

Phenomenological Prediction of Tensile Strength of *E*-Glass Composites from Available Aging and Stress Corrosion Data

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ABSTRACT: A simple model to predict the time- and environment-dependent degradation of tensile strength of unidirectional *E*-glass fiber composites is presented. The model is phenomenological; that is, based on curve-fits of data for the individual time- and environment-dependent behavior, for which data is available in the literature. These include stress corrosion, zero-stress aging, interphase aging, and moisture-dependent matrix stiffness. The ineffective length at fiber break sites is corrected for debonding length. The average strength of the fiber is reduced to account for zero-stress aging. The concept of inert aged strength is proposed to be able to use data developed under different environmental exposure and load-testing conditions. The conditions for which exposure and aging affect the composite significantly are discussed. Different exposure and loading times are accounted for in the model. Model predictions are compared with available experimental data.

1. INTRODUCTION

ALTHOUGH OTHER FIBERS have similar and even superior performance, the main attractive of glass fibers is that they are inexpensive.

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In addition, they have high strength, good fatigue life, good corrosion resistance in most common environments (in conjunction with a polymer matrix) and they are good electrical and thermal insulators. However, there are certain long-term phenomena that need to be accounted for successful application of glass fibers to structures with long expected life cycle, such as civil infrastructure. First, the strength of glass fibers is a function of time when subject to permanent loads (stress corrosion). Second, strength is affected by the environment (aging) even if no stress is applied. Third, the fiber-matrix interphase also ages, which is detrimental for the strength of the composite. Finally, the matrix plasticizes in the presence of moisture, thus impairing the ability to transfer the load among broken and sound fibers.

Numerous studies are being carried out to assess the effect of aging and environmental exposure on strength of composites. Many fiber-matrix combinations, in many laminate stacking sequences, and many hybrid systems involving composites and conventional materials are being investigated experimentally. Aging under exposure is being recorded with and without applied stress. A simple procedure is necessary to interpret these data, one that does not require us to go back to measure parameters that were not measured in the first place.

Most studies report a small number of parameters that are practical to measure. These include the age, conditions of exposure, value of applied stress during exposure, remaining strength after exposure, and conditions of strength testing. In addition, the type of fibers, matrix, and processing technique used to manufacture the samples is reported. More sophisticated data, such as variability of Weibull modulus with age and so on, are not available nor are they feasible to measure because of the complexity of the material and structural systems being studied (e.g., concrete beams wrapped with carbon fabric impregnated and cured in-situ). Most studies on aging do not measure the Weibull modulus of their fibers, nor do they report the gage length used in strength testing. In view of this, a model that does not require such detailed knowledge is useful even if approximate. The proposed model provides a reasonable interpretation of the available data while using nominal values, taken from the literature, for parameters such as Weibull dispersion m , inert strength S_0 , and so on. The remaining parameters (aging a and b , stress corrosion susceptibility N , and so on) can be adjusted from the available data without the need for refined measurements. The proposed approach does not neglect such refined quantities but incorporates their effect via curve-fit of observed behavior for each degradation mechanism. The resulting model evaluates their combined effect on the life of the composite.

Most every new study changes the exposure conditions to better represent practical applications of the materials under study. For example, exposure

conditions for bridge decks and pier piles are completely different. Geographic location also plays a role. Testing conditions also vary broadly because of the particular dimensions and processing conditions of various systems. For example, concrete fiber wraps are usually thin, pultruded structural shapes may contain voids, VARTM-produced bridge decks samples do not resemble anything else, and so on. Therefore, because of the variety of exposure conditions and testing conditions being used, a simple phenomenological model is deemed necessary to allow for comparison among seemingly different studies. Simplicity of the resulting model and the scarcity of sophisticated measurement mandates that the model includes only the mechanistic aspects that most dramatically impact the observed behavior. The present work is developed under such premises. More sophisticated models have been proposed [11,15,21–23,38,39] but so far they have not found its way into applied durability studies because of complexity and the concomitant need for parameters that are either very difficult to measure or for which no measurement technique has been proposed.

Quasi-static tensile strength of unidirectional composites can be predicted by the weakest link model [10,12,44]. The main feature of this model is to consider the influence of fiber average strength, Weibull dispersion, and matrix shear stiffness. The influence of initial fiber damage and creep of the matrix were added in [3,27]. The weakest link model highlights the importance of the shear-lag zone at the fiber break points, since fiber–matrix debond at the same points has a detrimental influence on composite strength. The debond length is a function of time and environment [49]. Available experimental data is used to quantify its effect.

An extensive review of the effects of chemistry, structure, and morphology of the effects of the interphase on the durability of composites is available in [45,47]. Fiber–matrix adhesion has been measured by fragmentation tests [14,17,33,50], micro-bond tests [19], fiber pull-out [40], and micro-indentation [29]. A round-robin study revealed large difference in bond strength among these measurement techniques [41]. Because of this, [49] used the surface energy to quantify the fiber–matrix debonding. The results of their study provide a practical procedure to measure debond length as a function of time and environment of exposure. Such data is incorporated into the predictive model developed in this work.

In addition to time- and environment-dependent debonding length, the influence of time- and environment-dependent fiber strength is integrated into the proposed model, by including the degradation of the average fiber strength as a function of time and environment, which is called zero-stress aging. Zero-stress aging data is available for exposure in air at 0% RH and 100% RH [48], air at 50% RH [18], in distilled water [34], all at 20°C, and 100°C distilled water [34].

Further fiber degradation is caused by stress corrosion. Stress corrosion data is available for exposure in air at 100% RH [35], air at 50% RH [2,37], and in distilled water [2], all at 20°C. The scope of this study is limited to E-glass composites, unidirectional and some laminates. Only data that is available for both, stress corrosion and zero-stress aging, for the same environmental conditions of exposure is used whenever possible.

Fiber stress corrosion reduces the strength of the fiber and thus the strength of the composite. In order to quantify stress corrosion of glass fibers under various environmental conditions, several authors have used a linear fit in logarithmic scale of the time to failure versus applied stress. The stress corrosion susceptibility is computed as the negative of the slope of the linear fit. The data deviates from the linear fit for long testing times, suggesting that other mechanisms act to degrade the fiber beyond the phenomena of stress corrosion [9,13,16].

Fiber strength also reduces when fibers are aged without applied stress, in what is called zero-stress aging. Since zero-stress aging takes place whether or not a stress is applied, the phenomenon takes place concurrently with a stress corrosion test, but it is not noticeable at short times. *This concurrent action of two phenomena causes long-term stress-corrosion data to deviate from a line.* An approximate solution to the interaction problem assumes that stress corrosion along acts for the first half of the time-to-failure and aging dominates that last half of the life of the sample [43]. An alternate solution is presented in this work by using the concept of inert aged strength.

Each of the models, corrosion, zero-stress aging, and debond length, are fitted with experimental data, which are available in the literature. By combining these models into one it is possible to predict the strength of composite fiber bundles and laminates. Predicted values are then compared to independent available experimental data that was not used to fit the parameters of the individual models. The model seems to predict well the strength of unidirectional composites and of some laminates [5], when the strength is controlled by the unidirectional layers in the laminate. Different exposure and loading times are accounted for in the model as required by seasonal exposure of composites in civil infrastructure.

2. QUASI-STATIC FRACTURE

When a fiber breaks, it carries no load at the break point. However, the same fiber is fully loaded a certain distance away from the break point. The load carried by a broken fiber is transferred from the fiber into the matrix, into the adjacent composite, then back into the broken fiber on the other side of the break point. Since stress transfer takes place through the interphase and the matrix, both play a crucial role in the strength of the composite.

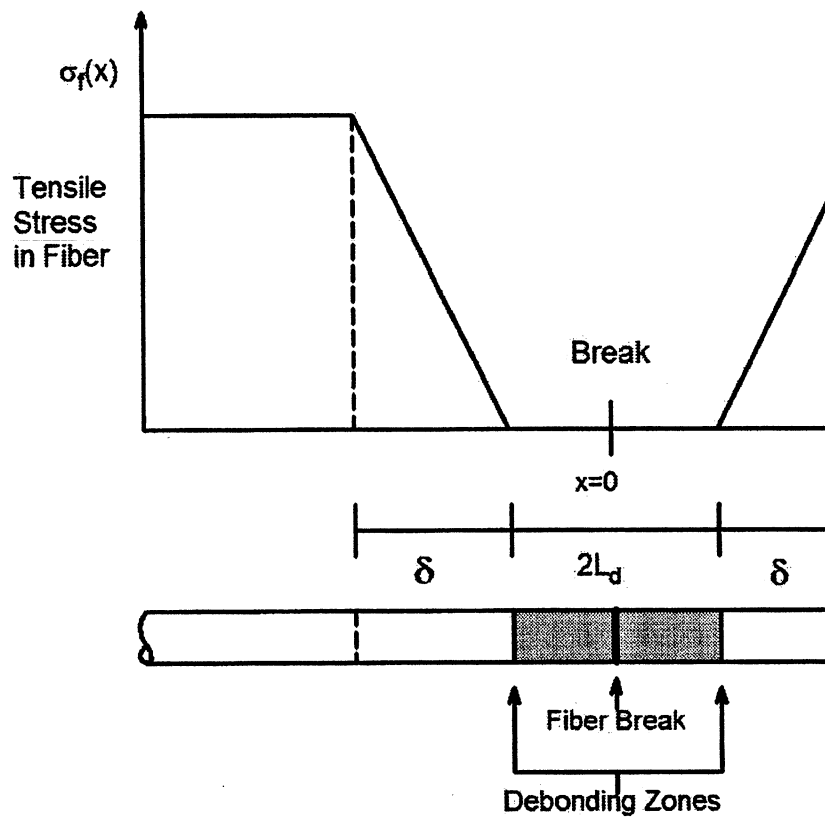


Figure 1. Schematics of a fiber break.

A fiber break is illustrated in Figure 1. A debonded length $2L_d$ was created upon fracture of the fiber. The ineffective length δ is the distance required to recover the stress in the fiber almost to the far-field stress, or $\sigma(\delta) = \phi * \sigma_{f0}$, where $\phi = 0.9$ means a recovery of 90% of the far-field stress σ_{f0} [44].

Fiber strength data follows a Weibull distribution with dispersion m and characteristic value μ . The characteristic value μ of the Weibull distribution is related to the average strength σ of the fibers by the Gamma function [36] as

$$\mu = \frac{1}{L} \left[\frac{\Gamma(1 + 1/m)}{\sigma} \right]^m \quad (1)$$

where L is the fiber length used while testing for average strength σ and Weibull dispersion m [26,31,32,46]. In this work, the Weibull dispersion for E -glass used was $m = 8.89$ [26]. The average strength as function of time is given by the modified stress-corrosion model (Equation (16)) developed in Section 6.

The debonding length $2L_d$ increases the ineffective length to $\delta + L_d$. Using the weakest-link model of [10,12,27,44] but with provision for the debond

length, yields a prediction for the strength of the composite as

$$F_{1t} = [\mu(\delta + L_d)me]^{-1/m} \quad (2)$$

where e is the base of the natural logarithms. For an elastic matrix with shear modulus G_m , the ineffective length can be estimated as [44]

$$\delta = \frac{d_f}{2} \left[\left(\frac{1 - \sqrt{V_f}}{\sqrt{V_f}} \right) \left(\frac{E_f}{G_m} \right) \right]^{-1/2} \cosh \left[\frac{1 + (1 - \phi)^2}{2(1 - \phi)} \right] \quad (3)$$

It can be inferred from the model that the longer the ineffective length the lower the composite strength. As shown in [27,28], the ineffective length can increase due to the viscoelastic reduction of G_m with time, so the long-term modulus $G_{m\infty}$ should be used in conjunction with long-term tests. Another cause for increase of δ is the reduction of shear modulus with moisture. In this work, we used the retention factor ([4] Equation (2.5)) to modify the shear modulus in account of temperature and moisture content as

$$G_m = \left(\frac{T_{gw} - T}{T_{gd} - T_0} \right)^{1/2} G_{m\infty} \quad (4)$$

where T_0 is the reference temperature, T_{gd} is the glass-transition temperature of the dry matrix. The glass-transition temperature of the wet polymer can be estimated ([4] Equation (2.4)) as

$$T_{gw} = (1 - 0.1m_{\text{sat}} + 0.005m_{\text{sat}}^2)T_{gd} \quad (5)$$

in terms of the saturation moisture content, which can be estimated by a power law of the relative humidity RH [8] as

$$m_{\text{sat}} = a \left(\frac{\text{RH}}{100} \right)^b \quad (6)$$

where $a = 0.018$ and $b = 1$ for epoxy matrix composites [8,13].

3. INTERPHASE DEBONDING

The fiber-matrix interphase is a thin layer that bonds the fiber to the matrix. Temperature, time, moisture, and other solvents tend to degrade

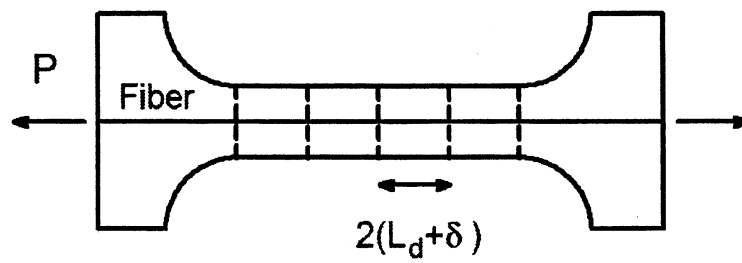


Figure 2. Fragmentation test for determination of fiber-matrix debond length L_d .

the interphase, causing fiber-matrix debond near the fiber breaks. The strength of the composite reduces when the fiber-matrix debond length increases.

The strength of the interphase can be measured in several experimental methods, such as fiber fragmentation [14,17], micro-bond [19], fiber pull-out [40], and micro-indentation [29]. The fragmentation test consists of a single fiber embedded in a polymer sample, as depicted in Figure 2. The sample is loaded in tension and fiber breaks are observed. The breaks reach saturation at a distance $\delta + L_d$ because the matrix is unable to load the fiber unless it has room to transfer the load by shear. Then it is possible to measure the debonding length from the measured saturation spacing and knowledge of δ from Equation (3). Also, it is possible to directly measure the debonding length by optical observation [49]. By measuring the debonding length as function of time, it is possible to infer the degradation of the interphase due to aging. Debonding length as function of time for *E*-glass fibers in epoxy matrix, immersed in 95°C water are reported in Table 3 from [49]. The data was fitted with the following equation

$$L_d = \kappa + \lambda \ln(t) \quad (7)$$

where $\kappa = 1822 \times 10^{-6}$, $\lambda = 179 \times 10^{-6}$, time is in days and length in meters. Equations (2)–(7) can then be used to predict the time-dependent strength of unidirectional *E*-glass composites, provided the time- and environment-dependent strength of the fibers σ_{av} is known. A model for fiber strength is developed in the next sections.

4. FIBER ZERO-STRESS AGING

Zero-stress aging is defined as the reduction of strength when no stress is applied during the time of exposure to a given environment. For determination of zero-stress aging, samples are aged in a given environment

at constant moisture, temperature and so on; then load-tested for strength. No load is applied during the time of exposure. The data is then fitted with

$$\sigma(t) = \sigma_0(1 + \alpha t_a)^{-\beta} \quad (8)$$

where σ_0 is the strength at time zero, at the environment of exposure, α and β are empirical constants adjusted to fit the experimental data. For example, fiber strength aged in various moisture environments is shown in Figure 3, fitted with Equation (8).

In the sequel it is necessary to distinguish between exposure and load-testing conditions. In most studies available in the literature, load testing takes place after exposure to determine the remaining strength, due to practical reasons. Load testing is not necessarily performed under identical environment as during aging. Some of the available data have been load-tested at the conditions of exposure while other were tested at room temperature after removing the samples from the environment of exposure. The initial strength σ_0 (at $t=0$) is a strong function of the environment at which the sample is load-tested to failure, and it is obviously independent of subsequent aging. This is evident in Figure 3, where the initial strength (at $t=0$) varies from one data set to the next even though they are all *E*-glass fibers.

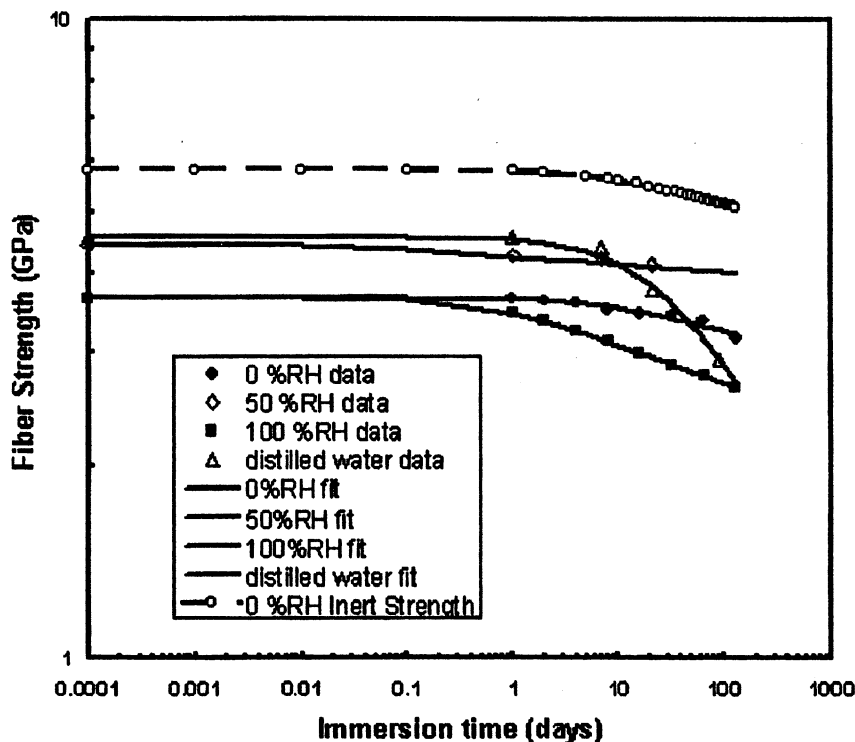


Figure 3. Zero-stress aging data and fit for all environment exposures.

Optical fibers aged at 20°C were load-tested at inert conditions (zero moisture and very low temperature), and at room temperature ambient (RTA) conditions yielding data of “inert strength” and “RTA strength”, respectively. The inert strength of aged fibers fits an equation similar to Equation (8), namely

$$S(t) = S_0(1 + \alpha t)^{-\beta} \quad (9)$$

where S_0 is the inert strength at time zero, load-tested at inert conditions, α and β are the same empirical constants determined by fitting Equation (8) to the data load-tested at RTA. That is, the curves represented by Equations (8) and (9) are parallel on a log-log plot. The ambient strength was measured at 20°C and the inert strength in liquid nitrogen (LN2) at -196°C [16].

No aged inert strength data exists for *E*-glass but the initial inert strength of *E*-glass is $S_0 = 5.817$ GPa, as measured in [6]. Based on the observations for optical fibers, we postulate that for *E*-glass fibers, the effect of environment during load-testing is independent of the age of the sample. In other words, the reduction of strength from its inert value S to its value when tested at other environment should be independent of the age of the sample, resulting in a parallel shift of strength, downward in log-log scale. This is illustrated in Figure 3 by the two curves corresponding to 0% RH. The inert strength curve for any condition of exposure can be obtained by an upward shift of the curve obtained by load testing at RTA.

The only effect of inert load-testing conditions is to shift up the strength curve by a constant. The shift can be easily computed for any material if the inert strength at zero time S_0 is known. Then, the inert aged strength curve can be obtained from available data as follows. First, determine the constants α and β by fitting Equation (8) using available data $(\sigma(t), t)$ of aged fibers which were load-tested at the condition of exposure, at RTA, or at any other condition. Then, simply use the same constants α and β into Equation (9). The value of the inert strength at time zero S_0 has to be determined independently by load-testing un-aged samples at inert conditions, but this data is available for *E*-glass [6,7]. *Therefore, all the curves available in the literature can be shifted to inert condition in order to compare them with each other.*

5. FIBER STRESS CORROSION

Stress corrosion, also called static fatigue, stress rupture, or delayed failure, represents the loss of strength as a function of time under a constant applied stress. The mechanism of failure of glass fibers is dominated by the growth of cracks and defects in the fiber. Surface energy is required to

produce the new surface associated to the growth of a crack. The external loads or the strain energy stored in the fiber can provide such energy. The Griffith energy approach states that a crack will grow only if the total energy of the system decreases [1]. The critical condition of imminent growth is given when the rate of change of the total energy is zero. In this case, the rate of change of the surface energy W_s with respect to crack length a equals the rate of change of potential energy W_p , which is the sum of the external work done by the applied loads and the strain energy stored in the fiber. The surface energy can be written as twice the area of the crack times the surface energy density γ_s , recognizing that two mirror images are produced when a crack opens. Therefore, the rate of change of surface energy with respect to crack area is $2\gamma_s$. The surface energy density is a material property that represents the ability of the material to resist crack formation. In fracture mechanics, it is called strain energy release rate, and it is proportional to the fracture toughness of the material.

The stress intensity represents the severity of the stress concentration at the crack tip. It is a function of the load, the geometry of the crack, and the geometry of the body in which it is immersed. For a crack in a uniaxial, uniform stress field we have [1]

$$K_I = Y\sigma\sqrt{\pi a} \quad (10)$$

where a is the crack length, σ is the far field stress, and Y is a geometric factor.

There are two mechanisms that bring about fracture as a function of time, the continuously decreasing surface energy density of the material and the continuous growth of the crack length that increases the stress intensity at the crack tip. The former effect is a strong function of the environment that corrodes the fiber, and we call it aging. The latter effect is a strong function of time and stress, since time is necessary to allow cracks to grow until they reach a critical dimension, and we call it stress corrosion.

A crack will grow if the stress intensity exceeds the fracture toughness of the material, which is proportional to the surface energy. The surface energy density of the material decreases as a function of time due to corrosion induced by the environment [5–7]. Eventually, the surface energy density falls below the threshold and fracture occurs. Such effect is accounted for in this work by a curve-fit of remaining strength of aged, unstressed fibers (see Section 4).

Since stress intensity is proportional to crack length, cracks grow (under permanent load) until they reach a critical dimension that causes fracture [20]. The slow growth of cracks is called stress corrosion and it is modeled

in this section with the slow crack model [1]. The relationship between crack growth velocity V and stress intensity K_I is Paris law:

$$V = \frac{da}{dt} = A K_I^N \quad (11)$$

where A and N are constants, N is called stress corrosion susceptibility. Proof of this model cannot be obtained by direct observation since it is nearly impossible to measure crack velocity. However, an indirect proof can be offered if it can be shown that A and N are constants, and they can be obtained from experimental data.

Solving Equation (10) for the crack length a and taking a derivative with respect to crack intensity yields an expression for the increment of crack length da , which can be set equal to da from Equation (11) to yield

$$\frac{dt}{dK_I} = \frac{2K_I}{\sigma^2 Y^2 \pi A K_I^N} \quad (12)$$

The time to failure is obtained by integrating over the range of stress intensity factors [16,25,43], as

$$t_f = \frac{2}{\sigma^2 Y^2 \pi A (2 - N)} [(K_{IC})^{2-N} - (K_{II})^{2-N}] \quad (13)$$

where the limits of integration are the initial stress intensity at time zero K_{II} and the final stress intensity at fracture K_{IC} . The latter is the fracture toughness of the material, which is proportional to the surface energy density. For typical values of susceptibility N (on the order of 10–20), the first term in the square bracket of Equation (13) is much smaller than the second and thus can be neglected [25]. Zero-stress aging can be interpreted either as a reduction of K_{IC} [23] or a reduction of the average strength of aged, unstressed fibers. We chose the latter because it leads to a simple curve-fit of available data (Section 4). Such data and the curve-fit for them are available in the literature. If on the other hand we were to model zero-stress aging as a change in K_{IC} , the first term in Equation (13) could not be neglected over long times [23]. Then, Equation (15) would not give a line in log–log scale, and the stress susceptibility could not be defined as the slope of such line. For our purpose, this would render impractical the classical stress-corrosion theory [34,35,37], which provides a credible interpretation of over fifty years of data (under conditions for which zero-stress aging is negligible, i.e., RTA). Therefore, we chose to leave the classical stress corrosion theory unchanged, and to model zero-stress aging as a reduction of the average strength of the fibers.

Since stress intensity is directly proportional to applied stress, the ratio of initial stress intensity to initial applied stress is the same as the ratio of fracture toughness to inert strength S , or

$$\frac{K_{Ii}}{\sigma} = \frac{K_{Ic}}{S} \quad (14)$$

That is, the fiber would break at time zero under inert environment at a stress S when the stress intensity equals the inert fracture toughness of glass K_{Ic} . The inert strength S and corresponding inert fracture toughness of glass K_{Ic} must be measured under dry conditions to avoid the detrimental influence of moisture. The most effective way of accomplishing perfectly dry conditions is to test at very low temperatures or in vacuum [43]. Using Equation (14), we can write the time to failure as

$$t_f = [BS^{N-2}]\sigma^{-N} = C\sigma^{-N}$$

$$B = \frac{2}{Y^2\pi A(N-2)K_{Ic}^{N-2}} \quad (15)$$

In this work, Equation (15) is called conventional stress corrosion (CSC) model. *A power-law regression of time-to-failure versus failure-stress data yields the susceptibility N and the coefficient C .* The coefficient B can be computed from C as $B = CS^{2-N}$. Stress-corrosion data of *E*-glass at 50% RH from two sources [2,37] is displayed in Figure 4.

Since the value of N can be found from time-to-failure versus applied stress data, it is not necessary to know the geometric factor Y in Equation (10) and the crack-velocity coefficient A in Equation (11). We postulate here that the inert strength must be independent of time for Equation (15) to truly represent the behavior of a material for which loss of strength is controlled only by slow crack growth according to Equation (11). Because of zero-stress aging (Section 4), the inert strength of the material remains constant only for a limited time. Therefore, the initial inert strength at time zero S_0 must be replaced for S in Equation (15) while determining the constant susceptibility N and coefficient C from stress corrosion data. This allows for a univocal definition of susceptibility N , which must be independent of time. *The inert strength of the material cannot change during the time interval used to compute N .* This imposes a restriction on the stress corrosion data that can be used to compute N , as we shall elaborate in Section 6.

The complete set of stress-corrosion data for *E*-glass at 100% RH from [35] is displayed in Figure 5. No data were censored in any way. The line fit

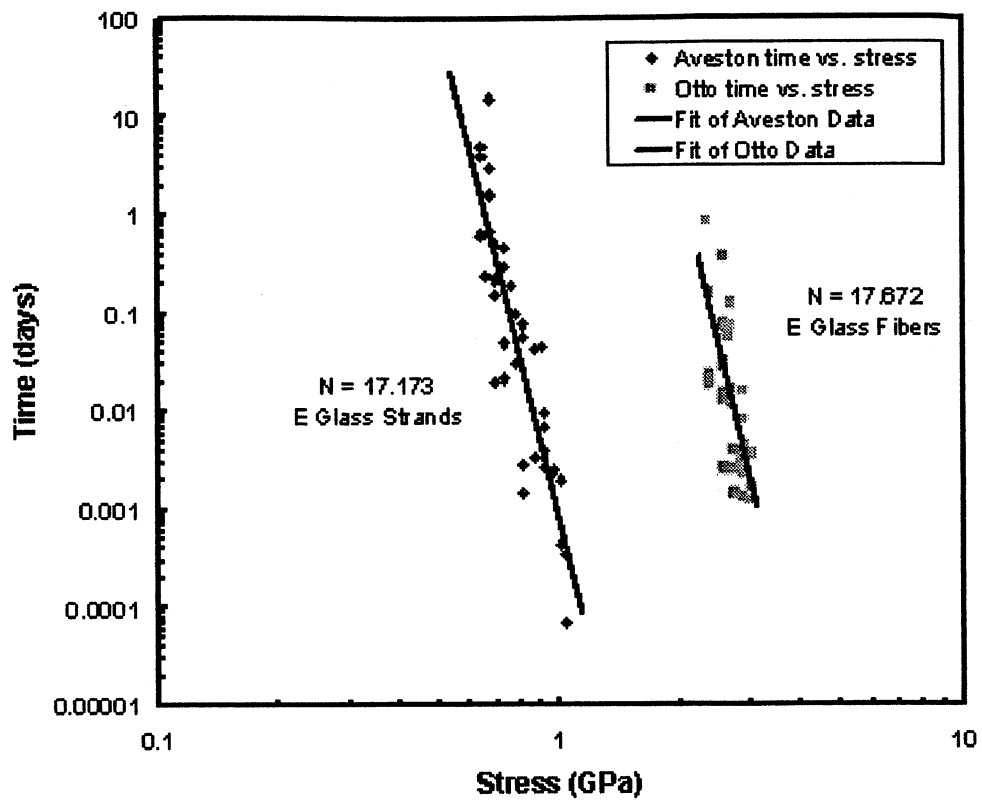


Figure 4. Stress corrosion susceptibility for 50% RH at 20°C.

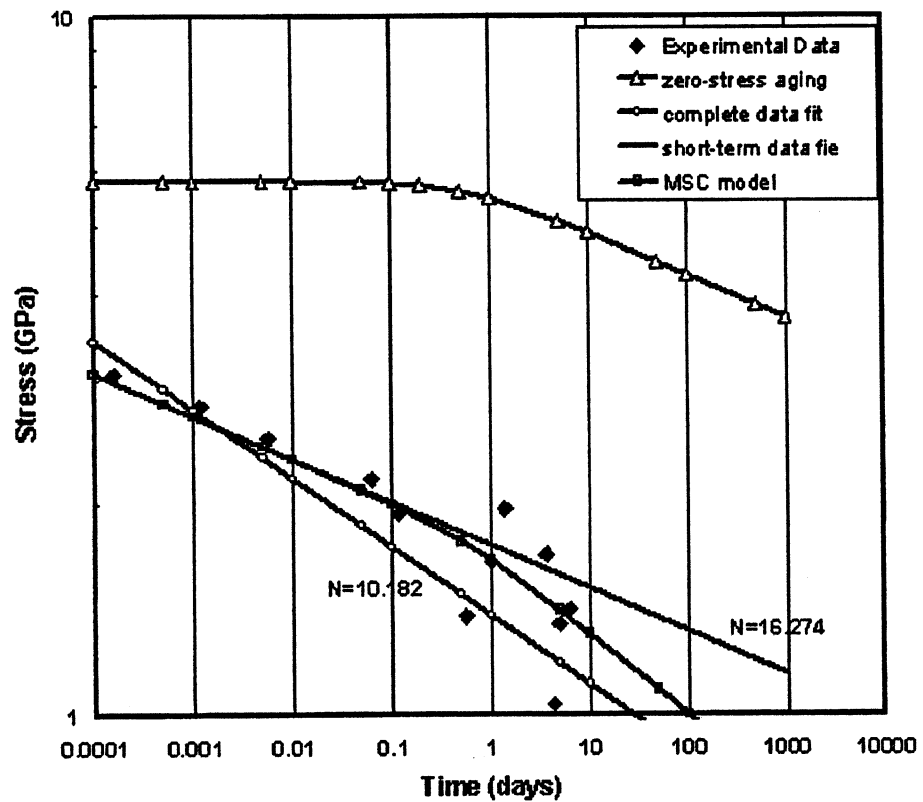


Figure 5. Stress corrosion susceptibility for 100% RH at 20°C.

was performed using short-term data, that yields $N = 16.274$. When longer test data is used, the incorrect value of susceptibility to stress-corrosion decreases to $N = 10.182$. Similar deviations from a straight line have been observed previously for optical fibers [16,42]. A reduction of N means a smaller time to failure for any given applied stress. *The parameters B and N are dependent on the environment of exposure but they must be independent of time.* Therefore, a second mechanism must be acting to further degrade the fiber. Since zero-stress aging takes place independently of the applied stress, it must be taking place concurrently with stress corrosion test. Therefore, all stress corrosion tests of long duration are affected by zero-stress aging, unless the environment is so benign (e.g., RTA) that zero-stress aging is not noticeable. *Since zero-stress aging is negligible at short times, the stress corrosion susceptibility can be found when short-term data is used.*

6. SIMULTANEOUS FIBER STRESS CORROSION AND AGING

To account for stress corrosion and zero-stress aging in a unified model, we replace the aged inert strength $S(t_a)$ as a function of aging time t_a from Equation (9) into the classical stress corrosion Equation (15). Then, we solve for the stress to obtain the proposed modified stress corrosion (MSC) model as

$$\sigma(t_f, t_a) = \left[\frac{t_f}{BS_0^{N-2}(1 + \alpha t_a)^{-\beta(N-2)}} \right]^{-1/N} \quad (16)$$

where t_f is the time to failure. Note that the values of N and B were determined with Equation (15); that is, with the short-term data for which $S = S_0$ is a constant. The susceptibility N represents the stress corrosion phenomena, which does not change for the entire life of the fiber. Any long-term reduction of fiber strength not accounted for by stress-corrosion is accounted for by a reduction of the inert strength S according to the zero-stress aging model Equation (9). Note further that no testing is necessary at inert conditions since only the values of α and β need to be found from aging data. The initial inert strength is known from un-aged tests at inert condition, which are available [6].

Since all the available stress corrosion data was obtained at constant environmental exposure, the aging time is the same as the time to failure ($t_a = t_f$). However, from practical applications of composites, aging at adverse exposure conditions may take place for a reduced length of time. For example, if seasonal conditions expose the material to high moisture only for a fraction of the service lifetime of the structure, then $t_a < t_f$.

This is particularly important since aging is only detrimental for severe conditions of exposure, as it is demonstrated using available experimental data next.

An environment at 20°C and 50% RH is known as RTA. Two sets of stress corrosion data are available for RTA exposure, from [2] for fiber strands and [37] for individual fibers. The load on a strand was used to compute the fiber stress dividing by the area of a strand, given as 0.0564 mm². The susceptibility coefficients N and B obtained by fitting Equation (15) are reported in Table 1 and the fit is shown in Figure 4. Zero-stress aging data at RTA is available in [18]. The parameters α and β are obtained by fitting Equation (8) to the data shown in Figure 3. The values are reported in Table 2. For RTA exposure, the zero-stress aging is negligible. The modified stress corrosion Equation (16) results in very small deviation from the straight line predicted by classical stress corrosion. At RTA exposure, the susceptibility N is independent of time. It can be seen in Figure 4 that very similar values of stress corrosion susceptibility N were obtained even though the time of exposure are different for the two sets of data.

Stress corrosion data for exposure at 20°C and 100% RH are available from [35]. The susceptibility coefficients N and B obtained by fitting Equation (15) are reported in Table 1 and the fit is shown in Figure 5.

Table 1. Stress corrosion parameters for each environmental exposure.

Environment	Relative Humidity (%)	Temperature (°)	N	B (Pa ² s)	Reference
Air	50	20	17.670	5.355E16	[37]
Air	50	20	17.173	1.82E16	[2]
Air	100	20	16.046	9.151E14	[35]
Distilled water	–	20	14.98	2.011E9	[18]

Table 2. Zero-stress aging parameters for each environmental condition.

Environment	Relative Humidity (%)	Temperature (°)	α (1/s)	β	Reference
Air	0	20	1.446E-6	0.04712	[48]
Air	50	20	3.880E-4	0.01248	[37]
Air	100	20	1.770E-5	0.06189	[48]
Distilled water	–	20	4.973E-7	0.27980	[18]
Water	–	100	7.490E-4	0.23192	[34]

Table 3. Debonding length L_d of E-glass-epoxy in 95°C water as function of time [49].

Immersion Time (Days)	Debonding Length L_d (μm)
0	35
0.01042	1934
0.02083	1379
0.04167	1710
0.08333	5200
0.58333	1734
4.08333	792
6.0	4854
13.0	7144
14.0	5292

Note that only the short-term data can be fitted with a line. The slope of such line is the susceptibility $N = 16.274$. The complete data, including long-term data, shows signs of zero-stress aging which results in a poor linear fit and an artificially lower value of $N = 10.182$. Therefore, we propose that N be computed with stress-corrosion data for samples that fail before zero-stress ageing becomes noticeable. The zero-stress aging curve in Figure 5 reveals noticeable aging by 1 day. Therefore, only data corresponding to applied stress bins for which all samples failed by 1 day were considered for the computation of the susceptibility $N = 16.274$.

Stress corrosion tests are done with many replicates at the same stress, which give a broad scatter of time to failure data. All data corresponding to the same applied stress is grouped into a data bin. The number of data points in each bin is not the same. Therefore, the susceptibility N should be calculated by a regression of the actual data, not of the average time to failure for each applied stress. The median time-to-failure values are shown in Figure 5 to avoid cluttering, but the slopes were computed using all the data. In terms of the median time-to-failure, the short-term data included all data points up to 0.2 days.

Zero-stress aging data at 100% RH is available in [48]. The parameters α and β are obtained by fitting Equation (8) to the data shown in Figure 3, then shifted to the inert condition and shown in Figure 5. The values are reported in Table 2. For 100% RH exposure, zero-stress aging is noticeable. The modified stress corrosion Equation (16) results in a reduction of 27% at one year from the strength predicted by classical stress corrosion. Stress corrosion data for exposure at 20°C immersed in distilled water are available from [18]. Zero-stress aging data in distilled water is available in [2]. Since zero-stress aging is significant for distilled water exposure, the modified

stress corrosion Equation (16) results in a reduction of 50% at one year from the strength predicted by classical stress corrosion.

The susceptibility decreases with moisture content, as shown in Table 1. A decreasing value of N represents faster reduction of strength with time and shorter time-to-failure for a given stress. Stress corrosion alone cannot model the observed reduction of strength at long times. Zero-stress aging, which is negligible for short time and for low moisture content, becomes important at long times and high moisture. In addition, time and moisture degrade the fiber-matrix interphase, which results in longer debonding lengths and consequent further reduction of composite strength, as modeled in Section 3. Therefore, the proposed composite model incorporates the degradation of the fiber and interphase, so that it can be used to predict the long-term strength of composites. Predicted values are compared next with available data for composite strands, laminates, and hand lay-up samples.

7. COMPARISON WITH COMPOSITE EXPERIMENTAL DATA

All the parameters of the model have been determined in previous sections. The stress corrosion susceptibility N and constant B were determined from fiber data for each type of environment (50 RH, 100% RH, water, all at 20°C) and reported in Table 1. The inert strength of E -glass is a known constant $S_0 = 5.817$ GPa. The parameters α and β of the zero-stress aging model were determined from fiber data for each type of environment and reported in Table 2. Experimental data required for determination of the parameters κ and λ of the debond-length model Equation (7) are available only for water immersion at 95°C, so this data will be used for the predictions. Since this is a more severe environment than the environments for which susceptibility and aging data are available, they are likely to result in conservative estimates of composite tensile strength.

Data and model predictions for unidirectional E -glass strands in epoxy matrix ($G_m = 1.130$ GPa) are shown in Figure 6. The samples were aged under load in distilled water at 20°C [2]. The fiber volume fraction is $v_f = 0.5$. The prediction by Equation (2), including stress-corrosion and aging (MSC, Equation (16)) as well as debond (Equation (7)) does match the data very well for the whole range of time. Conventional stress-corrosion cannot predict the long-term data accurately. It is worth emphasizing that the curves are not empirical fits of the data shown, but true predictions; that is, based on independently obtained fiber and interphase data.

Data from two sources were combined in Figure 7. First, unidirectional hand lay-up E -epoxy samples were aged in water at 20°C [24]. The fiber

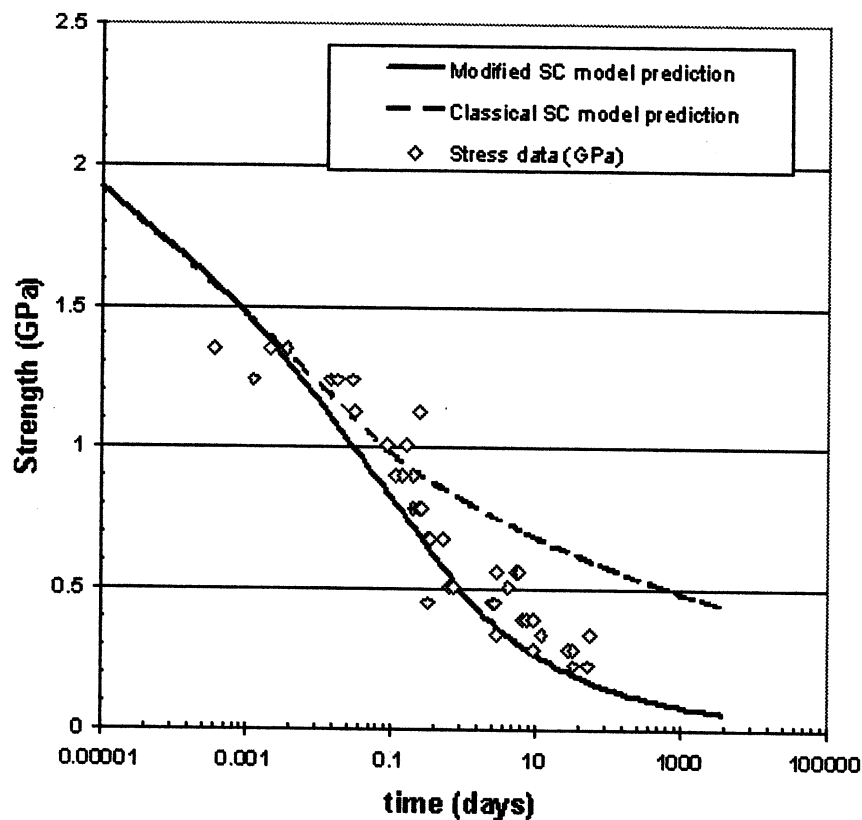


Figure 6. Experimental data and model predictions for E-glass-epoxy strands in distilled water, 20°C.

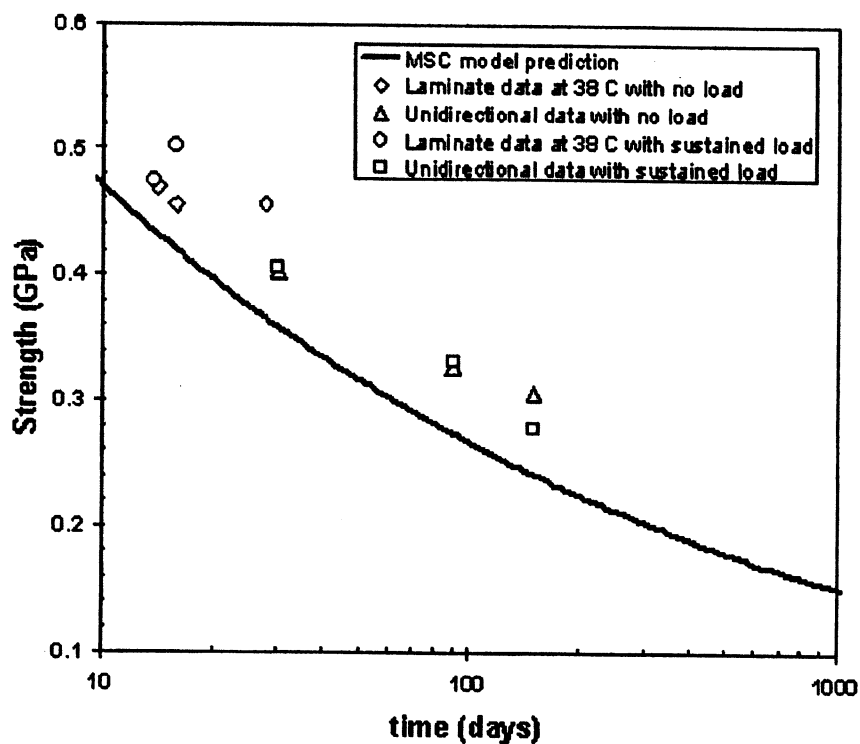


Figure 7. Laminate E-glass-vinylester and hand lay-up E-glass-epoxy data and model predictions.

volume fraction is $v_f=0.47$ and the shear modulus of the matrix is $G_m=1.274$. Some samples were unloaded during aging, while others were loaded during aging. All samples were then removed from the aging environment and tested at RTA conditions. The effect of sustained load was small and could be observed only past 100 days.

Next, laminated $[0/90/45/-45]_{2s}$ *E*-glass-vinylester samples were aged in water at 38°C. Some samples were not loaded during aging while others were loaded, then tested [5]. The effect of sustained load was not significant. The fiber volume fraction is reported in the range 0.48–0.57, so 0.525 was used in the analysis along with a shear modulus for the matrix $G_m=1.232$ GPa. Classical laminate theory was used to distribute the stress on the laminate into the layers and into the appropriate orientations. The laminate was assumed to fail when failure was predicted in the 0° layers. That is, it was assumed that while the 90 and 45 layers contribute to stiffness, they do not control the ultimate failure of the laminate. The MSF model (Equation (16)) was used to compute the average fiber strength to be used in Equation (2). The model matches the data reasonably well taking into account that fiber data, debond data, and composite data were measured on separate studies. Furthermore, the model predicts the correct trend (Figure 7).

8. CONCLUSIONS

The weakest link model was modified to include time- and environment-dependent reduction for fiber strength and fiber–matrix debonding length. The concept of inert aged strength was introduced to allow for the use of aging fiber data from various sources obtained in dissimilar conditions. The shift to inert conditions also allows for future aging studies to perform load-testing at ambient conditions rather than expensive load-testing at the conditions of exposure or at inert conditions. The same concept allowed us to derive an exact expression for the modified stress corrosion model. The fiber model seems to capture the essential features of stress corrosion and aging, which are displayed in long-term stress corrosion data of *E*-glass fibers. The composite model can predict the correct magnitude of strength and correct rate of degradation of composite samples when the environment of exposure is severe enough to trigger the same degradation mechanisms in the composite and the naked fiber. For mild conditions of exposure, the polymer matrix seems to protect the fibers resulting in degradation rates for the composite that are slower than for the fibers subjected to the same environment. Incorporation of a diffusion model is envisioned to be able to compute the actual environment inside the composite.

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