

# Environmental Influence on the Fracture Strength of Coated Glass Fibers

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## Synopsis

The effect of the environment on the fracture strength of coated glass fibers is described. Simple expressions relating the thermodynamic work of adhesion, in the presence and absence of stress to the permanence of the composite, are derived. The need for interactions other than dispersion-type interactions between silica and coating systems is emphasized. A prognosis is offered for achieving a permanently bonded structure, provided that reasonable wetting can be facilitated at the oxide-coating interface or that there is generated a strongly bound species to the silica, shifting the potential locus of failure.

## INTRODUCTION

Although the fracture strengths for long lengths ( $\sim$ km) of coated optical fibers have been reported to approach values of  $7 \text{ GN/m}^2$  ( $10^6 \text{ psi}$ ),<sup>1,2</sup> there is a serious degradation in strength when these same coated fibers are exposed simultaneously to high humidity and tensile stress.<sup>3</sup> Apparently, the diffusion of water vapor or bulk water through the coating may possibly displace the coating from the glass, exposing the pristine surface to environmental effects. While a variety of procedures have been adopted to prevent this premature failure, among them the use of silane coupling agents, it is not clear from the recent literature that this effect has been explained adequately. In this paper we shall present a simplified discussion of the interface and the principal factors involved in environmental failure. These considerations lead to a prognosis for premature failure of coated fibers when exposed to hostile environments.

## ENVIRONMENTAL EFFECTS ON ADHESION

A proper exposition of environmental factors and their influence on the permanence of coatings may best be viewed by considering some recent work in adhesive bonding.

Andrews and Kinloch<sup>4,5</sup> have described an adhesive failure energy  $\theta$ , which is based on the earlier efforts of Gent and Schultz.<sup>6,7</sup> The adhesive failure energy is comprised of two major components, namely, (i) the energy to propagate a crack through a unit area of interface in the absence of viscoelastic energy losses and chemisorption of the coating to the substrate, i.e., an intrinsic adhesive failure energy  $\theta_0$ , and (ii) the energy  $\psi$  dissipated viscoelastically within the adhesive in the propagating crack, again referenced to a unit area of interface.  $\theta_0$  should be rate and temperature independent since its value depends only upon the nature of the bonding at the interface. The energy  $\psi$ , dissipated viscoelastically, is by definition rate and temperature dependent. For cases where only secondary forces (dispersion forces) are operative, it has been shown<sup>4,5</sup> that  $\theta_0 \sim W_A$ , where

$W_A$  is the thermodynamic work of adhesion. When covalent bonding occurs across the interface,  $\theta \gg W_A$ .<sup>4,5</sup> Further,  $\theta_0$  was found to be independent of test geometry and should be appropriate for considering the cylindrical system of a coated glass fiber.

A more detailed look at environmental factors pertaining to adhesive joint strengths was undertaken by Owens<sup>8</sup> and Gent and Schultz.<sup>7</sup> Owens<sup>8</sup> demonstrated that in the presence of a particular liquid phase, if the thermodynamic work of adhesion of a composite AB is near or equal to zero ( $W_{AB} \simeq 0$ ), the composite would be unstable and delaminate in a relatively short period of time. In the absence of a liquid phase, the work of adhesion is large (corresponding to large values of  $\theta_0$ ), and  $W_{AB} \gg 0$ . Under these conditions, delamination may be retarded for an indefinite interval. Clearly, the lifetime of the composite in the absence of the liquid is considerably in excess of the composite aged in the presence of the liquid. The effect of simultaneous exposure to a liquid phase and stress was not considered. We shall consider that situation in the next section. Excluding chemisorption<sup>9</sup> (i.e., where  $\theta_0 \gg W_{AB}$ ) and interdiffusion,<sup>10</sup> it would appear that at least two criteria are necessary to predict premature failure of a composite in the presence of stress and a fluid phase:

1. The liquid must be immiscible with the polymer and substrate.<sup>8</sup> Clearly, immiscibility is a necessary criterion only for the application of classical surface energetics. Attack of the coating by the solvent phase to produce swelling or dissolution would facilitate separation of the coating and substrate.

2. The liquid or fluid phase must fully interact (i.e., in a surface chemical sense) with either one or both of the members of the composite. For example, in a composite consisting of polyethylene and another member, to facilitate environmental failure the fluid phase should react principally via dispersion forces ( $\gamma_{LV} \sim \gamma_{LV}^d$ ).

### THERMODYNAMIC WORK OF ADHESION IN THE ABSENCE OF APPLIED STRESS

Interaction of the environment with coatings may be visualized by considering the magnitude of the thermodynamic work of adhesion, that is, the free-energy change to create an organic-water and a substrate-water interface and to eliminate the original organic-substrate interface.

Consider a bonded composite AB. If water or other liquid delaminates the composite AB, then the work of adhesion in the presence of that liquid,  $W_{AB}^L$ , will be zero or negative. Obviously, to facilitate the permanence of the AB composite,  $W_{AB}^L$  should approximate  $W_{AB}$ , indicating that the energetics favor the A-B interface rather than the A-L-B interface. Clearly, if significant chemisorption had occurred across the interface, the likelihood of delamination would be reduced markedly. It will be assumed that formation of the interface has been maximized with respect to interfacial contact. The situation with coated glass fibers may be quite different, since we are concerned with dynamic wetting. For simple liquids, water or alcohol, the equilibrium contact angle on solids is reached in a relatively short time (seconds). However, for highly viscous liquids, similar to polymer melts, extended periods of time may be required to reach equilibrium contact angles. The dynamics of wetting is associated with viscosity, relative surface energetics of the solid and liquid, and velocity of the

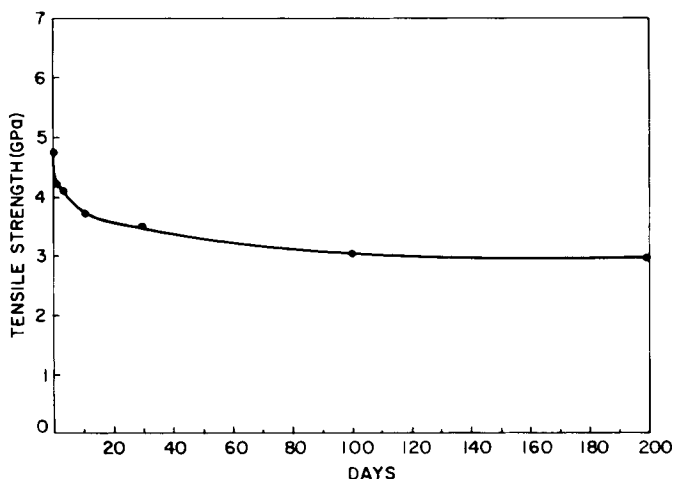


Fig. 1. Tensile strength of 110- $\mu\text{m}$  Suprasil-2 fibers coated with a UV-cured epoxy-acrylate. The fibers were drawn at 0.4 m/sec with a 250-watt  $\text{CO}_2$  laser. The coated fibers were aged in water at 23°C and zero applied stress.

liquid flow. In the fiber coating process, the contact angle appears to be associated with the dimensionless parameter  $\eta v/\gamma$ , where  $\eta$  is the viscosity of the liquid,  $v$  is the velocity of fiber drawing, and  $\gamma$  is the surface tension of the liquid.<sup>11</sup>

In the absence of a liquid phase, but in the presence of air ( $V$ ), the thermodynamic work of adhesion is

$$W_{AB} = \gamma_{AV} + \gamma_{BV} - \gamma_{AB} \quad (1)$$

where the  $\gamma$  values represent the solid surface tensions of the members of the composites. In the presence of a liquid phase, the thermodynamic work of adhesion becomes

$$W_{AB}^L = \gamma_{AL} + \gamma_{BL} - \gamma_{AB} \quad (2)$$

Since the work of adhesion for substrate A in contact with liquid L is

$$\gamma_{AL} = \gamma_{AV} + \gamma_{LV} - W_{AL} \quad (3)$$

and for substrate B, the work of adhesion in contact with liquid L is

$$\gamma_{BL} = \gamma_{BV} + \gamma_{LV} - W_{BL} \quad (4)$$

we obtain by combining eqs. (1)–(4)

$$W_{AB}^L = 2\gamma_{LV} + W_{AB} - W_{AL} - W_{BL} \quad (5)$$

The thermodynamic work of adhesion may be computed in the following manner by using the method of Fowkes,<sup>12</sup> which relates the polar and nonpolar contributions to the surface tension of solids. For polymers, wettability studies<sup>13</sup> provide a convenient way in which to compute the nonpolar and polar contributions to the solid surface tensions.<sup>14</sup> Table I lists the  $\gamma_S^d$  and  $\gamma_S^p$  values for some commonly used thermoplastics which could conceivably be used for the coating of glass fibers. It is apparent that nylon 66 has the largest fraction of polar interactions, while another polymer thought to be polar, i.e., poly(ethyleneterephthalate), is in fact relatively nonpolar. However, all the polymers are considered to be low surface-energy solids,  $\gamma < 100$  ergs/cm<sup>2</sup>.

TABLE I  
Polar and Dispersion Contributions to the Solid Surface Tensions for a Variety of Polymers and Silica

Polymer	$\gamma_s^d$ , ergs/cm <sup>2</sup>	$\gamma_s^p$ , ergs/cm <sup>2</sup>	$\gamma_s$ , ergs/cm <sup>2</sup>
Nylon 66	33.6	7.8	41.4
Polyethylene	31.3	1.1	32.4
Polystyrene	38.4	2.2	40.6
Poly(dimethylsiloxane)	20.5	1.6	22.1
Poly(ethyleneterephthalate)	36.6	2.9	39.5
Silica	123. <sup>a</sup>	637. <sup>b</sup>	760

<sup>a</sup> The value of 123 ergs/cm<sup>2</sup> is obtained from the physical adsorption of *n*-heptane on silica.

<sup>b</sup> The value of 637 ergs/cm<sup>2</sup> is obtained from adsorption of water on silica and eq. (10).

To obtain suitable values of  $\gamma^d$  and  $\gamma^p$  for silica, we resort to the physical adsorption of vapors on solids when the adsorbate is in equilibrium with the adsorbant. The total reduction in surface energy of the solid resulting from adsorption is  $\Pi_e$ , the equilibrium spreading pressure of the adsorbed film. Harkins<sup>15</sup> has shown that

$$\Pi_e = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \quad (6)$$

Using the expression formulated by Fowkes,<sup>12</sup> we obtain

$$\Pi_e = 2[(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} + (\gamma_{SL}^p \gamma_{LV}^p)^{1/2}] - 2\gamma_{LV} \quad (7)$$

If no polar interactions are operative,

$$\Pi_e = 2(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} - 2\gamma_{LV} \quad (8)$$

From the adsorption of hydrocarbons and water on silica, it is possible to compute reasonable values for  $\gamma_{SV}^d$  and  $\gamma_{SV}^p$ . Fowkes<sup>12</sup> reports the values shown in Table I. Owens<sup>8</sup> has shown that

$$W_{AB} = 2[(\gamma_{AV}^d \gamma_{BV}^d)^{1/2} + (\gamma_{AV}^p \gamma_{BV}^p)^{1/2}] \quad (9)$$

$$W_{AL} = 2[(\gamma_{AV}^d \gamma_{LV}^d)^{1/2} + (\gamma_{AV}^p \gamma_{LV}^p)^{1/2}] \quad (10)$$

$$W_{BL} = 2[(\gamma_{BV}^d \gamma_{LV}^d)^{1/2} + (\gamma_{BV}^p \gamma_{LV}^p)^{1/2}] \quad (11)$$

thereby facilitating a computation of  $W_{AB}^L$  since the appropriate  $\gamma^d$  and  $\gamma^p$  values are available.

Using the approach of Kaelble,<sup>14</sup> values of  $W_{BL}$  are computed and tabulated in Table II for the water-polymer systems. Table II illustrates the calculated work of adhesion,  $W_{AB}$ , for the silica-polymer composite in the absence and

TABLE II  
Thermodynamic Work of Adhesion of the Silica-Polymer Composite in the Presence of Water<sup>a</sup>

Polymer	$W_{AB}$ , ergs/cm <sup>2</sup>	$W_{BL}$ , ergs/cm <sup>2</sup>	$W_{AB}^L$ , ergs/cm <sup>2</sup>
Nylon 66	268.8	108.8	-162.4
Polyethylene	177.6	67.7	-212.5
Polystyrene	211.8	71.6	-182.2
Poly(dimethylsiloxane)	163.8	57.7	-216.3
Poly(ethyleneterephthalate)	219.6	84.1	-186.9

<sup>a</sup>  $W_{AB}^L = 2\gamma_{LV} + W_{AB} - W_{AL} - W_{BL}$ , where  $W_{AL} = 468$  ergs/cm<sup>2</sup> and  $\gamma_{LV} = 72.8$  ergs/cm<sup>2</sup>.

presence of water. What is striking is that for a variety of thermoplastic polymer coatings ranging from the rather polar nylon 66 to (nonpolar) polyethylene, the  $W_{AB}^L$  values are large and negative, indicating a tendency to delaminate spontaneously in the presence of water. Under these circumstances the silica surface would be under direct attack by the water.

To reduce the effect of the large value for  $W_{AL}$ , two approaches may be taken: (a) to form covalent bonds across the interface so that  $\theta$ , the intrinsic failure energy, exceeds the thermodynamic work of adhesion; this could be accomplished by forming Si–O–Si linkages or inducing suitable acid–base reactions; (b) to modify the surface of the silica by covalently bonding species onto the surface to reduce its interaction with water (surface modifier); these species could be of the nonreactive type, just to lower the  $\gamma_S$  value or the reactive type which could covalently bond to the coating (acid–base reaction).

**EFFECT OF STRESS AND HOSTILE ENVIRONMENT ON THE ULTIMATE STRENGTH OF COATED GLASS FIBERS**

A simple theory may be evolved which considers the features of the foregoing analysis and the Griffith approach.<sup>16</sup> Schonhorn and Frisch<sup>17</sup> have shown how this may be developed with regard to the permanence of adhesive joints.

The work  $W$  per unit length required to separate a composite AB may be represented as

$$W = W_S + W_P + W_E + W_T \tag{12}$$

where  $W_S$  is the reversible work required to form new surfaces,  $W_P$  is the work expended in plastic flow,  $W_E$  is the loss in stored elastic energy, and  $W_T$  is associated with the work to desorb chemisorbed sites. Employing a Griffith approach to crack propagation, we may represent the work required to form an elliptical crack of length  $2a$  as

$$W = 2aW_{AB} + W_p^{(a)}(a) + W_p^{(b)}(a) - \frac{\Pi a^2 \sigma_0^2}{E_e} + W_T a \tag{13}$$

where  $W_{AB}$  is the thermodynamic work of adhesion,  $W_p^{(A)}(a)$  and  $W_p^{(B)}(a)$  are assumed to be functions of  $a$ ,  $\sigma_0$  is the applied stress,  $E_e$  is the effective Young modulus, and  $W_T$  is associated with the work to desorb sites and fracture primary valence bonds. At a critical stress  $\sigma_f$  and critical crack length  $2a_s$ , beyond which crack propagation proceeds spontaneously,

$$2W_{AB} + W_p^{(A)'}(a) + W_p^{(B)'}(a) + W_T'(a) - \frac{2\Pi a_s \sigma_f^2}{E_e} = 0 \tag{14}$$

where the primes denote derivatives.

In the presence of a liquid phase, the above argument leads to

$$2W_{AB}^L + W_p^{(A)'}(a) + W_p^{(B)'}(a) + W_T'(a) - 2\Pi a_L (\sigma_f^L)^2 / E_e^L = 0 \tag{15}$$

If the liquid is immiscible with either member of the composite,  $E = E_e^L$  and  $a_s = a_L$ . Combining eqs. (14) and (15) yields

$$\frac{(\sigma_f^L)^2}{(\sigma_f)^2} = \frac{2W_{AB}^L + W_p^{(A)'}(a) + W_p^{(B)'}(a) + W_T'(a)}{2W_{AB} + W_p^{(A)'}(a) + W_p^{(B)'}(a) + W_T'(a)} \tag{16}$$

In the absence of plastic deformation and using eqs. (1)–(5), we obtain

$$\frac{(\sigma_f^L)^2_{AB}}{(\sigma_f)^2_{AB}} = 1 - \frac{2(W_{AB} - W_{AB}^L)}{2W_{AB} + W_T'(a)} \tag{17}$$

If only physical adsorption occurs,  $W'_T \cong 0$  and

$$\frac{(\sigma_f^L)_{AB}^2}{(\sigma_f)_{AB}^2} = \frac{W_{AB}^L}{W_{AB}} \quad (18)$$

For extensive chemisorption or the formation of covalent bonds across the interface,  $W'_T(a) \gg W_{AB}$  and

$$(\sigma_f^L)_{AB} \sim (\sigma_f)_{AB}$$

Once delamination occurs, either  $W_{AB}^L$  is zero, negative, or sufficiently small with respect to  $W_{AB}$  that a modest stress is required to facilitate the separation, the fracture of the glass may be viewed simply as the cohesive strength of the glass in the liquid environment (Fig. 1). Equation (18) becomes modified to

$$\frac{(\sigma_f^L)_{AL}^2}{(\sigma_f)_{AV}^2} = \frac{W_{\text{coh}}^L}{W_{\text{coh}}} = \frac{\gamma_{AL}}{\gamma_{AV}} \quad (19)$$

where  $W_{\text{coh}}$  is the work of cohesion. Using eq. (3) where  $\gamma_{AV} = 760$  ergs/cm,  $\gamma_{LV} = 72$  ergs/cm<sup>2</sup>, and  $W_{AL} = 468$  ergs/cm<sup>2</sup>, we find  $\gamma_{AL} = 364$  ergs/cm<sup>2</sup>. Since  $\gamma_{AL}/\gamma_{AV} \sim 0.5$ , we obtain

$$\frac{(\sigma_f^L)_{AL}}{(\sigma_f)_{AV}} = 0.7 \quad (20)$$

Wang et al.<sup>3</sup> (Fig. 1) and Kurkjian and Krause<sup>18</sup> have shown that epoxy-acrylate-coated fibers show a large initial drop in strength comparable to the drop predicted by eq. (20). Drying of coated fibers exposed to water for short periods of time show a recovery of initial strength. Apparently, insufficient time has elapsed for stress corrosion to occur to any appreciable extent. However, prolonged exposure (~200 days) does produce coated fibers that do not recover their strength upon drying.<sup>3</sup>

### PROGNOSIS FOR OBTAINING PREMATURE FAILURE IN WATER UNDER STRESS

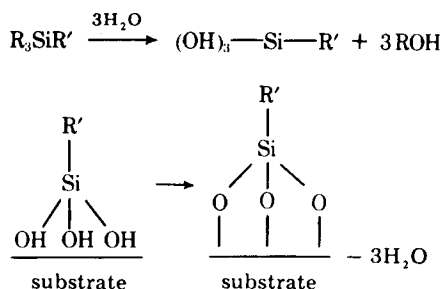
Clearly, from eq. (17) it becomes apparent that to maintain  $W_{AB}^L \sim W_{AB}$  chemisorption must occur across the interface to an appreciable extent. Although the epoxy-acrylate coating may have sufficient interfacial contact. We cite below several choices for precluding water at the interface.

1. To modify the interfacial tension of the silica so as to reduce the  $W_{AL}$  term substantially. If this is accomplished, coatings such as the polyolefins could be used with no delamination. For example, hydrophobic coatings with multiple adsorption sites which lower the solid surface tension to ~20 ergs/cm<sup>2</sup> and rely only on dispersion type interactions would drastically reduce  $W_{AL}$  and maintain  $W_{AB}^L$  equal to  $W_{AB}$ .

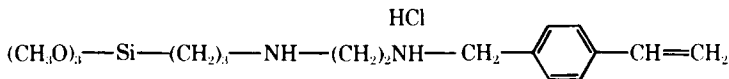
2. Modification of the silica surface with a reactive moiety which will not or chemisorb to the silica, but will have sufficient functionality to react (covalent bonds) to the resin phase.

This is precisely the approach we have taken by using a multifunctional silica coupling agent in a UV-curable epoxy-acrylate coating for glass fibers. Generally, silanes have been used mainly in conjunction with glass, metal,

metal oxide surfaces. However, it is clear from the chemical constitution of many of these species that much is to be gained by using them in conjunction with polymers. Silanes of most general utility have the basic formula  $R_3SiR'$ , where R is a hydrolyzable group,  $(OCH_3)$ ,  $(OC_2H_5)$ , etc., and  $R'$  is a group chosen so as to enter into chemical reaction with one or both of the substrates. Initially, there is hydrolysis followed by chemisorption to the substrate:



Ideally, the  $R'$  group is chosen to be reactive with the coating phase. In the UV-curable epoxy-acrylate, groups containing vinyl unsaturation are polymerized by UV radiation in the presence of a suitable sensitizer. In our study we have employed the cationic styryl functional silane Z-6032<sup>19,20</sup> (Dow Corning, Midland, Mich.):



The silane was blended into the resin prior to application on the glass fiber. To gain the full potential of this coupling agent, our method of application may have to be modified, since the dynamics of wetting may present a serious handicap.

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