BLISTERING OF GRAPHITE/POLYMER COMPOSITES GALVANICALLY COUPLED WITH METALS IN SEA WATER

By

Richard Brown
Thomas J. Rockett
Wayne C. Tucker
Shravan K. Miriyala

Materials Laboratory, Chemical Engineering
The University of Rhode Island
Kingston, RI 02881

A 1993 ANNUAL TECHNICAL REPORT

FOR

Dr. A. John Sedriks
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

ONR Contract # N0001491J1328

26pg

BLISTERING OF GRAPHITE/POLYMER COMPOSITES GALVANICALLY COUPLED WITH METALS IN SEA WATER

By

Richard Brown
Thomas J. Rockett
Wayne C. Tucker
Shravan K. Miriyala

Materials Laboratory, Chemical Engineering
The University of Rhode Island
Kingston, RI 02881

A 1993 ANNUAL TECHNICAL REPORT

FOR

Dr. A. John Sedriks
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

ONR Contract # N0001491J1328

ABSTRACT

The effects of bulk oxygen partial pressures on the galvanic blister growth in carbon fiber vinyl ester composites were studied. Varying oxygen concentrations significantly affected the corrosion currents when the samples were subjected to a cathodic potential of -900 mV (SCE). An increase in oxygen concentration proportionately increased the corrosion currents which is an almost certain evidence that oxygen reduction reaction occurs on carbon fibers in the composite. The blister detectability times decreased or the blister growth rates increased with increasing oxygen concentration.

Comparison of short beam apparent interlaminar shear strength test results of virgin, water saturated, electrolyte saturated and cathodically polarized (until blistered) samples of carbon fiber vinyl ester (CFVE) composite, revealed little changes in the interlaminar shear strength.The results indicated that galvanic blistering of CFVE samples subjected to galvanic conditions (applied potential: -900 mV (SCE)) for 7 days did not affect the apparent interlaminar shear strength of the composite. The implication of this result is that only galvanic blisters form only at surface layers for the given electrochemical conditions and the interior layers are protected from blistering because interior layers were depleted from oxygen. This depletion of oxygen in the inner layers is as a result of entire consumtion of available dissolved oxygen at the surface carbon layer (as evidenced by the diffusion controlled current). This must be further verified by conducting strength tests of samples subjected to cathodic potentials for longer periods (several months). A modification to the blister nucleation theory was suggested following the ILSS test results.

A semi-empirical model was developed to predict galvanic blister growth rates. The model is based on the galvanic blistering mechanism proposed by the authors.

TABLE OF CONTENTS

ANNUAL TECHNICAL REPORT 1992-93

1. INTRODUCTION

Several carbon fiber polymer composites undergo blistering when they are coupled to metals steel and aluminum in sea water or salt water. This blistering was linked to galvanic interactions of carbon fibers under these conditions (Tucker, 1989; Miriyala, 1991) and is termed *galvanic blistering or electrochemical blistering*. The blisters contain liquids with pH 14 and the blister opening was along the fiber/matrix interface (Miriyala, 1992). The research goals that constitute major part of the past year's efforts were:

(1) THE STUDY OF THE EFFECTS OF OXYGEN PARTIAL PRESSURES ON BLISTERING RATES: According to the galvanic blistering mechanism proposed by the authors (Miriyala, 1993), the galvanic blisters contain sodium hydroxide solution formed as a result of electrocatalytic reduction of oxygen on carbon fibers. As a consequence, partial pressures of oxygen in bulk electrolyte should affect the galvanic blistering rate and the study is necessitated since in actual sea environments highly aerated zones can be encountered where these materials are used. Therefore, the effects of oxygen partial pressures in the electrolyte on the galvanic blistering rates were investigated.

(2) THE STUDY OF THE EFFECTS OF APPLIED CATHODIC POTENTIAL ON THE INTERLAMINAR SHEAR STRENGTH OF THE COMPOSITE: The blisters nucleate and grow along the fiber/matrix interface according to the galvanic blister nucleation theory proposed by the authors. These defects introduced in the composite may affect the ultimate mechanical properties of the composite. The effects of applied cathodic potential (which is equivalent to a galvanic coupling) on the interlaminar shear strength of a composite laminate were studied.

(3) A SEMI-EMPIRICAL MATHEMATICAL MODEL TO PREDICT THE GALVANIC BLISTER GROWTH: A mathematical analysis of the galvanic blistering would help in verifying the theory of galvanic blistering mechanism and to quantify several elements in the blistering process. The ultimate goal of modeling is to predict accurately the blister growth rates as a function of time.

2. MATERIALS STUDIED

An orthotropic laminate with unidirectional T300 carbon fiber tapes in a DERAKANE™ 470-36 vinyl ester matrix (CFVE) was studied. The laminate was characterized by a fiber volume fraction of 26%. An attempt was made to use samples made by casting vinyl ester resin on flat, polished glassy carbon substrates to measure adhesive strength under shear. However, large residual stresses at the interface caused debonding of the cast film from the substrate and precluded testing of these samples.

3. EFFECTS OF VARYING BULK OXYGEN PARTIAL PRESSURES ON GALVANIC BLISTERING

3.1 INTRODUCTION

The cathodic reaction on many carbon surfaces in the presence of an aqueous electrolyte is the electro-catalytic reduction of oxygen to hydroxyl ions (Kinoshita, 1988).

The high pH of blister fluids suggests that this cathodic reaction occurs also on the surface of carbon fibers in a carbon fiber polymer composite. However, this needs further verification and is the theme of this chapter. Comparison of potential-current profiles obtained for samples of carbon fiber woven fabric and a CFVE, in a previous work by the authors, strongly supported the above cathodic reaction in cathodically polarized CFVE (Miriyala, 1992). The study of the effects of dissolved oxygen partial pressures in electrolyte on the rates of galvanic blistering may yield a positive correlation that would indicate a cathodic oxygen reduction reaction and help explain how blistering rates are affected by changes in the oxygen concentrations. The study of the influence of oxygen partial pressures on galvanic blistering is also important from a practical stand-point. There are regions of highly aerated zones encountered in marine environment such as boat propeller regions where thorough mixing or churning of sea water occurs, splash zones, etc., and the damage of carbon composites used in these regions could be exacerbated as would the associated anodic corrosion driven by the composite.

3.2 EXPERIMENTAL PROCEDURES

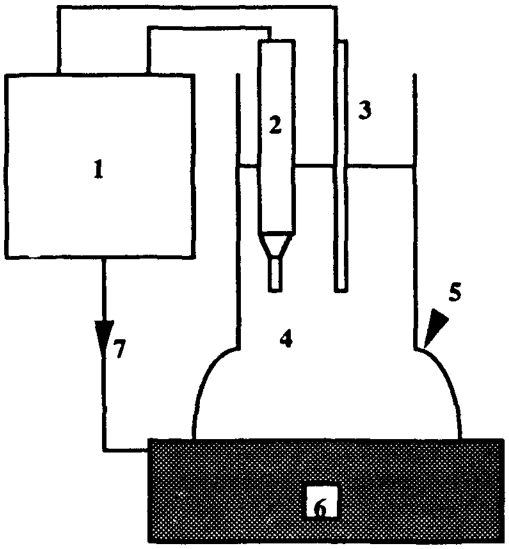
Samples of dimensions 6 cm x 6 cm x 3 cm were cut from a laminate of 3 cm thick. The resin-rich faces of the samples were exposed to the electrolyte. The composite has several defects in the form of air bubbles which formed during processing. The exposed area is a 5 cm diameter circular area.

The electrolyte used in the study is a 3.0 weight percent sodium chloride solution. Three different oxygen partial pressures in the electrolyte were chosen: (a) dissolved oxygen at 1 atmosphere by bubbling pure oxygen gas through the electrolyte; (b) dissolved oxygen at 0.2 atm. from dissolved air at one atmosphere in the electrolyte. (c) dissolved oxygen at 0.06 atms. attained by first preparing sodium chloride solution from a freshly boiled and cooled de-ionized, distilled water (this will drive away all dissolved gases) and subsequent bubbling of nitrogen gas. The electrolyte was not changed during the period of experiments. The experiments were conducted at average ambient temperature of 70°F.

The oxygen concentrations were measured using a ORION Model 97-08-00 electrode. Since, the instrument can measure oxygen concentration up to 14 ppm only, the oxygen concentration at higher partial pressures i.e. oxygen concentration at 1 atmosphere was estimated by extrapolation. The activity coefficient was assumed constant in estimating the concentration of oxygen at the partial pressure. Oxygen partial pressures used and the corresponding concentrations are given in the following table:

Oxygen Partial Pressures (atmospheres)	*Concentrations (parts per million by weight)*
1.00 (high)	41.25 (estimated)
0.20 (medium)	8.25 (measured)
0.06 (low)	2.25 (measured)

The electrochemical experimental set-up is shown in Figure (1). The cathodic potential applied to the samples was -0.9 volts versus a standard calomel electrode (SCE). A EG&G PARC model 273 and model 363 potentiostats were employed to apply and maintain the potentials.



1. potentiostat; 2. standard calomel reference electrode; 3. platinum counter electrode; 4. 3% sodium chloride solution; 5. glass tube with O-ring; 6. carbon fiber reinforced polymer composite sample; 7. electron flow direction.

Figure 1. Electrochemical Experimental Setup

Current values were recorded at different exposure times. Visual examination of samples was also conducted at these times to examine for blisters. The time for blisters to grow to a diameter approximately 1 mm size was arbitrarily termed as the *blister detectability time* (BDT). The BDT is used as a criterion to compare the rate of blistering of the samples. Lower the BDT, the greater is the rate of blister growth and *vice-versa*. The blister detectability times were recorded for the three samples.

3.3 RESULTS AND DISCUSSION

A cathode supports an electrochemical reaction in which electrons are consumed. The oxygen reduction reaction on a carbon cathode surface when coupled to steel is represented by the following stoichiometric half-cell equation:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH)^- \qquad ...(1)$$

The hydroxyl ions produced at the cathode are neutralized by the sodium ions (Na^+) in the electrolyte. As a result there is a high concentration of sodium hydroxide solution in the region near the cathode. Hence, the high pH of blister fluid in blisters formed on carbon/polymer composite is further evidence that oxygen reduction reaction occurs at the cathode, but it is not a conclusive evidence.

When carbon fibers are subjected to a cathodic potential within the range +0.2 volts (open circuit potential) and -0.9 volts versus SCE, the cathodic reaction rate (or current) was found to be controlled by diffusion of one or more of the species (oxygen, water, hydroxyl and sodium ions) away or towards the cathode surface. This effect is shown in Figure (2), (Miriyala, 1992). The figure shows a plot of applied cathode potential versus apparent current densities for both CFVE composite and free carbon fibers. The negligible change in the current density below -.4 volts potential indicates a diffusion or concentration controlled current. This type of behavior is observed when one or more of the species involved diffuses at a slower rate relative to the rate of the cathodic reaction. The diffusion controlled current is lower for the CFVE composite relative to that of free carbon fibers because of smaller diffusion rates of the controlling species through the polymer layer. *If indeed this diffusion controlled current results due to slower diffusion of oxygen towards the carbon surface, then changes in the current densities can be expected when the oxygen diffusion rates are changed.* The oxygen diffusion rates depend upon the bulk oxygen concentration. Therefore, in this research, the changes in the current for various oxygen concentrations in the bulk electrolyte were monitored for the CFVE composite samples subjected to a potential of -0.9 volts (SCE).

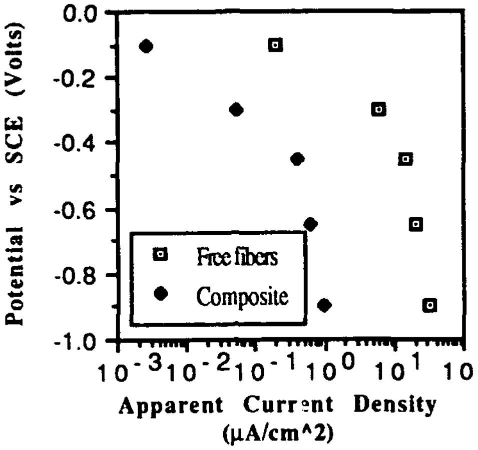


Figure 2. Tafel plots for carbon fiber polymer composite and carbon fiber roving exposed to 3% NaCl solution.

The changes in apparent current densities (current divided by exposed sample area) with increasing exposure time is shown in Figure (3). The current increases to a high value rapidly within a few hours and drops off to a steady value for the cases of high and medium oxygen concentrations. The steady state current density for the sample exposed to higher oxygen concentration is five times the current density for the case of medium oxygen concentration. The high oxygen concentration is five times the medium oxygen concentration. It follows therefore, that the current density is directly proportional to the oxygen partial pressures in the electrolyte. *This is a strong evidence that the carbon fibers in the carbon fiber vinyl ester composite support oxygen reduction reaction producing hydroxyl ions under the applied potential conditions.* The proportional increase of steady state current with increasing O_2 concentration from 0.2 atm to 1 atm indicates that the amount of debonded area of the polymer from the carbon fibers for these samples is same.

However, the steady state current value for the low oxygen case is same as that of the medium oxygen case. The reason for this behavior is as follows: The faces of the sample other than the exposed face to electrolyte were exposed to the ambient. Therefore, even though the electrolyte contains less oxygen for the low oxygen case, oxygen from the atmosphere (partial pressure = 0.2 atm) permeates through the sides of the sample, into the sample, resulting in higher current density.

The composite samples, before exposure, were all in equilibrium with atmosphere and therefore were saturated with air from the atmosphere. The higher current above the steady state values for the medium and high oxygen concentrations is due to the reduction of this oxygen present in the composite. Once this happens, the interior of the fibers will be devoid of oxygen and the current drops to a steady value. However, the high initial current greater than the steady state value is absent for the low oxygen case because of the negligible contribution of oxgyen from the electrolyte solution.

The mechanism of galvanic blistering in carbon fiber composites was earlier proposed by the authors based on electrochemical studies and blister fluid analyses (Miriyala, 1993). According to this mechanism, the galvanic blisters grow due to osmotic pressure developed at the fiber/matrix interface due to difference in the diffusion rates of sodium hydroxide solution (formed as a result hydroxyl ion production by oxygen reduction on the carbon fibers) and water through the polymer. Therefore, blister growth rate depends on the oxygen concentration in the electrolyte.

To determine how concentration of oxygen in the bulk electrolyte relates to the blister growth rate, the following analysis was conducted. The rate of increase of blister fluid volume V' (which represents blister growth rate) is given by:

$$V' = K(\gamma_1 - \gamma_2) \qquad .....(2)$$

where γ_1 = rate of production of OH^-

γ_2 = rate of diffusion of OH^- through the polymer layer.

K = proportionality constant which can be a function of time.

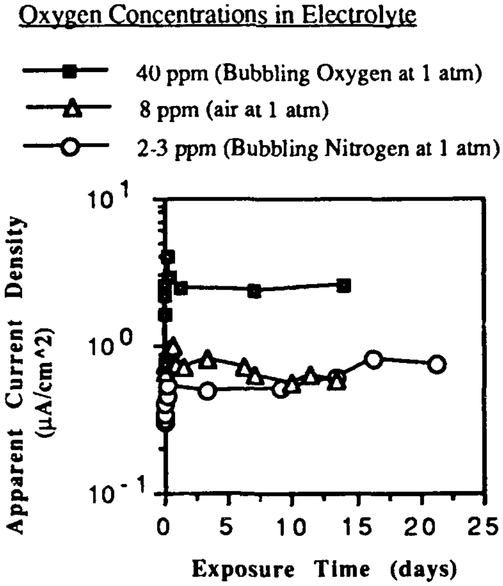


Figure 3. Temporal changes in apparent current densities for CFVE samples exposed to solutions with varying O_2 concentrations.

The γ_1 is proportional to the measured current I and the current I in turn is proportional to the concentration of oxygen in bulk electrolyte, given by, (Fontana, 1986),

$$I = \frac{nFC_oD}{\Delta x} \qquad \text{....(3)}$$

where n = stoichiometric coefficient of electrons involved in the cathodic half-cell reaction (1).
F = Faraday's Constant.
C_o = Concentration of oxygen in bulk electrolyte.
D = Diffusion Coefficient for oxygen diffusion through the polymer.
Δx = average thickness of polymer layer.

Therefore, the rate of increase of blister fluid volume V' becomes:

$$V' = \frac{K'C_oD}{\Delta x} - K\gamma_2 \qquad \text{....(4)}$$

where K' is another constant. Since, at blister detectability times, the polymer layer deformation configuration is similar, Δx is same for all the cases. The rate of diffusion of hydroxyl ions through the polymer layer into the bulk electrolyte, γ_2, remains constant assuming the diffusion rate of OH^- in the bulk electrolyte is much greater than in the polymer. Now, assuming the diffusion coefficient of O_2 is constant, the blister growth rate is proportional to the oxygen concentration in bulk electrolyte C_o. If the blisters grow at a constant rate, then the blister growth rate is inversely proportional to the BDT. According to equation (4), a plot of $(BDT)^{-1}$ versus oxygen concentrations in bulk electrolyte C_o should produce a straight line. 1/(BDT) as a function of oxygen partial pressure is shown in Figure (4).

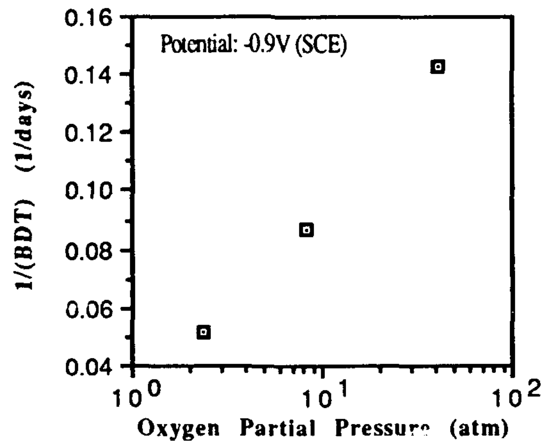


Figure 4. Effects of varying oxygen partial pressures on the blister growth rates

The plot shows a non-linear increase of $(BDT)^{-1}$ with increasing oxygen partial pressures. The conclusion is that the blister growth rate increases with increasing oxygen concentrations. This result is significant and validates the galvanic blistering mechanism proposed by the authors (Miriyala, 1993). However, the $(BDT)^{-1}$ increases non-linearly with slower increase at greater oxygen concentrations and does not follow equation (4). A possible cause of the non-linearity is the varying blister growth rate with exposure time for a given oxygen concentration. Under given conditions, the blister growth rate is a function of diffusion rates of species which are again function of the blister geometry and dimensions at any instant and also polymer creep properties. Future investigation is required to correlate these factors.

The BDT for oxygen partial pressure of 0.06 atms is greater than that for 0.2 atms even though the steady state current density is same for both as shown in Figure (4). The reason for this is galvanic blister size or the total blister fluid volume depends on the amount of hydroxide produced which in turn is proportional to the total or cumulative charge density on the cathode surface, but not on the current density at that time. The cumulative charge density Q at any instant 't' is given by:

$$Q(t) = \int I(t)dt \qquad \ldots.(5)$$

The current data of Figure (3) is numerically integrated with respect to time to yield the cumulative charge densities (CCD). The cumulative charge densities as a function of time are shown in Figure (5).

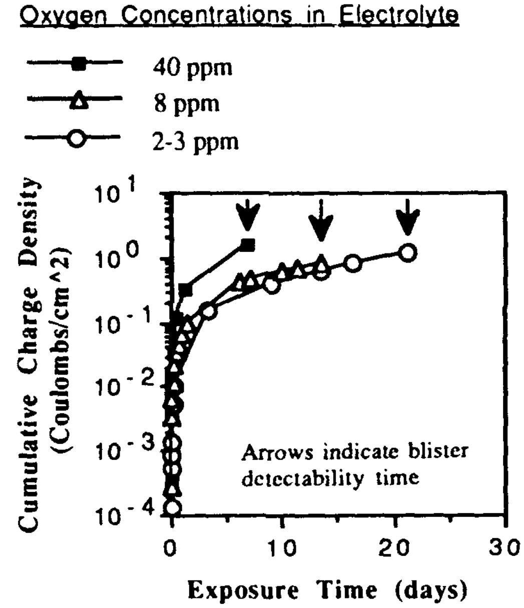


Figure 5. Apparent cumulative charge densities versus exposure time for CFVE composite samples. applied potential: -0.9V (SCE)

It can be seen that the charge densities exponentially increase with time initially and at very slow rates at large exposure times. The most interesting feature is that the cumulative charge densities increase by 4 orders of magnitude during the initial periods of exposure and at the blister detectability time, they all are within the order of magnitude of 1 coulombs per sq. cm. for this composite under the given experimental conditions. The rapid increase of CCD during the initial times was attributed to the combined effect of the increased area of exposure of carbon fibers to the diffusing electrolyte solution and also due to rupture of small blisters (formed on the fibers closest to the surface) that expose the fibers. It can be seen that the CCD reach 1 coulomb/cm^2 value at the BDT for all samples exposed to different oxygen concentrations. The conclusion is that the blister size or the blister fluid volume is proportional to the amount of sodium hydroxide solution (which is proportional to CCD) formed at the electrode.

4. EFFECTS OF CATHODIC POLARIZATION OF CARBON FIBER COMPOSITE ON ITS INTERLAMINAR SHEAR STRENGTH

4.1 INTRODUCTION

The study of the effects of cathodic polarization of the fibers in a carbon fiber composite on its ultimate properties is not only significant from mechanical design point of view but also would provide insights into the mechanistic aspects of blister nucleation and growth. The mechanical property chosen for study was the composite interlaminar shear strength. The ASTM D 2344-84 standard test method for apparent interlaminar shear strength of parallel fiber composites by short beam method was adopted to determine the shear strength.

4.2 EXPERIMENTAL PROCEDURE

Short beam samples of dimensions 3" x 0.5" x 0.5" were fabricated from a 1.5" thick carbon/vinyl ester composite laminate. Different sets of samples were exposed to the following conditions, prior to testing:

(1) samples exposed low relative humidity (RH) (oven conditions) and @ 60°C temperature for 80 days;
(2) samples immersed in deionized, distilled water (100% RH) @ 60°C for 80 days;
(3) samples immersed in 3% (by weight) NaCl solution @ 60°C for 80 days;
(4) samples immersed in 3% (by weight) NaCl solution @ 60°C for 80 days, and then subjected to -900 mV versus a standard calomel electrode in the same solution @ 60°C for 7 days (after blisters were detected).

The weight gain of two samples of (2) and (3) categories was monitored over the period of exposure. All samples were cooled to room temperature prior to testing. The cathodically polarized samples formed blisters within 4 days of exposure. These samples were *uncoupled* , cooled to room temperature and then were tested. An INSTRON model 1125 testing instrument was employed for the testing program. A constant cross-head speed of 0.05 inches/min was used during the testing. The width and depth of each sample was measured to 0.001 inches accuracy using a precision vernier calipers.

4.3 RESULTS AND DISCUSSION

The weight gain curves for the samples immersed in water and sodium chloride solution are shown in Figure (6). The weight gain curves reveal a non-Fickian mode of diffusion in the samples. The samples did not reach saturation at the end of exposure period of 80 days, but it appears they are nearing saturation. The weight gain of the samples immersed in sodium chloride solution was considerably less than that for the samples in pure water by about 27%. This value is not consistent with the theoretical prediction of about 3%. The reason for this greater difference in weight gain is not yet clear.

The samples were tested at room temperature for apparent interlaminar shear strength. A schematic of a typical load-time curves obtained for the 3-point bend tests is shown in Figure (7). The load increases linearly with time to failure. The failure was always in shear in the one of the inner layers followed by multiple shear failures. The apparent shear strength τ was estimated using the following expression:

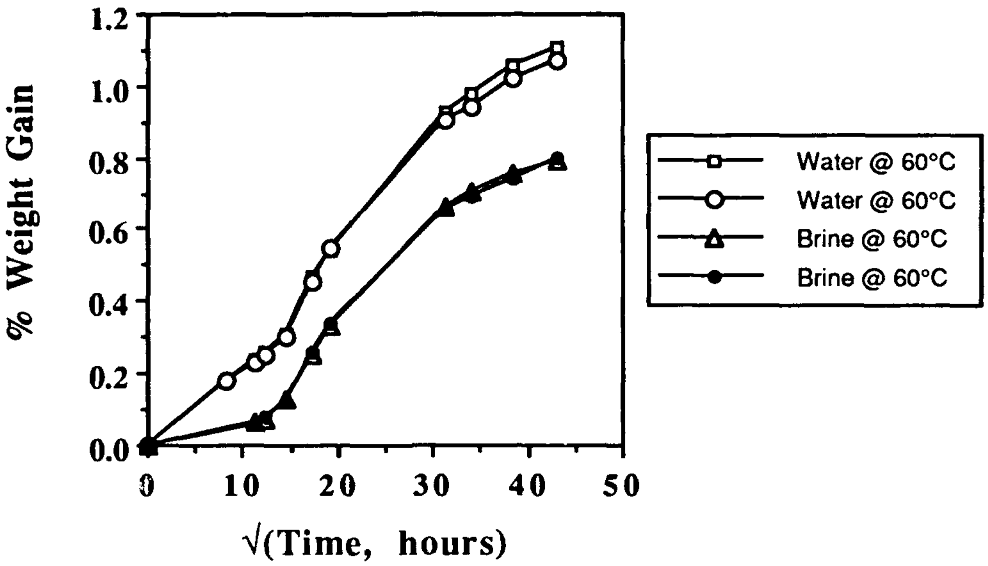


Figure 6. water and electrolyte absorption curves for carbon/vinyl ester composite

$$\tau = \frac{0.75P}{bd} \qquad \ldots(6)$$

where
P = maximum shear failure load (N)
b = width of sample at loading nose (m)
d = depth of sample at loading nose (m)

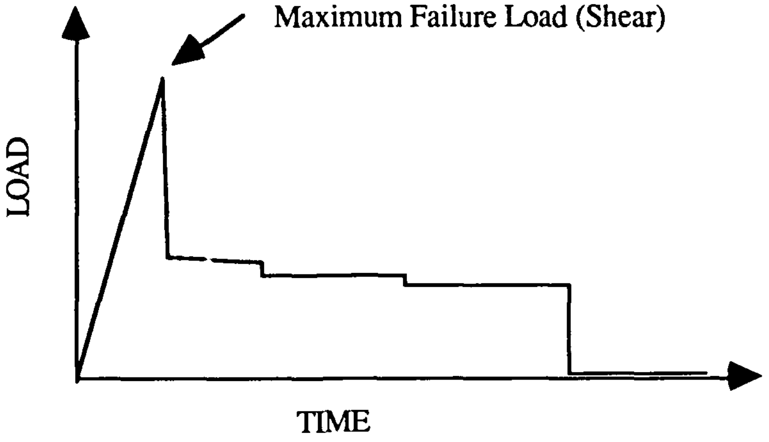


Figure 7. Schematic of Load-Time Diagram in the 3-point bend test

The apparent shear strength data for various environmental conditionings is presented in Table (1) and in the bar chart shown in Figure (8). The limited accuracy of the testing instrument and vernier causes uncertainty in the calculated shear strength data and this uncertainty in the estimated shear strength data was calculated by a precise method suggested in the literature (Kline and McClintock, 1953). The maximum uncertainty is about 14% of the average.

The results indicate a little improvement in the average apparent shear strength when the samples have moisture and electrolyte present in them. The reason for this small increase in the average shear strength could be the plasticization of the vinyl ester matrix by the presence of moisture or electrolyte which enables the matrix sustain more deformation, thus reducing the induced shear stress at the fiber/matrix interface.

The galvanic blistering of the composite when subjected to a cathodic potential of -900 mV (SCE) did not result in degradation in the composite's apparent shear strength. This is an intriguing and a significant outcome of this research. The interface damage in the surface layer due to blistering did not affect the overall apparent shear strength. The explanation for this behavior is as follows:

It can be recalled that the corrosion current, due to -900 mV potential applied to the composite, is limited by diffusion of oxygen towards the carbon fibers (figure 2). Therefore, the entire oxygen will be consumed at the surface carbon fiber layers, depleting oxygen in the interior layers of the composite. According to the galvanic blistering mechanism (Miriyala, 1993), oxygen reduction to hydroxyls results in the formation of sodium hydroxide solution at the carbon fiber surface which causes osmosis and blistering. Since the oxygen reduction is shut-off inside by lack of oxygen in inner layers of the composite, the inner layers are protected from blistering. The fact that no blisters or debonded zones were observed at the deeper layers even at higher magnifications could be because no blisters were formed at all at the inner layers.

A modification of the galvanic blister nucleation theory is required in light of the above result. The earlier theory is restated as follows (Miriyala, 1993):

<u>Blister Nucleation Theory</u>: The carbon fibers are negatively charged (electron rich) as soon as the galvanic couple is established. The polymer layer adhering to the carbon fiber surface experiences an electric field due to the fiber charging. The electron dense regions of the polymer chains close to the carbon surface tend to move away from the negatively charged carbon surface. This will result in some adhesive bonds being broken. Due to zero partial pressure of water in the debonded regions, water molecules in the surrounding electrolyte-saturated-polymer diffuse into these regions and a layer of water molecules condensed as an aqueous film is created.

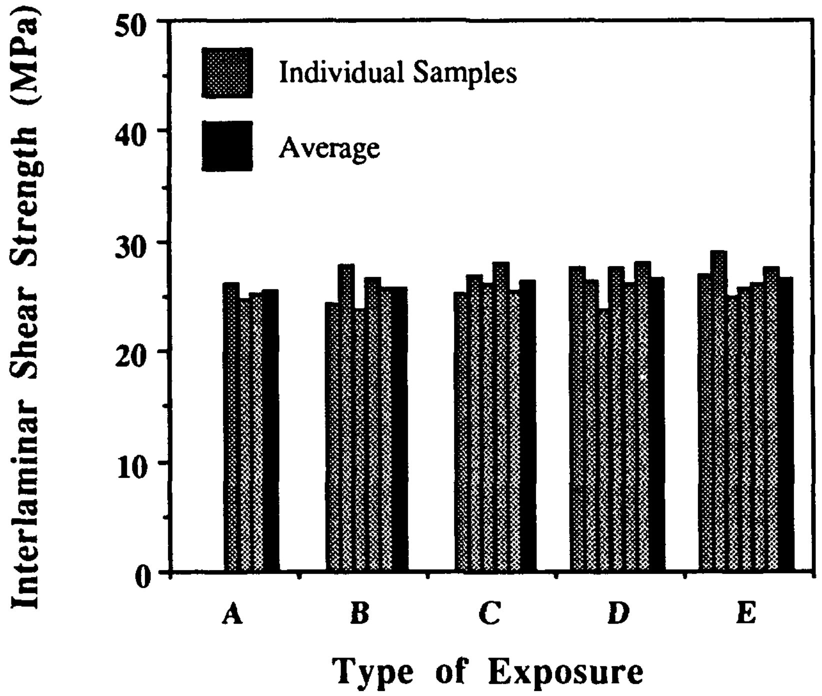
If the above phenomenon is irreversible, the debonded zones containing aqueous solution will exist even after galvanic <u>decoupling</u> (removal of applied potential) of the carbon composite. This must cause permanent defects at the fiber/matrix interface in all the layers of the composite. If this is true, then there should be a drop in the ultimate mechanical properties of the composite, especially those which are controlled by the interface bonding such as the interlaminar shear strength. However, the relatively no change or drop in ILSS of the blistered composite samples suggest that there were no permanent defects introduced in the composite after decoupling.

Thus, the blister nucleation might be a reversible phenomenon. The galvanic decoupling causes the electron dense regions of the polymer chains to return to their original configuration that causes the nucleated water to redissolve in the polymer. For a permanent debonding to result, oxygen reduction reaction should take place in these nuclei that introduces osmotic pressures and debonding. However, since the inner layers are devoid of oxygen, a galvanic decoupling would leave the fiber/matrix interfaces at the inner layers unaffected.

TABLE I

Interlaminar Shear Strength Data from 3-point Bend Tests of Short Beam Samples of a Carbon Fiber Reinforced Vinyl Ester Composite Laminate Exposed to Various Environments

Exposure Condition	*Shear Strength (psi)*	*Shear Strength (MPa)*	*Uncertainty (%)*	*Arithmetic Mean psi(MPa)*	*Standard Deviation (%Mean)*
Virgin samples @ room temperature	3668	25.4	±12.1	3673(25.4)	2.8
	3572	24.7	±11.8		
	3780	26.1	±12.5		
Virgin samples @ 60°C for 80 days and tested @ room temperature	3718	25.7	±12.4	3713(25.7)	6.5
	3871	26.8	±12.8		
	3437	23.8	±11.4		
	4020	27.9	±13.4		
	3519	24.3	±11.6		
Samples immersed in water @ 60°C for 80 days and tested @ room temperature	3689	25.5	±12.2	3814(26.4)	4.3
	4059	28.1	±13.4		
	3795	26.2	±12.6		
	3876	26.8	±12.8		
	3651	25.2	±12.1		
Samples immersed in 3% NaCl solution @ 60°C for 80 days and tested @ room temperature	4058	28.0	±13.4	3847(26.6)	5.9
	3787	26.2	±12.5		
	3976	27.5	±13.1		
	3439	23.8	±11.3		
	3823	26.4	±12.6		
	4001	27.7	±13.2		
Samples immersed in 3% NaCl solution @ 60°C for 80 days, later subjected to -900 mV (SCE) potential @ 60°C for 7 days and tested @ room temperature	4003	27.7	±13.3	3860(26.7)	5.5
	3772	26.1	±12.6		
	3720	25.7	±12.3		
	3602	24.9	±11.9		
	4192	29.0	±13.8		
	3874	26.8	±12.7		



A: Virgin samples at room temperature

B: Virgin samples at 60°C for 80 days

C: Samples immersed in deionized, distilled water at 60°C for 80 days and tested at room temperature

D: Samples immersed in 3% NaCl solution at 60°C for 80 days and tested at room temperature

E: Samples immersed in 3% NaCl solution at 60°C for 80 days, later subjected to an applied cathodic potential of -900mV (SCE) for 7 days and tested at room temperature

Figure 8. Short Beam Interlaminar Shear Strength Test Results for a Carbon Fiber Vinyl Ester Composite

These conclusions are based on ILSS test results of blistered samples polarized for 7 days. A long term polarization studies are required to further verify the proposed modified theory.

5. A SEMI-EMPIRICAL MODEL FOR GALVANIC BLISTER GROWTH

5.1 INTRODUCTION

A formal mathematical analysis of galvanic blistering process based upon the mechanism proposed by the authors is necessary not only to verify the proposed mechanism but also to quantify and predict several elements of the process, and ultimately the blister growth rates. The galvanic blister growth rate for a given carbon fiber composite will be a function of several electrochemical variables, diffusion rates of species involved, mechanical properties of the polymer and polymer/fiber interface and temperature. If 'A' represents the rate of increase of delaminated or debonded area, then,

$$A = f\{X, c_i, D_i, z_i, I'', E_p, \sigma_{fail}, \sigma_t, Y, B, T, \Delta\}$$

where X = electric field produced by the electrode potential E
i = chemical species involved: Na^+, OH^-, Cl^-, O_2 and H_2O
c_i = concentrations of the species *i* in the blister fluid and the electrolyte assuming these are ideal solutions
D_i = diffusion coefficients of the species *i* in the given system (diffusion coefficients of species *i* will be different in the polymer layer and the electrolyte.
z_i = oxidation number of ions *i*
I'' = current density on the debonded carbon surface under the polymer layer
E_p = Young's modulus of the polymer
σ_{fail} = tensile failure stress of the polymer
σ_t = failure strength of the fiber/matrix interface under a normal load
Y = yield criterion
B = creep criterion
T = temperature
Δ = geometric configuration of the blister including blister shape, size, etc.

5.2 A COMPLETE MATHEMATICAL ANALYSIS

A complete and accurate analysis of galvanic blistering phenomenon to predict the blister growth rates involves the following steps:

(a) Develop gradient flux equations for all species by applying conservation of mass and conservation of charge principles:

The flux of a neutral species such as oxygen anywhere in the system can be evaluated by Fick's laws of diffusion. However, the flux of ionic species *i* is given by the Nernst-Planck equation (Bockris, 1973):

$$J_i = -(D_i c_i / RT)\nabla\mu_i' \qquad \text{...(7)}$$

$$\text{where} \qquad \mu_i' = \mu_i + z_i F \varphi \qquad \ldots(8)$$

$$\mu_i\,(P,T) = \text{chemical potential of species 'i'} = \mu_i^\circ + P\underline{V}_i + RT\ln(\gamma_i c_i) \qquad \ldots(9)$$

μ_i° = reference chemical potential for species 'i'
P = pressure
$\underline{V}_i$ = molar volume of species 'i'
γ_i = activity coefficient for species 'i'
φ = electrical potential

Using the flux definition, the conservation equation for each of the species must be obtained. The electrostatic term in equation (8) will be absent for the neutral species such as oxygen and water. The species mass conservation equation can then be obtained as:

$$\partial c_i/\partial t = \nabla J_i \qquad \ldots(10)$$

where 't' is the time.

The species mass conservation equation obtained for a species *i* in a one dimensional cartesian coordinate system is given below, as an example:

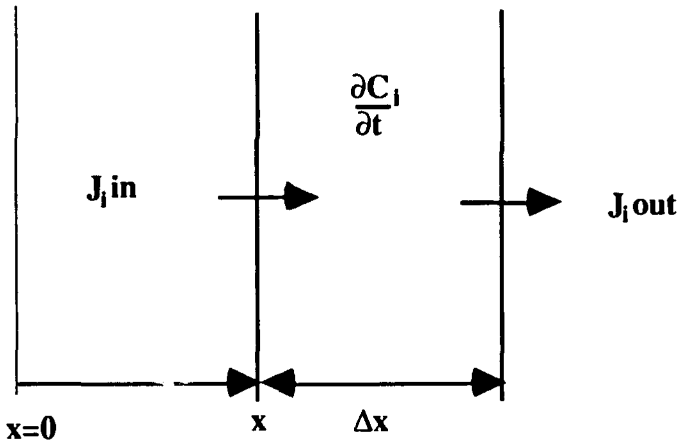


Figure 9. Schematic showing control volume in one-dimensional cartesian coordinate system over which mass and charge were balanced to obtain equation (9)

$$\partial c_i/\partial t = \partial J_i/\partial x \qquad \ldots(11)$$

(b) *determine the rate of volume increase of water V_w' cm^3/s in the blister cavity by the following expression*:

$$V_w' = \partial V_w/\partial t = \int^{a^\circ} (J{\cdot}v/c_w)\,\big|_o\, da \qquad \ldots(12)$$

where the subscript 'w' corresponds to water, 'o' indicates that the integral is evaluated at the inner surface of the polymer layer, 'a' is area, and 'a°' is the inner area of the polymer layer. If the rate of change of volume of the blister fluid is positive then there will be a net increase of volume in the blister fluid, which will be the case for blistering phenomenon.

(c) analyze the stresses and displacements induced in the polymer and the fiber/matrix interface region due to the above volume change: The volume increase of the fluid in blister given by equation (12) yields displacement boundary conditions for the polymer layer for a given geometric configuration of the blister. Using theories of elasticity and plasticity, perform stress and displacement analysis for the polymer and interface for the given geometric configuration of the blister. The induced stresses if exceed the ultimate properties of the polymer and/or interface, result in further debonding, yield and creep of the polymer. *The displacement field in the polymer would give the rate of increase of the blister size.* The stress field yields the pressure P applied on the blister liquid and the chemical potentials μ_i will be a function of P as per equation (9).

Since the deformation of the polymer layer is a function of volume increase of water in the blister solution and the internal pressure, the rate of blister growth can be obtained by simultaneous solution of the non-linear partial differential equations (10), (12) and the stress-displacement field equations. These extremely complex set of equations may not yield a complete and closed analytical solution but could be solved by numerical methods using computers.

The knowledge of several properties and parameters will be necessary to obtain an analytical solution which actually discourages any attempt to solve these equations. However, based on experimental observations as well as making some assumptions, it may possible to simplify the solution procedure. However, a simple semi-empirical model was developed that eliminates several of the complex steps involved in a complete analytical solution.

5.3 ASSUMPTIONS IN THE SEMI-EMPIRICAL MODEL

The less complicated method suggested below is characterized by assumptions some of which are based upon experimental observations. This semi-empirical model requires experimental data that can be easily be measured. The data required and the assumptions made are discussed below:

(1) **empirical current -time data**: The corrosion current can be measured using a simple multimeter and this current can be monitored over the period of exposure for composite samples subjected to galvanic potentials. The transient current density I(t) is proportional to and therefore incorporates in itself the following: (a) electrical field (b) rate of production of the hydroxyl ions by the reduction of oxygen at the carbon cathode and (c) diffusion rates of oxygen.

(2) **empirical $[OH^-]$ - time data**: The concentration of hydroxyls in the blister fluid as a function of time can be measured by titration of blister fluid collected at different time intervals. The pH of the blister fluid is not a correct measure of hydroxyl ion concentration above pH 14 because hydroxyls will not be in a completely dissociated form as speciation of sodium hydroxide occurs. The pH of blister fluids in carbon fiber vinyl ester composite was found to be 14. This remained almost constant throughout the period of blistering. A blistered sample of graphite flat disks coated with vinyl ester was *uncoupled* and immersed in a 3% NaCl solution. The chart showing pH decrease versus time is shown in the following figure (10). It can be seen that the pH stays constant for a long time before it starts dropping indicating that we have a higher concentration of $[OH^-]$ than suggested by the pH value. For this reason, to obtain the hydroxyl ion concentration, titration methods must be employed. The hydroxyl ion concentration of the blister fluid at any instant is controlled by (a) the rate of production of hydroxyl ions, (b) the rate of diffusion of

hydroxyl ions away from the blister region, (c) the mechanical properties of the polymer layer and fiber/matrix interface. The latter is an important element that controls the hydroxyl ion concentration in the blister fluid by controlling blister geometry and therefore diffusion rates of species. Therefore, the knowledge variation of hydroxyl ion concentration with time greatly simplifies the analysis since the deformation behavior of the polymer layer reflects in the hydroxyl ion concentration values. The simplification is significant also because the actual failure mechanisms (polymer creep or debonding at the interface and to what extent) were unknown.

(3) **no OH^- concentration gradients exist within the blister**: This is an important and a reasonably valid assumption. It implies that the rate of production of OH^- ions is much greater than the diffusion of OH^- through the polymer film into the bulk electrolyte. In fact, this rate difference is the causative of the osmotic pressure, according to the galvanic blistering mechanism. Thus, the OH^- ion concentration within the blister fluid is a single, lumped value.

(4) **the significant species in the blister fluid are Na^+, OH^- ions and their associated pairs**: The concentration of Na^+ ions will be atleast as much as that of the OH^- ions and therefore will be significant. Moreover, at the high levels of pH noted for the blister fluid (pH = 14), sodium hydroxide may not completely dissociate into ions. Therefore, the so called *associated pairs* of the these ions can exist in the blister fluid whose concentration is controlled by the dissociation constant K_d. The concentration of Cl^- in the blister fluid is neglected relative to the concentrations of Na^+ and OH^- because (a) the blisters are in the close vicinity of the cathode and the high transference number of Cl^- ions which is one-and-a-half times that of Na^+ (transference numbers: Na^+=0.396; Cl^-=0.604) and therefore, its concentration will be low near the cathode region.

(5) **constant blister cavity shape at all times**: The blister geometry and configuration at the initial point of time are known, and the shape remains constant with time while the size increases as blister grows. This will be the case for a polymer coated flat carbon substrates.

(6) **sodium hydroxide concentration in the blister liquid is below the solubility limit for the given temperature:** If the sodium hydroxide concentration in the blister fluid is greater than the saturation value, sodium hydroxide will precipitate out and alters the blister characteristics such as its effective volume, carbon fiber surface as a result of scale formation, etc. Therefore, it was assumed that we are at current densities that yield concentration values below the solubility limit.

(7) **diffusion coefficient of OH^- ions through the polymer is known**: the diffusion coefficient of hydroxyl ions through must be known. This can be found by techniques such as titration in a diffusion cell. Several other techniques can be found in the literature.

5.4 THE SEMI-EMPIRICAL MODEL

Based on these assumptions, the following semi-empirical model is developed. Consider a cross section of a axisymmetric blister cavity as shown in Figure (11). The rate of accumulation of OH^- ions in the blister liquid is given by mass balance:

$$\partial M/\partial t = q\{\text{rate of production } OH^- \text{ ions}\} - j\{\text{ rate of } OH^- \text{ diffusion through the polymer }\} \quad ...(11)$$

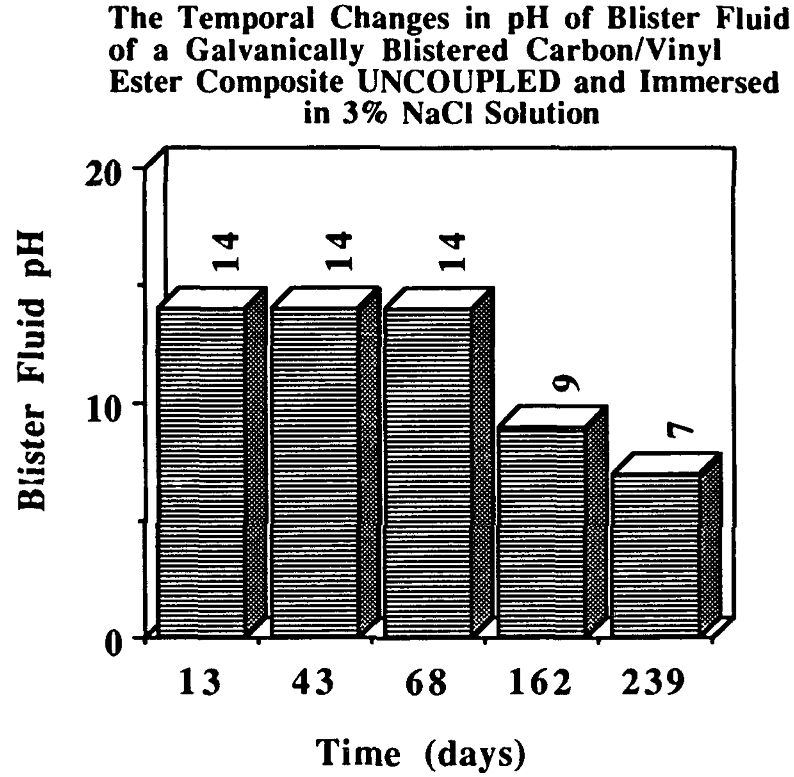

The Temporal Changes in pH of Blister Fluid of a Galvanically Blistered Carbon/Vinyl Ester Composite UNCOUPLED and Immersed in 3% NaCl Solution

Figure 10

where M = # of moles of OH^- ions accumulated in the blister liquid
t = time

The rate of production of OH^- ions is given by:

$$q(t) = A_c I(t)/F \quad ...(12)$$

where $I(t)$ = current density (amperes/cm^2)
F = Faraday's constant = 96500 coulombs/g equi
A_c = debonded cathode area exposed to the blister fluid

Let the average flux of OH^- ions through the inner polymer surface be j''. Then the rate of diffusion of hydroxyl ions through the polymer j is given by:

$$j = j''A_p \quad ...(13)$$

where A_p = area of the polymer film surface facing the blister cavity

Substituting the values 'q' and 'j' from equations (12) and (13) into equation (11), we get the general expression for the rate of accumulation of OH^- ions in the blister liquid:

$$\partial M/\partial t = A_c I(t)/F - j''A_p \qquad \text{...(14)}$$

The rate of increase of the volume of the blister fluid V' is given by:

$$V'(t) = (\partial M/\partial t) \div [OH^-] \qquad \text{...(15)}$$

$$\text{or} \quad V' = \frac{A_c I(t)}{[OH^-]F} - \frac{j''A_p}{[OH^-]} \qquad \text{...(16)}$$

where $[OH^-]$ = hydroxyl ion concentration obtained from titration of blister fluid.

This is the important working equation in this analysis.

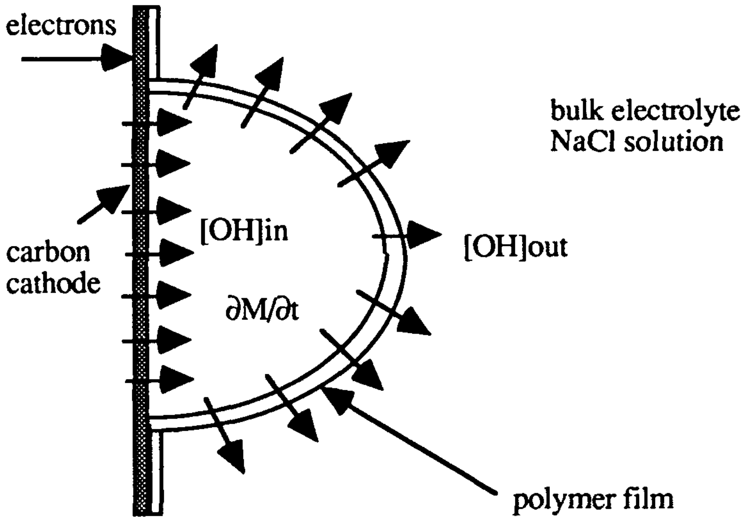


Figure 11. Schematic of a arbitrary blister showing hydroxyl ion transport

5.5 THE SEMI-EMPIRICAL MODEL APPLIED TO A SPHERICAL BLISTER

Blister shapes can be approximately spherical when the polymer has very low stiffness and a strong interfacial adhesion bonds. With a little consideration, the steady state diffusion rate of OH^- ions through the polymer film of a hemispherical blister can be shown as:

$$j = \frac{2\pi D(C_i - C_o)}{\{1/r_i - 1/r_o\}} \ \text{(moles/s)} \qquad \text{...(17)}$$

where D = diffusion coefficient of $[OH^-]$ ions through the polymer, cm^2/s
C_i = concentration of $[OH^-]$ inside the blister, $moles/cm^3$
C_o = concentration of $[OH^-]$ in the bulk electrolyte, $moles/cm^3$
r_i = inner radius of the spherical blister cavity, cm
r_o = outer radius of the spherical blister cavity, cm

Then the rate of increase of blister fluid volume is given by substituting (17) for $j''A_p$ in equation (16):

$$V'_{spherical} = \frac{\pi r_i^2 I(t)}{[OH^-]F} - \frac{2\pi D([OH^-]-C_o)}{[OH^-]\{1/r_i - 1/r_o\}} \quad \ldots(18)$$

The volume of a hemisphere $V = 0.667\pi r_i^3$ and its base being $A_c = \pi r_i^2$. Therefore, $V = 0.667Ar_i$. Substitution of this expression in the above equation and integrating with respect to time with the initial condition, $t=0$; $r_i = a$; $r_o = b$, and assuming the volume of the polymer film to be a constant, we can derive an expression for the debonded area $A_c(t)$.

5.6 SEMI-EMPIRICAL MODEL APPLIED TO A FILM-TYPE BLISTER

The blister can take a film shape when the polymer stiffness is very high and the fiber/matrix interface bond is weak. During the initial stages of blistering, the blister may be of this form. The film type blister model is diagramatically illustrated below in figure (11). Let the film thickness be '*h*' cm and be constant with time. Let the thickness of polymer film be *k* mm. For this model, the debonded area and area for diffusion of OH^- through the polymer will be same i.e. $A_c = A_p$. Then, the diffusion rate through the polymer 'j' will be $D(C_i-C_o)/k$. Substituting these in the equation (16), we get the volume growth rate as:

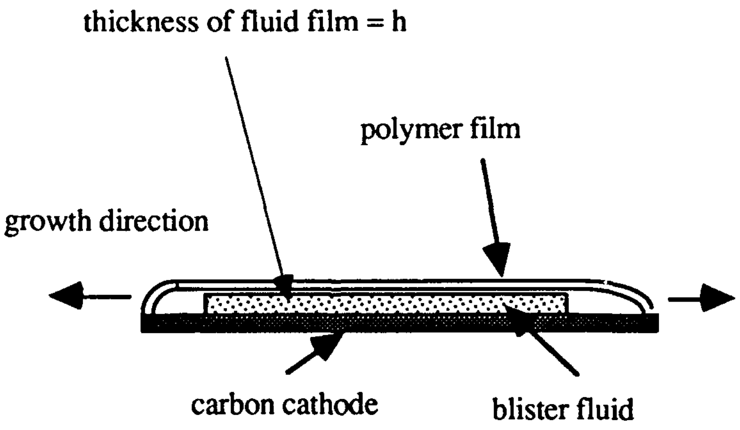


Figure 12. Film-type blister model

$$V' = \frac{A_c I(t)}{[OH^-]F} - \frac{A_c D(C_i-C_o)}{[OH^-]k} \quad \ldots(19)$$

The volume $V = hA_c$. Therefore, $V'=hA_c'$. Thus, with the initial condition $t=0$; $A_c=A_{co}$ the growth rate of the debonded area is given by:

$$A_c(t) = A_{co}\exp\{h^{-1}[\int^t I(t)dt/F - D([OH^-]-C_o)t/k]\} \qquad \ldots(20)$$

The semi-empirical model needs rigorous verification by comparison with experimentally measured growth rates. Since composite geometries are complicated to incorporate, an equivalent regular model must be defined for a given composite's polymer and fiber geometry.

6. SUGGESTED IMPLICATIONS TO DESIGN

- The materials that were found to undergo galvanic blistering were carbon fiber reinforced vinyl esters, polyesters, epoxies and polyamides. Other carbon/polymer systems need to be investigated for galvanic blistering. Several of the conclusions presented here hold for carbon/vinyl ester composites. These conclusions may also hold for other carbon/polymer composites but further research is required for verification.

- Galvanic blistering in carbon/vinyl ester composites results in debonding of surface polymer layer from the carbon fibers. The polymer layer may be completely removed subsequently with continued galvanic conditions resulting in the exposure of surface carbon fibers directly to the electrolyte.

- Galvanic coupling of carbon composites to steel or aluminum metal structures such as fasteners, substructures, etc.will pose a threat to the mechanical integrity of the metal structures , because they will undergo rapid corrosion under the galvanic conditions.

- The exposure of carbon fibers due to rupture of blisters increases galvanic power, and further may accelerate the metal corrosion.

- The galvanic coupling of carbon fiber vinyl ester composites to metals steel and aluminum results in corrosion potentials above -.900 mV (SCE). This potential is above the water breakdown potentials, therefore oxygen reduction reaction is the only significant cathodic reaction.

- Since the oxygen reduction reaction above -900 mV (SCE) potential is limited by oxygen diffusion rates, the inner layers of the composite are protected from blistering since in the inner layers, no oxygen will be available to trigger the oxygen reduction reaction that leads to galvanic blistering. This is evidenced by relatively little change in interlaminar shear strength of a carbon/vinyl ester composite subjected to a potential of -900 mV(SCE) at 60°C for 7 days (the composite blistered in 4 days under these conditions). Extended periods of exposure beyond 7 days may not affect the ultimate mechanical properties since the oxygen reduction reaction that causes the defects at the interface is limited to the surface carbon fibers only. However, this needs further verification and will be part of the work of the fiscal year 1993-94. Reduction in interlaminar shear strength by 30% in carbon/epoxy composites galvanically coupled to magnesium (equilibrium potential: -1500 mV(SCE)) for 180 days (Sloan et al, 1991) must be due to water breakdown that can occur in the deeper layers of the composite. Similar to oxygen reduction reaction, electrochemical breakdown of water results in the production of hydroxyl ions at the carbon fibers that can lead to galvanic blistering. The conclusion is that as long as the applied cathodic potentials are above the equilibrium potential for water breakdown, the composite strength may remain unaffected as the electrochemical reactions are confined to surface layers only.

- The sodium hydroxide solution that constitutes galvanic blister liquid may attack (saponification) and degrade certain polymer matrices. This matix chemical breakdown may affect the composite integrity.

7. CONCLUSIONS

(1) The varying oxygen partial pressures in the bulk electrolyte significantly affected corrosion currents and blister initiation times in the carbon/vinyl ester composite. The corrosion current was found to be proportional to the bulk oxygen partial pressure. The blister detectability time (BDT) was defined as the time required for blisters to grow to a size of 1 mm diameter. The blister growth rate therefore will be inversely proportional to the BDT. The blister growth rates increased with increasing bulk oxygen concentration. This effect almost certainly is an evidence of electrocatalytic reduction of oxygen on the carbon fibers in the composite. The cumulative charge density (obtained by integrating current over the time period) increased 5 orders of magnitude in the early stages of exposure and stayed at around 1 coulomb/sq cm until blisters formed. This was true for different cases of varying oxygen concentrations. The cumulative charge density when blisters formed was found to be within an order of magnitude at BDT for the three different oxygen concentrations: 2, 8 and 40 ppm. This result suggests that the blister size is a function of the total charge passed and the same is independent of oxygen concentration. It further implies that the oxygen reduction reaction rate controls blister growth.

(2) The apparent interlaminar shear strength (ILSS) tests were designed according to the ASTM D 2344-84 standard test method using short beam samples. Short beam samples were exposed to 60°C temperature at low relative humidity; to deionized, distilled water at 60°C; 3% sodium chloride solution at 60°C for 80 days. *Comparison of ILSS of these samples showed little variation in their average interlaminar shear strength.* Some of the latter samples exposed to the NaCl solution were subjected to a cathodic potential of -900 mV versus a standard calomel electrode for 7 days until blistered. These samples were uncoupled and tested. *The data did not reveal any changes in the average interlaminar shear strength.* In spite of the formation of galvanic blisters, the shear strength was unaffected. This leads to the conclusion that the interior layers of the composite were unaffected and blistering and debonding takes place only on the surface layers where all the oxygen was being consumed. It can be recalled that the corrosion current was limited by oxygen diffusion and therefore, all the oxygen was being consumed at the surface carbon layer, thus not allowing any electrochemical reaction at the inner carbon fiber layers. This conclusion is also supported by the fact that blisters were never observed at the deeper layers of the composite.

(3) An accurate mathematical analysis and methodology was suggested to predict the galvanic blister growth rates. However, since an analytical solution involves solution of complex differential equations and also demands experimental property data, a simple semi-empirical model was sought. The semi-empirical model to predict the blister growth rates developed requires corrosion current density - time data and hydroxyl ion concentration in blister fluid versus time data. The model evaluates the rate of volumetric increase of the blister fluid. The growth rate of debonded area can be calculated using the volumetric growth rate for a given geometric model of the blister.

8. REFERENCES

Bockris, J. O'M, Reddy, A.K.N., 'Modern Electrochemistry', Vol. 1, *Plenum Publishing Corp.*, New York, 1973

Fontana,M.G., *Corrosion Engineering*, McGraw-Hill, Inc., New York, USA, pp.43, 1986

Kinoshita, K., 'Carbon - Electrochemical and Physicochemical Properties', *Wiley-Interscience*, New York, 1988

Kline, S.J. and McClintock, F.A., 'Describing Uncertainties in Single Sample Experiments', *Mechanical Engineering*, January, 1953

Miriyala, S. K., Rockett, T. J., Tucker, W. C. and Richard Brown, 'Degradation of Polymeric Matrix Materials in Sea Water', *Proceedings of NACE Conference on Environmental Effects on Advanced Materials*, San Diego, February, 1991

Miriyala, S. K., Rockett, T. J., Tucker, W. C. and Richard Brown, 'Degradation of Carbon Reinforced Polymer Composites Under Galvanic Coupling Conditions', *Proceedings of the 33rd ASME/AIAA Structures, Structural Dynamics and Materials Conference*, Dallas, Texas, April, 1992

Miriyala, S. K., Rockett, T. J., Tucker, W. C. and Richard Brown, 'Corrosion Activated Degradation of Composites in Sea Water', *Proceedings of the Annual Tri-Services Conference*, Boston, Mass., May, 1992

Miriyala, S. K., Rockett, T. J., Tucker, W. C. and Richard Brown, 'The Mechanism of Galvanic Blistering in Carbon Fiber Composites', *Proceedings of the 9th International Conference on Composite Materials*, Vol. 5, Madrid, Spain, July, 1993

Miriyala, S. K., Rockett, T. J., Tucker, W. C. and Richard Brown, 'Blister Formation in Carbon Fiber Composite Materials Exposed to the Marine Environment', *Technical Symposium Series on Applying Composites in the Marine Environment*, American Society of Naval Engineers, Savannah, Georgia, November, 1993

Tucker,W.C., Brown,R., *Blister Formation on Graphite/Polymer Composites Galvanically Coupled with Steel in Seawater*, Journal of Composite Materials, Vol. 23, pp. 389-395, April 1989