, but additional experiments using an ellipsometer revealed that on the contaminated surfaces the water adsorbed as clusters, presumably around regions of contamination. They pointed out that only a small amount of hydroscopic contamination is needed to give multilayer adsorption. At a relative humidity of 50%, a surface contaminated with 10^{-7} gm/sq. cm. of potassium hydroxide would "adsorb" the equivalent of five molecular layers.

The question of long-range surface forces and the adsorption of many multilayers of water has been revived recently. Claims have been made that pristine glass and silica surfaces adsorb thick water films and that part of this water is converted into a new form of water variously known as anomalous water[20], ortho-water[21] or polywater[22]. In these experiments water is condensed from subsaturation vapor pressures ($\sim$95% RH) into extremely narrow ($<50\mu$) glass or silica capillaries. The greater part of the research on anomalous water has been done by Deryaguin and his co-workers in Russia [20,21,23]. They have established many of the physical properties of the condensate and have shown that these properties cannot be explained by the leaching of electrolytes from the glass surfaces. British[24] and American[22] workers have established that the anomalous condensate invariably evaporates to a gel-like residue. Lippincott *et al.*[22] determined the infrared and Raman spectra of this gel and conclude from their results that the gel is a polymeric form of H-bonded water in which the H-O distance is unusually short. Their chemical analysis of this "polywater" failed to show the presence of any significant amount of silicon.

The evidence for the existence of polywater is not unambiguous. We have already mentioned that at high relative humidities thick films of water adsorb on the hydroscopic regions of pristine glass surfaces and that this adsorbed film is alkaline. It is quite probable that an alkali accelerated surface corrosion occurs on the glass capillary wall and that as this film thickens it pulls up into a column of condensate. This corrosion process will lead to the formation of a colloidal silicate sol. In silica capillaries the surface corrosion process would be acid-catalyzed and lead to the formation of a silicic acid sol. In addition any contaminating salts on the glass or silica would also contribute to water adsorption and surface corrosion. Although Deryaguin has shown that simple electrolyte solutions do not exhibit the properties of anomalous water, these properties can be attributed to colloidal silicic acid sol-gel systems. The results of Lippincott *et al.* would appear to rule out the presence of silica but the amounts of material that they analyzed were so minute that their results cannot be considered conclusive.

Surface Diffusion

Adsorbed molecules are in more-or-less continual motion over the surface[4, 25]. We have already mentioned the mobility of adsorbed water on the

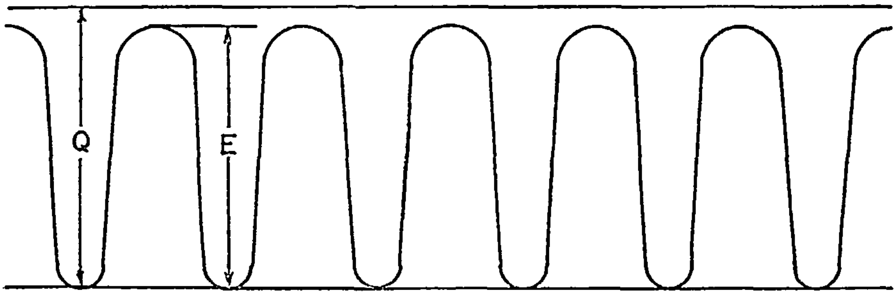


Figure 4. Schematic diagram of the relationship between the energy of adsorption, Q, and the activation energy for surface diffusion, E.

inorganic oxide surfaces and, in the next section, surface diffusion over fracture surfaces will be a major consideration. When dealing with fracture surfaces, we are concerned with the diffusion of water at low surface coverages. Under these conditions diffusion occurs by water moving from one adsorption site to another without encountering another molecule of adsorbed water.

Figure 4 illustrates the energy barrier to surface movement assuming an energetically homogeneous surface. For a heterogeneous surface there would be a random distribution of energy wells and we would need an expression for this distribution. In the homogeneous case, the lifetime a molecule spends at a given site, τ, is given by

$$\tau = \tau_0 \, e^{E/RT} \qquad (2)$$

where τ_0 is a function of the substrate, and E is the activation energy for surface diffusion (Figure 4). From equation 2, we can write an expression for the surface diffusion coefficient, D_s,

$$D_s = \frac{\lambda^2}{2\tau_0} e^{E/RT} \qquad (3)$$

where λ is the distance between sites. The surface flux, F_s, is given by the usual expression involving the concentration gradient dc/dx,

$$F_s = -D_s \, dc/dx. \qquad (4)$$

A major obstacle to applying these equations to stress-corrosion experiments is the lack of information about the activation energy E or the site distance λ for fracture surfaces. Any comparison of fracture surfaces with the surfaces of the inorganic oxide powders described above would not be realistic. In the process of fracture the separated surfaces are frequently left with unsaturated bonds and electrical charges not usually encountered on the powders which have usually had ample time for surface relaxation.

Frequently, the activation energy, E, is assumed to be some large fraction of Q, the heat of adsorption. Even this assumption can be quite incorrect if the high energy sites have a low barrier between them due to overlapping force fields.

MOISTURE-ASSISTED CRACK PROPAGATION

Fracture mechanics provides a fundamental and quantitative means of describing material failure including the effects of environment. Failure begins with the formation of one or more minute flaws or cracks, usually at the surface. Stress applied to the material is magnified at the crack tip until the crack begins to propagate. Propagation usually begins slowly followed by an abrupt increse in the rate of extension which may eventually reach a limiting or terminal velocity of about 40% of the speed of sound. The stage of crack growth at which the specimen fails catastrophically depends on its dimensions and the manner in which load is applied. Through the proper design of test specimen and test method, it is possible to control crack growth and to measure the energy expended. From this information a fracture toughness can be computed that is a characteristic property of the material.

The following equation gives an accounting of the energy dissipation at the moment a crack propagates[26],

$$\delta E_c > \delta\sigma + \delta W \tag{5}$$

This expression states that a crack will advance when the elastic strain energy (δE_c) due to the applied stress exceeds the energy needed to create new surface ($\delta\sigma$) plus the energy expended in plastic deformation (δW) all per unit area of crack extension. The strain energy is concentrated in a zone radially distributed about the crack tip (Figure 5). Neither σ or W is available from first principles except for the simplest of materials. However, Irwin[27] has shown that δE_c can be evaluated experimentally to obtain the "rate" of released elastic strain energy, G, a fundamental measure of fracture toughness.

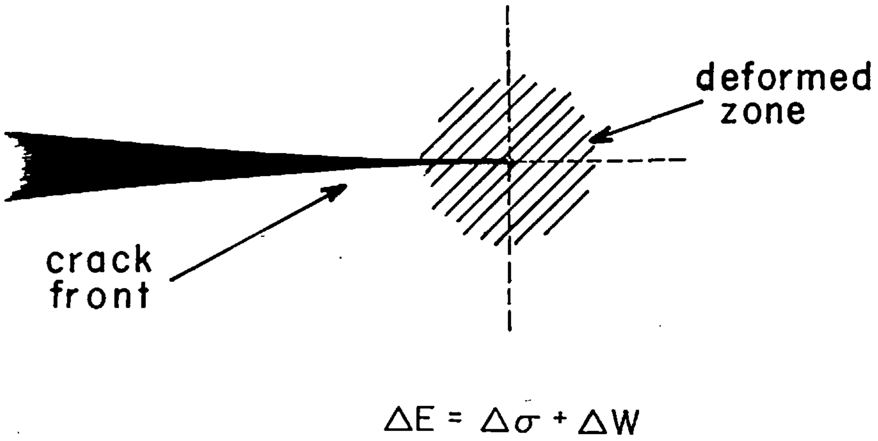


Figure 5. Crack tip and advance deformed zone.

The energy used in plastic deformation, δW, usually outweighs the surface energy term, $\delta\sigma$, in determining fracture toughness. Thus, a brittle material such as glass has little ability to deform plastically and so has a low fracture toughness even though it has a very high cohesive strength (high surface energy). Copper, on the other hand, has a much lower cohesive strength than glass but is more resistant to fracture because it can deform.

Strictly speaking, Equation 5 applies to the onset of fast crack propagation and not to the regime of slow propagation which is of most significance to moisture-assisted failure. However, the equation provides a convenient formalism for discussing the effect of water. In the past a decrease in strength due to moisture or other adsorbate was usually explained as a reduction in surface energy due to adsorption from the gas phase onto the surface as the crack propagated. Obviously, the adsorbate cannot influence crack extension through a reduction in σ by adsorbing onto crack surfaces that have already formed. The action of the adsorbate must be to alter the bond strength at the crack tip, i.e. a reduction in σ by reducing the cohesive energy. However, Equation 5 offers an alternate mechanism in which the water embrittles the material around the crack tip thus reducing δW, the amount of deformation that can occur ahead of the crack. This is an unlikely mechanism when the crack is propagating rapidly (approaching the terminal velocity) because it requires a very rapid water diffusion to the crack tip and into the deformed zone. Indeed, we will see in the next section that crack velocity in glass plates can exceed the rate of water transport to the crack front.

Moisture can assist failure in at least two other ways besides its effect on σ and W. Surface corrosion can lead to surface flaws, i.e., surface pits or inclusions of a weak corrosion product. Also, water condensing into a crack tip can exert considerable capillary pressure acting to open the flaw[28]. However, significant condensation does not usually occur up to relative humidities of 90% or greater so that this last mechanism will not be important except at high relative humidities.

These explanations of environmental failure say nothing about the atomic or molecular processes involved. In recent years, interest in molecular mechanisms has been mounting to the point where it is now a very active area of materials science research.

However, efforts to establish the atomic mechanisms of moisture-induced failure in composite materials have been rather limited compared to the studies of metals and ceramics. This is not to say that valuable research has not been reported. However, much of this work has been to determine the sensitivity of a particular material to a specific environment without any attempt to derive meaningful failure mechanisms. The studies reviewed in the following section have been selected because they at least suggest the molecular events occurring during failure. Also, they serve to illustrate sound approaches to establishing stress-corrosion mechanisms.

Glass Plates and Filaments

Two of the more definitive studies of glass corrosion are those by Mould[29] and Charles[30,31]. Mould compared the strengths of glass plates in moist air, σ, relative to their strengths in dry air, σ_n, as a function of temperature and obtained curves of the form shown in Figure 6. Up to 75°K the relative strength (σ/σ_n) was unity, which indicates that the rate of moisture attack is too slow to have a discernible effect. Between 75°K and 500°K the rate of attack increases with the temperature (decrease in strength). Above 500°K this trend is reversed. Mould explains this reversal as either a decrease in the amount of adsorbed water with increasing temperature or as an increase in plastic flow at the crack tip (increase in δW in Equation 5). Mould and Southwick[32] found that for glass of a specified composition but subjected to a variety of pretreatments, the fatigue data fit a universal fatigue curve (stress vs. time to failure).

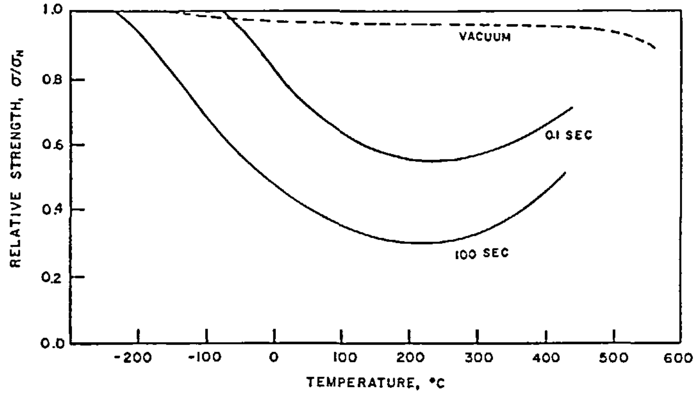


Figure 6. Relative strengths of glass plates (moist vs. dry air) as a function of temperature at load durations of 0.1 sec and 100 sec (reference 31).

Charles[31] studied stress corrosion as a function of temperature and showed that it is an activated process with an activation energy of 18.8 kcals/mole. Later, Hillig and Charles[35] derived an expression for fatigue failure that adequately predicted the shape of the stress-temperature curves (Figure 6), the universal fatigue curve obtained by Mould and the energy of activation obtained by Charles. They developed their equation by combining a thermodynamic expression for the rate of reaction at the crack tip with an expression for the stress distribution around the crack assuming the crack tip to have an elliptical shape. Included in the reaction rate equation was a term for the change in free energy of activation with stress, $\delta\Delta F/\delta E$. They note that this term should be negative if the stress at the flaw tip tends to expand the material and positive if the stress is compressive.

Charles and Hillig propose that, at the crack tip, water hydrates sodium ions (or other cations) to form the metal hydroxide which in turn hydrolyses siloxane bonds thus weakening the silica network structure. They identify the experimental activation energy of 18.8 kcal/mole with the activation energy for sodium ion diffusion in glass (20-25 kcal/mole).

In measuring and analyzing fatigue stress data, Mould and Charles were not dealing directly with the fundamental phenomena of crack propagation. Direct studies of moisture-induced crack propagation have been reported by Weiderhorn[34] and Irwin[35]. Weiderhorn measured crack velocities through microscope slides submerged in water or held in air (or nitrogen) having different water vapor contents. A crack was started from a notch cut into one of the short edges of the slide and the crack was guided through the slide by a scratch parallel to the long dimension and through the center of one side of the specimen. Crack velocity as a function of applied force is given in Figure 7 for experiments in 1.5 mole percent water in air, 0.001 mole percent water in nitrogen and in nitrogen gas dried over liquid nitrogen. In air containing 1.5 mole percent water (and also when submerged in water), crack velocity is a linear function of applied force. At the lower moisture contents, the data show a distinct plateau at velocities of about 10^{-7} cm/sec. Weiderhorn suggests that at this velocity, crack propagation exceeds the rate of diffusion of water vapor to the crack tip. Note that the data taken in dried nitrogen also show a plateau, indicating that the gas was not anhydrous.

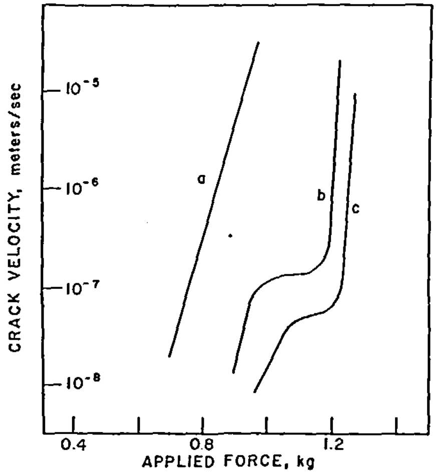


Figure 7. Crack velocity vs. applied force for glass slides in 1.5 mole % water in air (a), 0.001 mole % water in N_2(b) and N_2 dried over liquid nitrogen (c) (reference 34).

Weiderhorn found that the crack velocity-stress curves obtained as a function of temperature fit an expression similar in form to that derived by Charles and Hillig. He obtained an activation energy of 19.5 kcal/mole, in reasonable agreement with the 18.8 kcal/mole found by Charles. Weiderhorn also believes that cation diffusion is the activated process.

The mechanical aspects of Irwin's study of moisture-induced crack propagation[35] are particularly noteworthy, although his data were not as extensive as those of Weiderhorn. Irwin chose the shape of the glass test plates and the loading method so that cracks propagated across the plate with no tendency to wander out of the horizontal plane. This means that the crack is guided by the stress field alone with no need to cut a scratch across the length of the plate. With crack propagation so stabilized, Irwin was able to compute G, the crack extension force, from the applied stress, crack length and test specimen dimensions for G. We will consider the actual expression for G in a later section. Having G values, the analytical methods of fracture mechanics permit formal estimates of the size and shape of the crack opening near the leading edge, and the size of the zone of deformation ahead of the crack. These computations are open to criticism in that microscopic dimensions (< 100A) are being calculated from macroscopic measurements. Nonetheless, the calculated values are reasonable approximations useful in considering the events at or near the crack tip.

In addition to the mechanical aspects of Irwin's study, the results provide other pertinent points. He observed plateaus in plots of crack velocity *vs* stress similar to those observed by Weiderhorn (Figure 7). Irwin's data included crack velocities higher than those in Figure 7 and he found evidence for a plateau region in very moist air, comparable to the condition of curve 7a. Another significant result was that the G values were in the range of 3000-5000 ergs/cm^2 which are a factor of ten greater than any reasonable estimate of the surface energy of glass (300-800 ergs/cm^2). Clearly, much more energy is being expended than is needed to simply overcome cohesive energy (twice the surface energy). Presumably, most of this excess energy is used to deform the stress zone ahead of the crack tip. In glass, as in concrete[36], there is probably very little plastic strain in the zone ahead of the crack. Instead, stress relief occurs by advance cracking of the weak alkali regions.

It is Irwin's suggestion that the effect of water on crack propagation is to diffuse into the deformed zone via these microcracks to hydrate the alkali microheterogeneities so as to weaken them further and to form corrosive products. Above a certain crack velocity, the water is unable to penetrate these advance cracks and the data show a plateau. One reason for this limiting velocity is that the crack speed exceeds the rate of water diffusion to the crack tip, as suggested by Weiderhorn. However, Irwin points out that with increasing stress there is the possibility that the advance cracks became narrower. His argument is that, at low G values, the advance cracking is mainly by single, essentially coplanar cracks (Figure 8). As G is increased, the

Figure 8. Advance cracking in glass at slow crack velocities (A) and fast cracks (B).

advance is by multiple cracking throughout the deformed zone. Thus, the total opening by advance cracks increases with G but the average size of the opening decreases.

It is not unreasonable to identify the activation energy of 18-20 kcal/mole obtained by Charles and Weiderhorn with water diffusion into the crack front rather than with cation diffusion. The ingress of water to the crack front and into the micro-cracks must occur by surface diffusion. Irwin's calculations indicate the crack tip opening to be about 20A and the advance crack openings to be much less. These dimensions are too small for significant gas transport of water molecules. The heat of activation for the surface diffusion of water on silica powder is about 12 kcal/mole[25] but we can expect higher values for diffusion on the strongly adsorbing glass fracture surfaces.

We now shift our attention from glass plates to the glass filaments used as reinforcement in glass-resin composites. Because these filaments have such small diameters ($<10\mu$), a surface flaw 20A in depth can cause catastrophic failure at stresses only a fraction of the tensile strength of an undamaged filament. Consequently, the principal consideration in the stress corrosion of filaments is the formation of surface flaws by the hostile environment. Thomas[37], Otto[38], Hollinger and Plant[39] and Schmitz and Metcalfe[40] have made major contributions in this area. Schmitz and Metcalfe determined the fatigue data (stress *vs* time-to-failure) for E-glass filaments at 50% and 99% RH. From failure time probability plots, they determined a life increase of 40% for the lower humidity. The data were obtained by testing a statistically significant number of filaments at each stress level from which they determined the failure probability. The surprising result of their work was that the fibers which survived static loading at 100% RH and tested for ultimate strength at 50% RH were found not to have suffered any weakening due to exposure to the high humidity. They concluded that the stress-corrosion mechanism (Figure 9) must involve a long induction time during which no

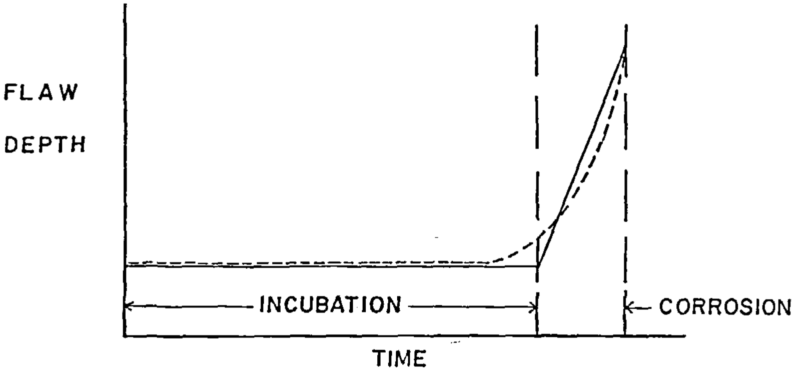


Figure 9. View of stress-corrosion of glass filaments given by Schmitz and Metcalfe (Reference 40).

flaws are formed. When a surface flaw does develop, its formation is relatively rapid compared to the incubation time and the flaw causes catastrophic failure. They estimate that the stress concentration is a factor of 5 in which case a flaw 10-15A deep would lead to failure in the observed stress range (1—5 $\times$ 10^5 psi). They give further support to their explanation by pointing out that for continuous flaw growth a logarithmic plot of time-to-failure against the reciprocal of the failure stress should be linear. Such was not the case for their data. In fact, a better fit was obtained by assuming a two stage process.

Schmitz and Metcalfe suggest that the incubation period involves the gradual adsorption of water to form a surface film having a high enough hydroxyl concentration that flaw growth can occur. However, this explanation is somewhat unsatisfactory in that water adsorption on glass involves the progressive hydration of cation sites so that the highest "alkaline" condition occurs at early stages of hydration. Thus, if alkalinity is the criteria for failure, then there would not be an incubation period. Actually, it is the mobility of the adsorbed film that increases with time so that the incubation period may represent the time needed to establish a film capable of the material transport necessary for the corrosion step.

Stress Corrosion at Adhesive/Adherend Interfaces

The matrix/reinforcement interface has long been considered the most moisture sensitive region in composites. Evidence for interfacial attack is based on a loss of flexural strength or interfacial shear strength after exposure to water vapor or boiling water[11]. These tests give valuable engineering data, but until the micromechanics of composite failure is better understood these methods have limited use in evaluating the mechanism of moisture attack. There has been some progress in developing the fracture mechanics of composites, notably the work by Kies[12] and Corten[13]. A fracture study of composite failure in wet environments has been initiated by Mast, Mulville and Wolock[14] but the work is in the preliminary stages.

For the present we must resort to the much simpler geometries used in adhesive testing such as double beam, lap and "napkin-ring" joints. Studies of breaking strength or times-to-failure with these type specimens have demonstrated that water can cause very substantial losses in adhesive strength. Unfortunately, when these specimens are stressed to complete failure it is often difficult to judge the locus of failure. To even begin considering failure mechanisms, it must be known where failure initiated and slow crack propagation took place. An examination of the fracture surface usually reveals where catastrophic failure occurred but tells little about the earlier stages of failure. The problem lies in the fact that the locus of failure depends on both the material characteristics and the manner in which the specimen is loaded. For example, a failure that appeared to occur at or near the interface may indicate a weak boundary or it may mean that failure initiated away from the interface but that the particular method of loading forced the crack to run near the interface.

Much of this uncertainty can be avoided by studying crack extension rather than ultimate failure. This approach is being successfully used in the work of Ripling, Mostovoy and Patrick[45,46,47]. Their specimen design shown schematically in Figure 10 is a tapered, double cantilever beam. The adherends were either an aluminum alloy (2024-T351) or plate glass and the adhesive was an amine cured epoxy resin (100 parts by weight bisphenyldiglycidyl ether—DER 332LC, 15 parts tetraethylenepentamine, post-cured at 150-180°F). The tapered configuration was selected so that the crack extension force, G, is a linear function of the applied force, the specimen dimensions and the modulus of the adherend[46]. In general, the crack extension force, G, is given by

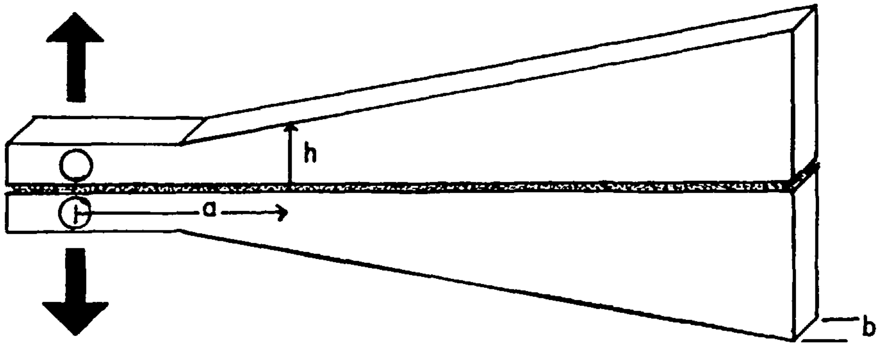


Figure 10. Tapered specimen for crack propagation studies of adhesive-adherend systems. a, crack length; b, specimen width; h, specimen half-height at crack tip.

$$G = \frac{P^2}{2b}\frac{dC}{da}$$

where P is the applied force, b is the specimen thickness, a is the crack length (measured from the point of loading) and C is the specimen compliance. For the tapered beam they have shown[46] that dC/da is a function of crack dimensions and adherend modulus, E,

$$G = \frac{4P^2}{Eb^2}\left(\frac{1}{h} + \frac{3a^2}{h^3}\right)$$

where h is the specimen half-height. The crack extension force at which the crack propagates is designated G_c.

They investigated various curing agent-resin compositions, curing schedules and surface cleaning methods for the adherend to obtain conditions that would give center of the bond (cohesive) failure when the load was increased continuously. They determined G_c to be about 44,000 ergs/cm^2 for the particular resin used and the value was the same for both glass and aluminum

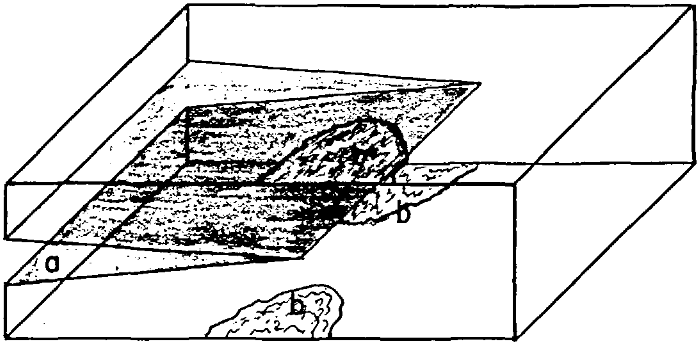


Figure 11. Diagram of adhesive layer at crack tip (a) showing the position of moisture-induced, interfacial cracks (b) above and below crack front.

adherends. Note here, as with glass, that the fracture energy, G_c, is almost 1000 x the surface energy.

Moisture-induced failure was investigated by the static loading of precracked specimens in 58% and 99+% RH at stress levels of about $0.2G_c$. Invariably, they observed the development of cracks very near the adhesive/adherend interface above and below the advance front of the preformed crack (Figure 11). These apparently interfacial cracks initiated at the specimen edge and propagated inward until they reached the other side of the bond or intersected another crack front coming from the other side. At the higher humidity of about 99% RH, cracks initiated above and below the precrack front and from both sides of the bond. At the lower humidity, 58% RH, only one or two cracks developed. Once an interfacial crack had extended across the bond width, it would continue to propagate lengthwise away from the loading points.

When the load was returned to the G_c value, the locus of failure shifted from the interface back to the preformed crack in the adhesive layer. Actually, to restart the center-of-bond crack, the initial load had to be somewhat higher than G_c because of a slight toughening of the resin at the crack tip due to exposure to water during the static test.

These workers have examined the center-of-bond and the interfacial fracture surfaces with a scanning electron microscope. Within the resolution of the instrument, about 200A, the moisture induced fracture appeared to have propagated at the resin/adherend boundary. So far as fracture mechanics is concerned, this represents interfacial failure since the deformed zone ahead of the moisture driven crack is easily 200A in diameter. In others words, fracture mechanics forces us to recognize that failure occurs in a zone having dimensions much greater than one or two molecular layers. It remains to identify the material in this zone that is water sensitive. This material may be a hydroscopic oxide on the adherend or some component of the resin that has accumulated near the interface.

TECHNICAL APPROACHES TO IMPROVING COMPOSITE WET-STRENGTH

An obvious precaution that can be taken to reduce the adverse effects of water is to prevent water from ever reaching the interface. A good start in this direction is to avoid surfaces that expose filaments, especially cut edges. Water can also gain entry by diffusion through the resin. This point has been emphasized by Regester[48] and by Quick and Griffith[49] who have been investigating hydrophobic fluoroepoxy resins for possible use in filament-wound composites.

Voids created by air trapped in the composite during fabrication are another cause for poor reliability in wet environments. These air pockets cause internal cracking when the composite is stressed and so create paths for the entry of moisture. Large voids with dimensions many times those of the fibrous reinforcement are not uncommon but can be avoided by proper fabrication techniques. On the other hand, the entrapment of microvoids is inherent in the fabrication of composites whenever a viscous resin impregnates a strand or cloth of filaments[50]. At normal rates of impregnation the resin is unable to completely displace the air between filaments and the result is the entrapment of elongated air voids with diameters comparable to the filament diameter. Entrapment of these microvoids cannot be prevented but their numbers can be greatly reduced during fabrication[51]. A reduction in microvoid content improves composite strength[51] and resistance to degradation by water[52].

Adhesion Promoters

Shortly after the introduction of glass-resin composite materials, various treating agents were found that when applied to the glass filaments improved composite wet-strength. Principal among these agents are the so-called silanes. These compounds have the general formula, $R\text{-}Si\,(OR')_3$, and are more properly called H-substituted trialkoxysilanes; the OR′ groups are alkoxy functions and the $-R$ group is referred to as the organofunctional group. An example of a silane adhesion promoter is γ-aminopropyltriethoxysilane, $NH_2CH_2CH_2Si\,(OC_2H_5)_3$.

The silanes have been the subject of much research and speculation in an effort to understand how they work. A number of explanations have been offered, the principal one being the coupling theory (Figure 12) which proposes that the trialkoxysilane chemically bonds to the adhesive by reaction of the organofunctional group with the resin molecules and bonds to the glass surface through interaction of the alkoxy groups with surface silanols[41]. This explanation has been useful in guiding the search for improved adhesion promoters.

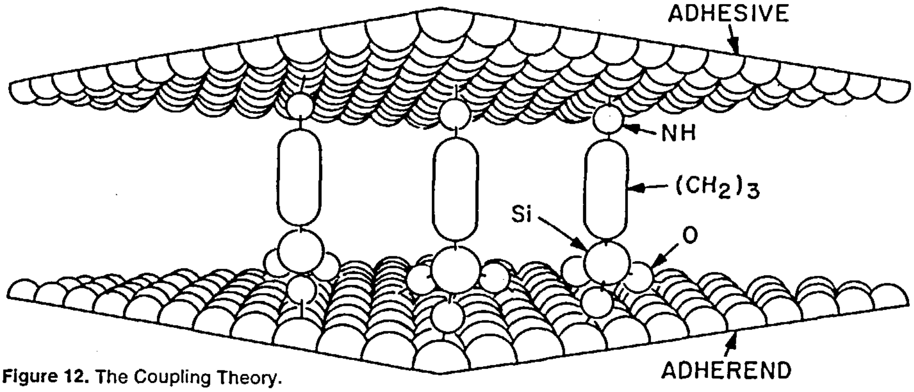


Figure 12. The Coupling Theory.

The coupling theory is not consistent with all the facts. First, it does not explain why certain silanes are effective adhesion promoters even though they have organofunctional groups incapable of reacting with the resin. Secondly, the silanes are used successfully as adhesion promoters on metals as well as glass, and although the trialkoxysilanes may form metallosiloxane bonds to metal surfaces, such bonds are easily susceptible to hydrolysis. According to the coupling theory, part of the ability of a silane to improve adhesive bond wet-strength is attributed to the formation of hydrolytically stable -Si-O-Si- bonds with the glass.

Part of the difficulty with the coupling theory is that it over-simplifies the structure of both the resin and the adsorbed silane film. The resin is incorrectly viewed as a uniform polymer structure. The silane film is viewed as a monolayer of adsorbed silane monomer when actually it is seldom a monolayer and is usually adsorbed as the siloxane polymer.

Consider first the structure of the silane film. The trialkoxysilanes readily undergo hydrolysis-polymerization to the corresponding three-dimensional polysiloxane. These reactions are acid-base catalyzed[53]. The methods used to apply silane adhesion promoters usually include water and an acid (or base) so that the deposition of a polymer film is quite probable. Experimentally, silane films have been found to be polymeric by Tutas el al.[54], Schrader et al.[55], Johannsen et al.[56], and Bascom[57]. Generally, these films were much thicker than a monolayer of silane monomer and appeared to be composed of a strongly held polysiloxane network along with some hydrolyzed or partially hydrolyzed silane and small polysiloxane molecules. These lower molecular weight materials could be easily removed from the substrate by rinsing with organic solvents or even by prolonged contact with water. On the other hand, the high molecular weight polysiloxane network resisted desorption by either water or organic solvents. This resistance to solvent removal held true whether the films were formed on glass, stainless steel or gold[57]. In the case of the gold substrate, it is very unlikely that the trialkoxysilane formed metallosiloxane bonds with this inactive metal. However, if the film were a high molecular weight siloxane polymer network it would resist desorption due to its low solubility and to the fact that a polymer segment has multiple bonds to the surface and to remove the polymer these bonds must be broken simultaneously; a process that requires a large activation energy even when the individual attachments are weak, nonspecific dispersion forces.

The structure of the resin has also been oversimplified. Electron microscopy and optical microscopy[58,59] of epoxy, phenolic and phthalate resins reveal that these materials are not homogeneous but consist of micelles or granules of high-density polymer separated by narrow boundary regions of lower-molecular-weight material. These micelles probably originate because polymerization initiates from random points and proceeds radially and as these regions approach one another, they are unable to coalesce into a homogeneous network. Instead, the polymerization is terminated, leaving unreacted or partially reacted material at the periphery. At an interface, this low-molecular-weight material may exist as a thin, continuous film or as channels between micelles. Either way, the low density regions offer pathways for the easy entry of water into the interfacial region. The silane film would act to prevent or compensate for the incompletely polymerized resin at the interface. Entanglement of this low-density resin into the siloxane films would increase its density and thus hinder water penetration. Alternatively, the silane film may initiate polymerization of the resin so that there is a high percentage of dense polymer at the interface. The polymerization would be initiated if, (a) the organofunctional group on the silane were a reactant in the polymerization or, (b) the film were capable of selectively adsorbing one of the resin constituents which in turn initiated interfacial polymerization.

Evidence that the silane film and the reinforcement surface itself can influence resin structure comes from the work by Arnheim, Kwei and Kumins[60] who studied water sorption by a polyester resin containing E-glass powder as a filler. They observed that films of the filled polymer absorbed less water than would be expected if the polyester and glass were separate. The effect could not be explained by the polyester preventing the water vapor from reaching the glass powder. They further observed that when the E-glass powder was first coated with vinyl-triethoxysilane, water sorption by the polyester-filler film was even lower. This silane treatment did not significantly lower the ability of the E-glass powder to take up water. When they pretreated the glass powder with ethyltriethoxysilane, water sorption by the polymer-filler film was not decreased relative to the film containing untreated filler.

This work was an extension of their earlier studies in which they found that vapor sorption by various resins was notably decreased by the addition of less than 10% TiO_2 or other inorganic powders[61]. To explain their results they proposed a model in which the filler particle increases the degree of local ordering of the polymer segments and that the water uptake by this bound polymer is much less than by free polymer. On the basis of this model they conclude that the filler-polymer inter action extends as much as 1500 A from the particle surface. They suggest that this same ordering of the polymer takes place in the polyester-untreated E-glass system. Treating the E-glass with vinylsilane enhances the ordering effect because the vinyl end groups are capable of entering into the polyester polymerization reaction. However, their model does not consider the inhomogeneous (micellar) resin structure and the effect the filler may have on this structure. They assume a homogeneous network and then consider how it might be disturbed by the filler. The actual situation may be much more complex. Despite these reservations about their model, the polymer-filled interactions that they observed point up the fact that in composite materials the resin matrix can be profoundly altered by the reinforcement and by silane films applied to the reinforcement.

NONSILICATE REINFORCEMENTS

Other than glass, the principal composite reinforcements are carbon filaments, alumina whiskers and filaments of high strength metals such as boron. None of these materials are immune to moisture (not even carbon). Much of the interest in carbon-resin composites stems from the belief that they will not be as water sensitive as the glass resin materials. This expectation may not be entirely justified. Carbon filaments are partly graphitized, and it is known that the mechanical behavior of graphite crystals is sensitive to various adsorbates including water. The use of graphite as a dry-film lubricant requires the presence of adsorbed gases such as oxygen, water vapor or organic vapors[62]. The film lubricity is lost in high vacuum. It was at first believed that these gases adsorbed on the basal planes of the graphite crystals so as to reduce the inter-crystalline attraction and allow the crystals to slide past each other[62]. It has since been determined that the amount of adsorbate needed to affect lubricity is much too small to give significant coverage of the basal plane area and most of the adsorbate would be held by polar sites at the crystal edges. The actual role of adsorbates in graphite dry-film lubricants is still very uncertain[63]. Its possible implications to carbon filaments has been recognized[64] but no detailed study of the matter has been published as yet.

The mechanical properties of the crystalline reinforcements, e.g. alumina whiskers and boron filaments, are largely determined by their crystal lattice defects. Thus, the yield and fracture of crystalline materials involves the movement of dislocations. There are various ways in which adsorbed water can interfere or enhance dislocation mobility. This type of stress-corrosion has been the subject of much study and is too extensive to be reviewed here. Instead, the reader is referred to the proceedings of a recent conference which includes an excellent review by Westwood[65].

SUMMARY

We have touched on the essential aspects of water adsorption on glass and the elementary theory of fracture. Despite all that has been accomplished in these areas, there remain some unanswered questions critical to the problem of moisture-induced failure. First of all, the state of knowledge about fracture surfaces is very meager. We can anticipate that water arrives at the crack front by surface diffusion but we cannot describe this surface flow in any quantitative way until more is known about the energies involved in water adsorption on fracture surfaces. It is also uncertain what the water encounters when it arrives at the crack front. The micromechanics of crack propagation teaches that surrounding the crack tip is a deformed region, but it is not always certain whether this deformation is elastic, plastic or involves microcracking of the material.

Even if the material is unstressed, water can reach and weaken the adhesive/adherend interface by diffusion through the resin or along the interface itself. It would appear that this water migration is sensitive to the resin structure. This structure is complex, especially in the interfacial region since there is evidence that the surface can influence the polymer configuration by influencing the polymerization.

The questions posed here are not unanswerable. Experimental approaches are available that are sound from both a surface chemical and mechanics point of view and meaningful progress can best be achieved when both these aspects of the problem are respected. Empirical approaches to reducing the moisture sensitivity of composite materials can be very valuable. However, technological demands for new, reliable composites can best be met if these materials are designed on a scientifically sound basis.

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