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The Effect Of Carbon Fiber Type On The Electrochemical Degradation Of Carbon Fiber Polymer Composites

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ABSTRACT

The galvanic interaction between metals and carbon fiber/polymer matrix composite degrades not only the metals but the composite itself. The objective of this study was to investigate if the fiber type influenced either the mechanism or form of damage. Two different composites were examined. Both have same epoxy matrix, 3501-6 epoxy, but contain different carbon fibers, either AS4 or IM6. The surfaces of the composite materials were exposed to 0.5 N NaCl solution to simulate sea water at open circuit condition or cathodic potentials to simulate galvanic coupling of metals. Electrochemical impedance spectroscopy (EIS) was employed to monitor changes in the behavior of the composites. Modeling of experimental data indicated that the parameter, Rp, representing the polymer resistance decreased with increasing time of exposure for both open circuit conditions and applied cathodic potentials. The value of Rp also decreased with increasingly cathodic applied potentials. This suggested that a damage process for the polymer involving increased access of solution to the carbon fibers. SEM examination showed that cracks and polymer separations on the exposed but not on the unexposed surfaces. The fiber type did not appear to influence the damage mechanism in this study.

INTRODUCTION

Advanced carbon fiber reinforced polymer composites are currently being developed for numerous applications because of the important potential benefits of light weight, high specific modulus and good corrosion resistance. Various applications can be found in marine, aerospace, automotive and commercial structures. However, these materials are not used in isolation. They are connected to metallic materials such as fasteners and other components. As carbon is conductive and a very noble cathodic material, the coupling will result in accelerating corrosion of metal by anodic reactions and degrading the composite by cathodic reactions. Earlier studies indicated electrochemical degradation of carbon fiber composite materials. A time dependent phenomena of blistering was reported for several combinations of polymer on carbon fibers [1-4]. The blisters were filled with solution of high pH, greater than 10 [1]. Although a few degradation mechanisms were proposed and discussed, the effects of material parameters on the mechanisms of composite degradation are still poorly understood.

The objective of this study was to investigate if the fiber type influences either the mechanism or form of damage electrochemically induced in carbon fiber/polymer composites. Electrochemical impedance spectroscopy (EIS) was employed to monitor the behavior of the composites. This method, previously used to evaluate the protective coatings on metals [5,6], has recently been applied for the quantitative electrochemical studies of carbon/polymer composites [2-4]. Scanning electron microscopy was performed on both exposed and unexposed surfaces of the specimens to better understand the electrochemical degradation mechanism. The relationship between impedance data and surface features were examined. Solution chemistry resulting from degradation processes was monitored by pH measurement during the surface exposure.

EXPERIMENTAL PROCEDURES

Materials

The materials examined in this study were carbon/polymer composite materials. The composites were prepared using prepregs with the same polymer matrix, 3501-6 epoxy, but containing different carbon fibers, either AS4 or IM6. One other difference was that a sizing agent was used on IM6 fibers but not on AS4. The manufacturers standard processing cycle (350°F cure temperature) was used for both materials.

The materials were then post-cured in a convection oven for four hours at 350°F. The stacking sequence of both composite laminates (AS4/3501-6 and IM6/3501-6) were identical $(0°/90°)_{4S}$ as was the laminae thickness at 0.005 in nominal. The microstructure of composites is shown in fig. 1. The composites are 65% volume of fibers and 35% polymer for both materials.

Principle and technique of impedance measurements

Electrochemical impedance spectroscopy testing was conducted to investigate the electrochemically induced degradation mechanisms of the composites. The experimental setup for impedance measurement is schematically shown in fig. 2. With this arrangement, the solution must permeate through the polymer to contact carbon fiber. The surface area exposed to the electrolyte of 0.5 N NaCl for simulated sea water is 5.73 cm^2. A platinum sheet and a standard calomel electrode (SCE) serve as counter and reference electrodes respectively. EIS measurements in the frequency range between 1mHz and 100kHz were carried out using a frequency response analyzer (Solartron 1255) and a PAR 273 potentiostat interfaced to an IBM PC.

The experimental tests were performed on open circuit conditions or with negative potentials applied, $-0.65V_{SCE}$ and $-0.90V_{SCE}$, to simulate galvanic coupling of anodically active metals such as steel and aluminum alloys. The impedance data were displayed as Bode plots (impedance modulus |Z| vs. frequency and phase angle vs. frequency).

pH Measurement

Solution pH was measured using a digital pH meter during exposure.

Scanning electron microscopy (SEM)

Scanning electron microscopy was conducted on both exposed and unexposed specimen surfaces for AS4 and IM6 composites. Evidence of surface changes was evaluated by comparison of these two surfaces.

EXPERIMENTAL RESULTS

Open Circuit Conditions

Long term exposure tests up to 360 days were conducted on both AS4 and IM6 composites under open circuit conditions. Bode plots of

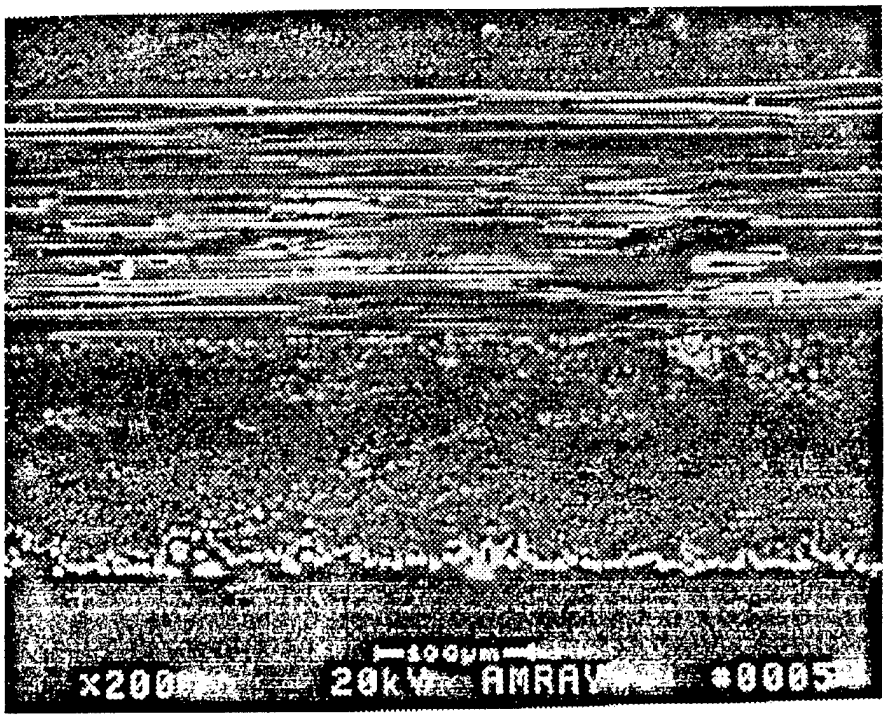


Figure 1. Microstructure of IM6/3501-6 Composite Material

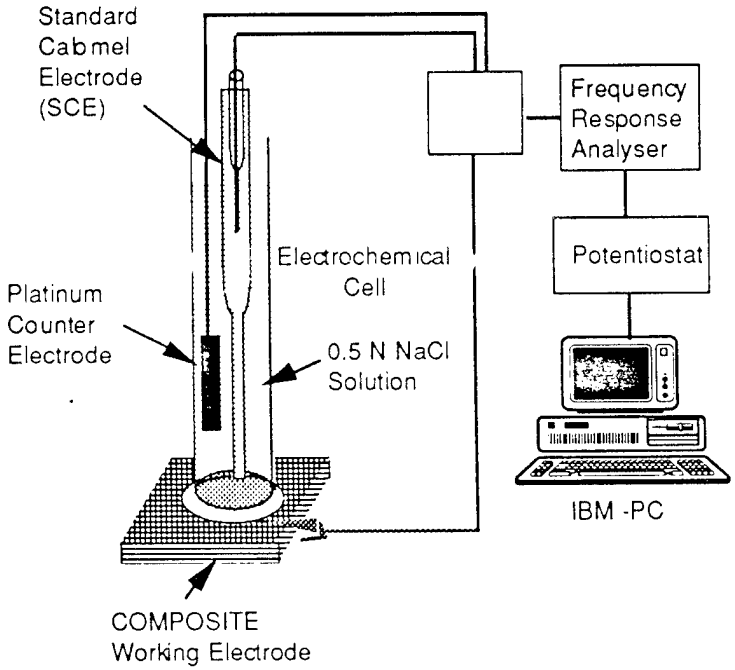


Figure 2. Experimental Setup for Impedance Spectroscopy

experimental data for the open circuit condition are shown in fig. 3 for AS4/3501-6 composite. The plots show the impedance responses from 5 hours up to 140 days of exposure. A decrease of impedance with increasing time of exposure was noticed. The most significant changes in impedance occurred in the first 100 days for both materials. The high frequency phase angle decreased in magnitude and shifted initially to the lower frequencies and then moved back to the higher values as the impedance response decreased. Identical behavior was also found for IM6/3501-6 material.

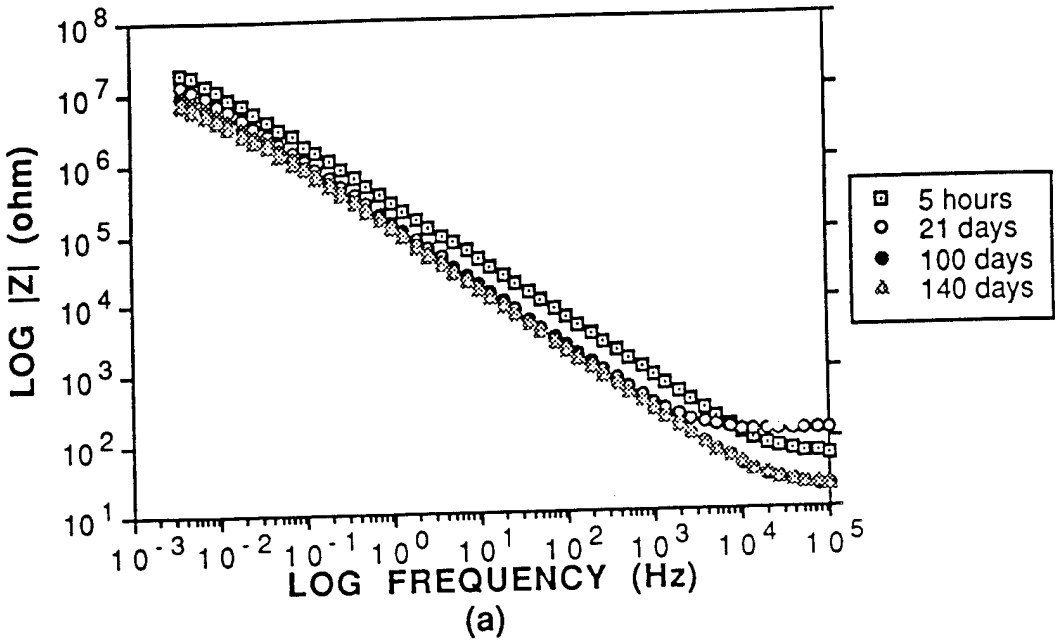
Applied Negative Potentials

Under polarized conditions, the exposure periods were up to 30 days at -650mV potential and 15 days at -900mV potential for both AS4/3501-6 and IM6/3501-6 materials. Bode plots of experimental data as the symbols at -650mV are shown in fig. 4 for AS4/3501-6 material and in fig. 5 for IM6/3501-6 material. The results reveal that the initial impedance response for cathodically polarized specimens was lower than open circuit conditions up to the high frequency arrest region. The phase angle maxima moved to the lower frequency and decreased in magnitude as the time of exposure increased. For IM6 composite, the impedance also decreased with the time of exposure. However, with AS4 composite, differences were found at applied -650mV potential. The solution resistance for AS4/3501-6 increased more than that of IM6/3501-6 material. In addition, the impedance at lower frequency increased with the time of exposure for AS4/3501-6 until 21 days then decreased.

The significant changes occurred in the first week at -900mV applied negative potential for both materials, as shown in fig. 6 for AS4/3501-6 composite. Similar features were also observed in the Bode plot for IM6/3501-6 material. It should also be noted that the indication of diffusion control was present for both -650mV and -900mV polarized materials. This was shown by a phase angle of 45^{o} .

Modeling of Experiment Data

The impedance response was simulated using equivalent circuit modeling EQUIVCRT software. The two RC circuit model, first proposed by Mansfeld and Kendig [5] for most polymer-coated metals shown below was used to provide the best fit of impedance behavior of composites and extract the parameters which provide significant information of composite degradation due to electrochemical reactions.



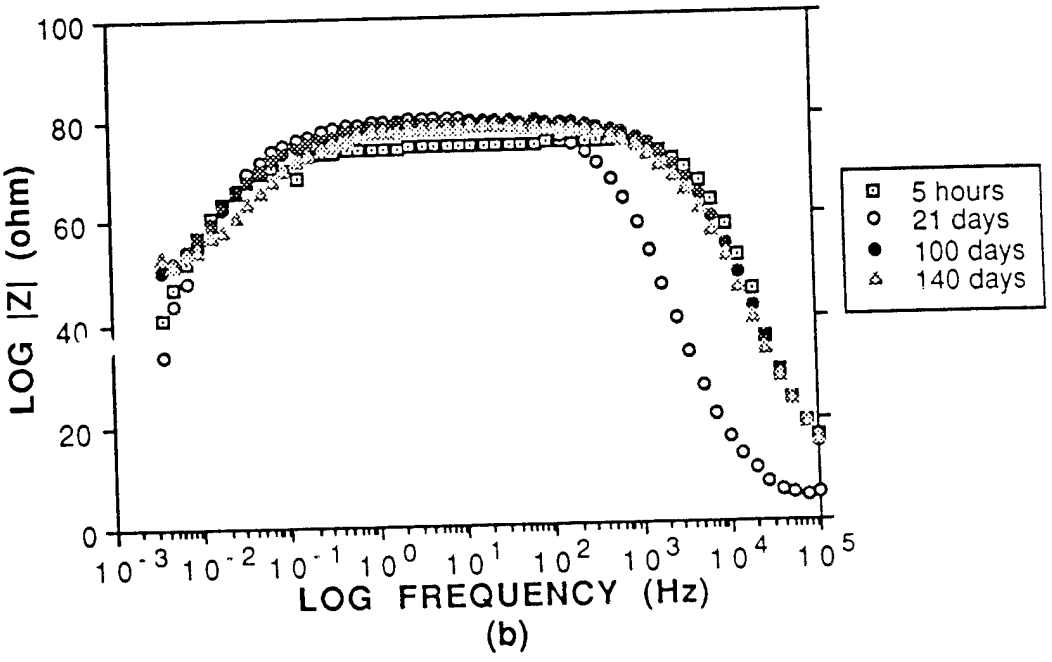
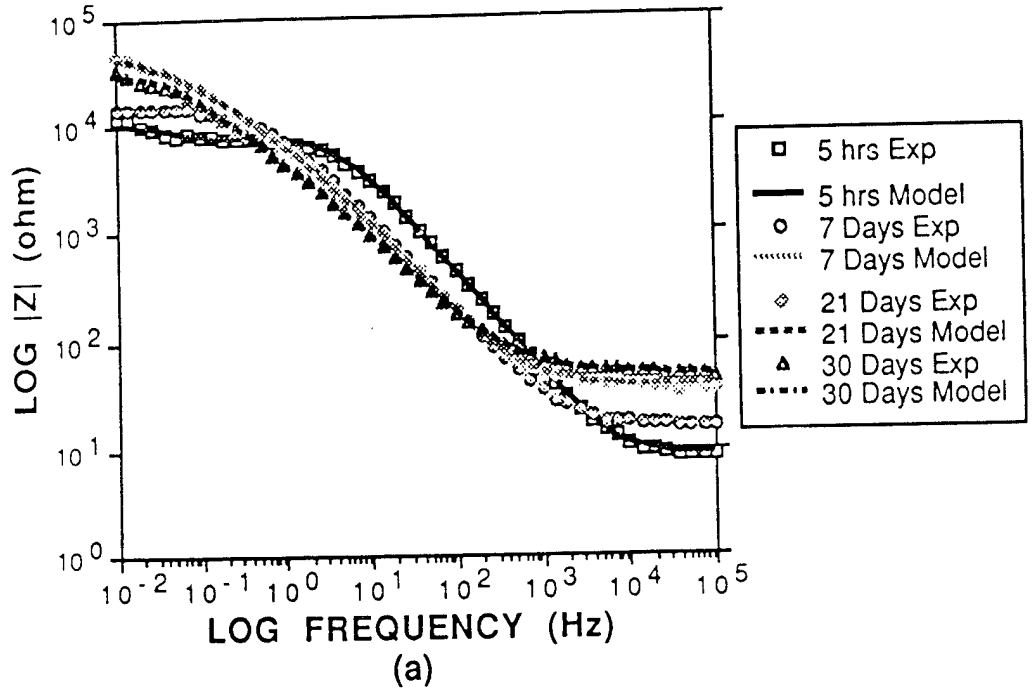
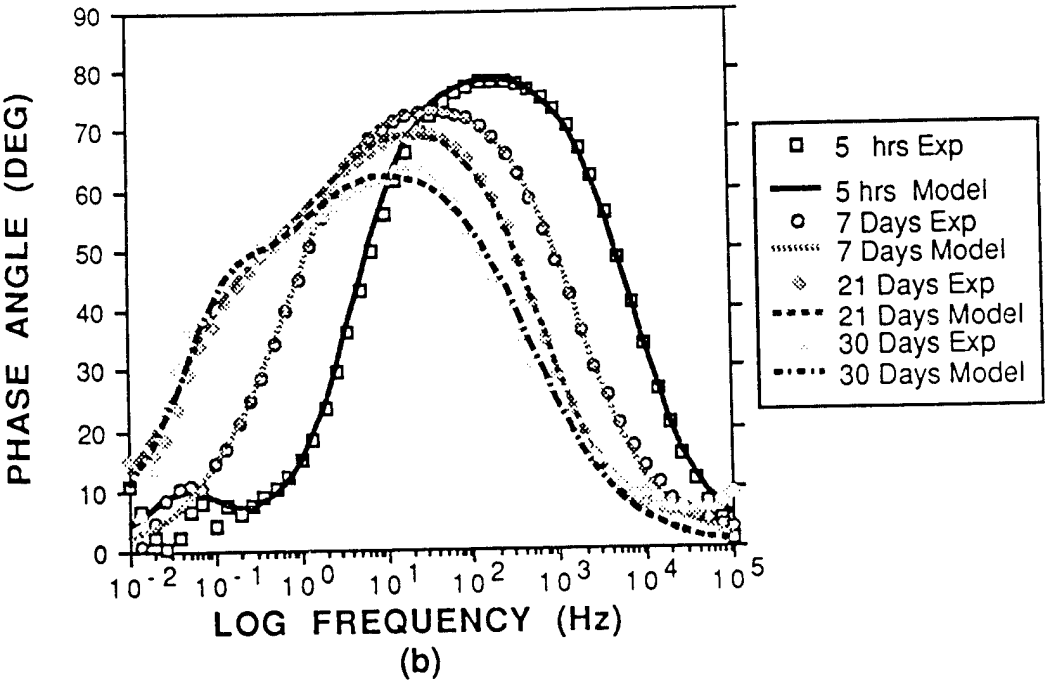


Figure 3. Bode Plot for AS4/3501-6 Composite at Open Circuit Condition

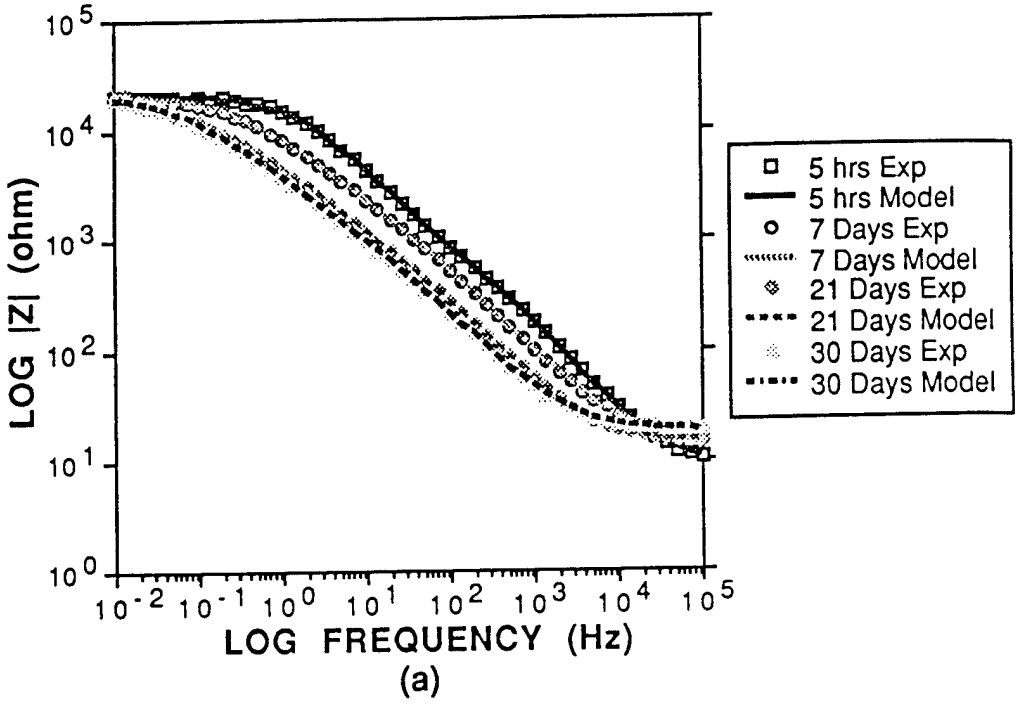


(a)



(b)

Figure 4. Bode Plot for AS4/3501-6 Composite at -650mV Applied Potential



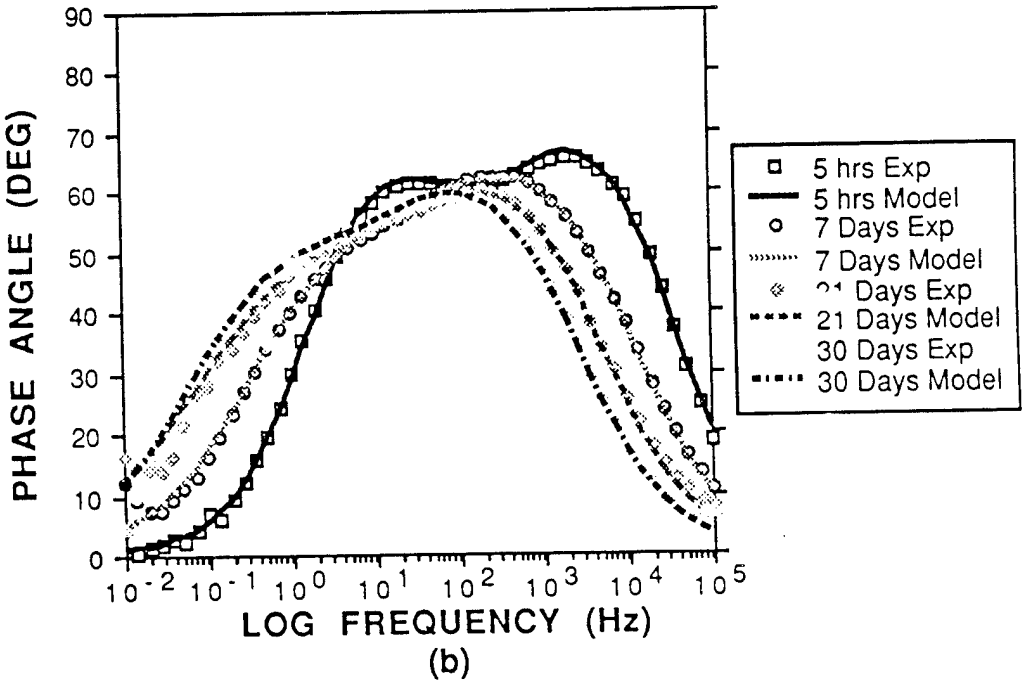
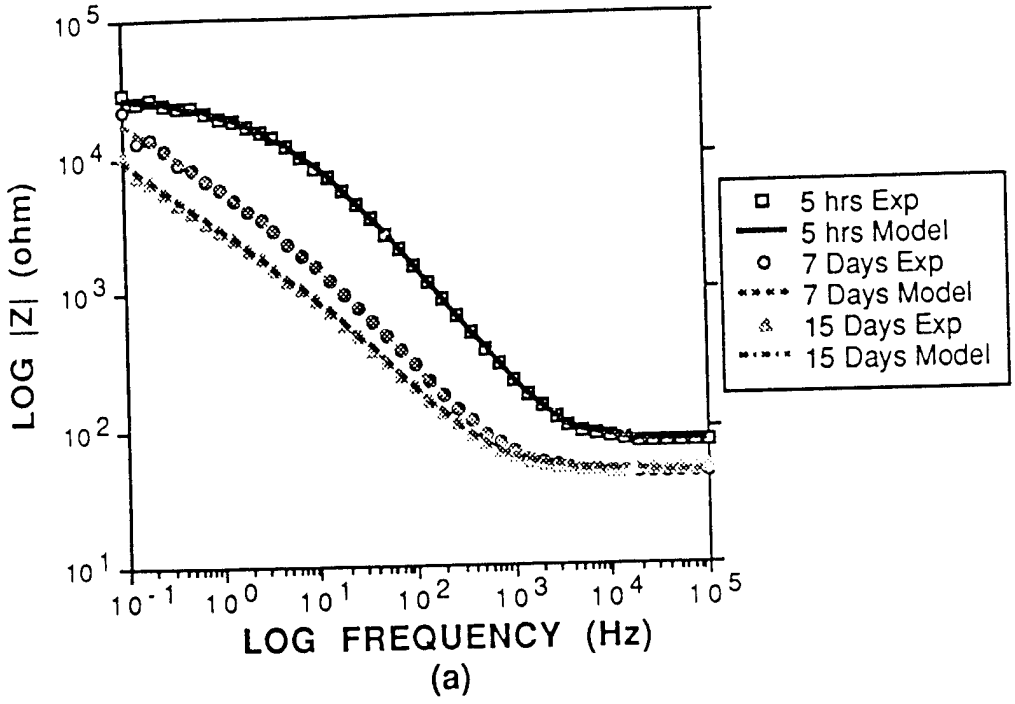


Figure 5. Bode Plot for IM6/3501-6 Composite at -650mV Applied Potential



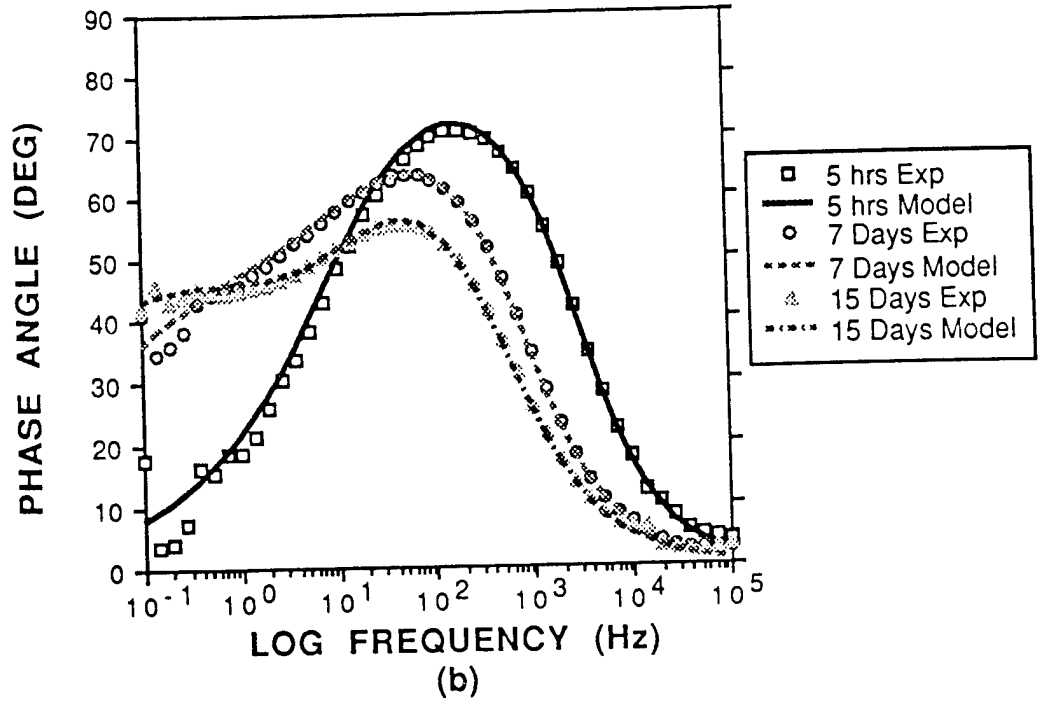
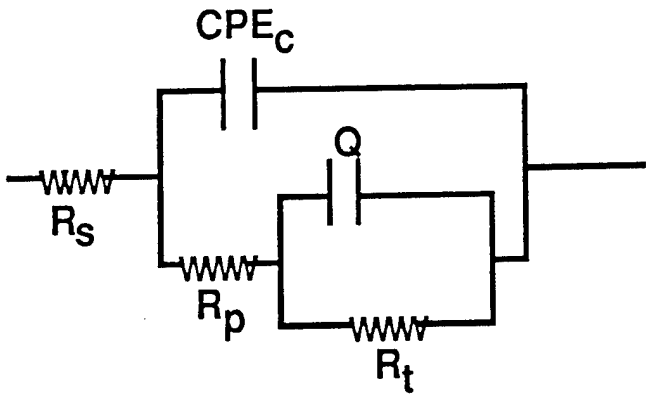


Figure 6. Bode Plot for AS4/3501-6 Composite at -900mV Applied Potential



where Rs is the solution resistance, CPE_C is the constant phase element of the polymer dielectric and Rp is the resistance of the polymer matrix due to the penetration of electrolyte through the defects and pores in the matrix. Q ($Q=Zo(j\omega)^{-n}$) is a constant phase element which allows contribution of diffusion at the carbon fiber/moisture interface region. When n=0 and 1, Q represents pure resistance and pure capacitance respectively. In the case of n=-0.5, Q behaves as a true diffusion impedance. Rt is the charge transfer resistance at the carbon fiber/polymer interface.

The simulated data from the equivalent circuit modeling are plotted as the lines together with the experimental data, as shown in fig. 3-6. The model provides a good fit to the data.

The parameters extracted through the equivalent circuit modeling varied significantly with different conditions. The parameter, Rp, representing the resistance of the polymer matrix separating fibers from electrolyte decreases rapidly with increasingly negative applied potentials, as shown in fig. 7 for AS4/3501-6 material and fig. 8 for IM6/3501-6 composite. The value of Rp also decreased with exposure time for both open circuit and applied cathodic potentials o -650mV and -900mV

Solution pH variations

An increase in solution pH was found for both materials under cathodic polarized conditions. The pH variations for AS4/3501-6 material are shown in fig. 9 . The value of pH was not significantly changed for open circuit condition. Similar results were also found on the second composite IM6/3501 system.

Microstructure Characterization

Detailed surface examinations were performed for both exposed and unexposed surfaces of composite specimens by SEM for better

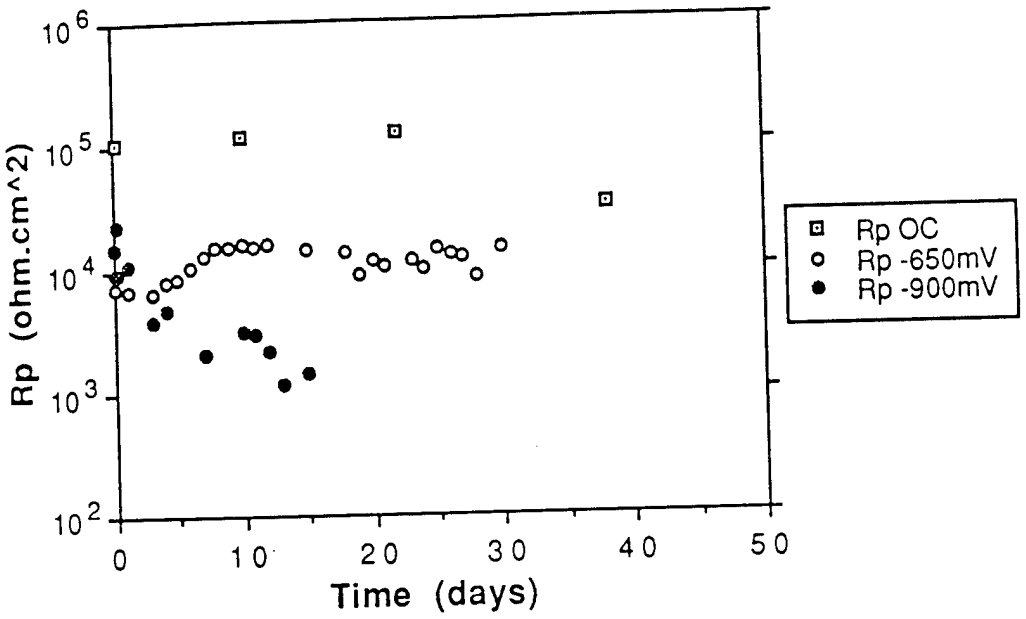


Figure 7. Polymer Resistance Rp vs. Time for AS4/3501-6 Compsite

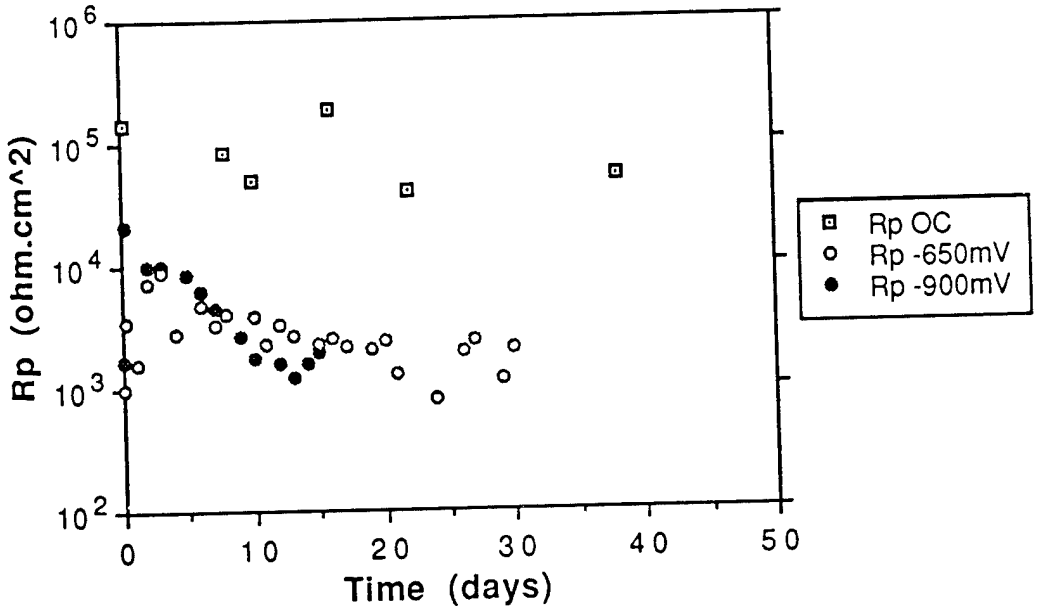


Figure 8. Polymer Resistance Rp vs. Time for IM6/3501-6 Composite

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understanding of the degradation mechanisms. The results indicated that damage features were present on the exposed surfaces of different composites, but that features changed in size and density with exposure period and potential.

In general, the unexposed composite showed a very smooth surface, fig. 10. However, cracks and polymer separation were found running along the carbon fibers for all polarized samples, fig. 11 for IM6/3501-6 material and fig. 12 for AS4/3501-6 composite after exposed to the electrolyte at -650 mV applied potential for 30 days . For IM6/3501-6 composite, it appeared that large portion of polymer were removed exposing carbon fibers directly to electrolyte. The joining of several cracks can produce this effect.

DISCUSSION

Electrochemical impedance study

Open Circuit Conditions

With increasing exposure time, impedance decreased for both composite materials. One possible reason for time dependent decrease in impedance at open circuit conditions is moisture absorption and pre-existing defects in the polymer matrix.

The effects of moisture on composite materials have been studied in detail [7-8]. It was shown that moisture has a potentially degrading effect on epoxy matrix materials. Moisture is present in many forms such as contained in the polymer free volume after manufacture or the electrolyte solution and eventually penetrates by diffusion until the moisture equilibrium or saturation concentration is achieved. The absorbed water as well as ionic solutions may also be transported along fiber-matrix interfaces and cause delamination of the interface.

The electrolyte can also permeate through pre-existing defects to contact the cathodic site. Therefore the decrease in polymer resistance as a function of time represents damage to the composite from moisture induced processes. It was shown previously that impedance spectroscopy can monitor damage of composites under open circuit condition when osmotic blistering was noted after extended periods in both distilled water and sodium chloride solutions [9]. In this case, in addition to monitoring existing defects in the composite at initiation, the defects created during exposure were also identified.

Cathodically polarized conditions

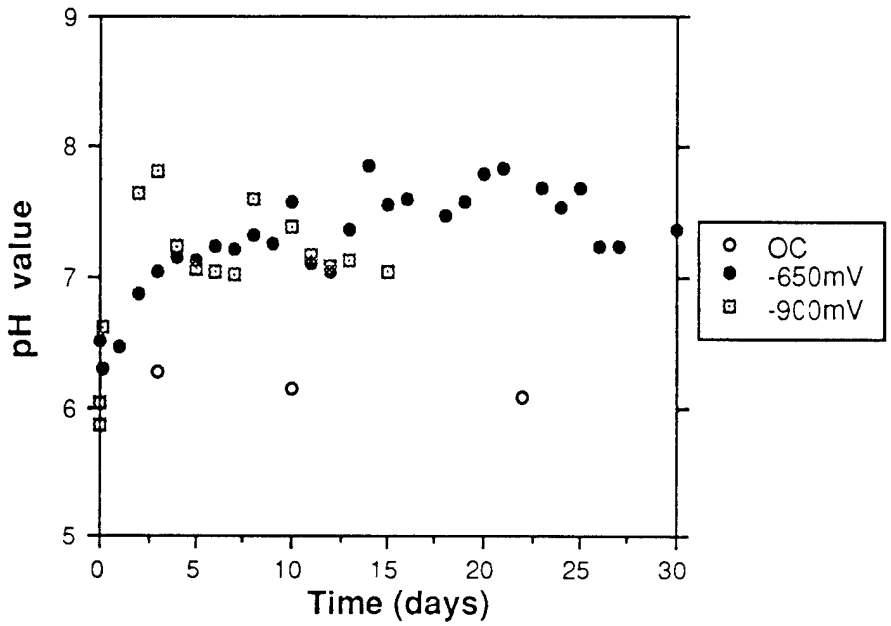

Figure 9. pH value vs. Time for AS4/3501-6 Composite

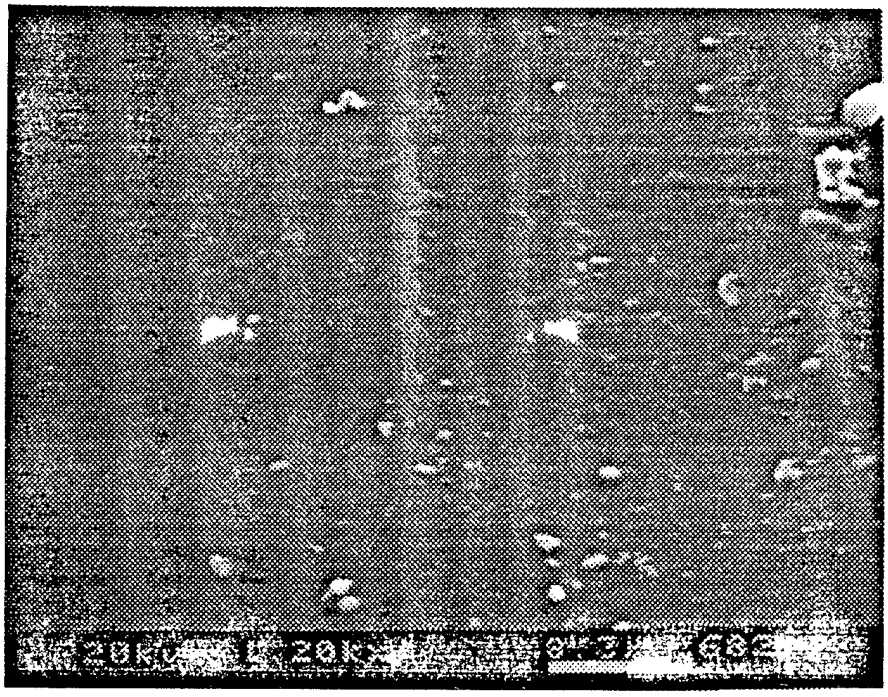

Figure 10. Unexposed Surface of IM6/3501-6 Composite Materials

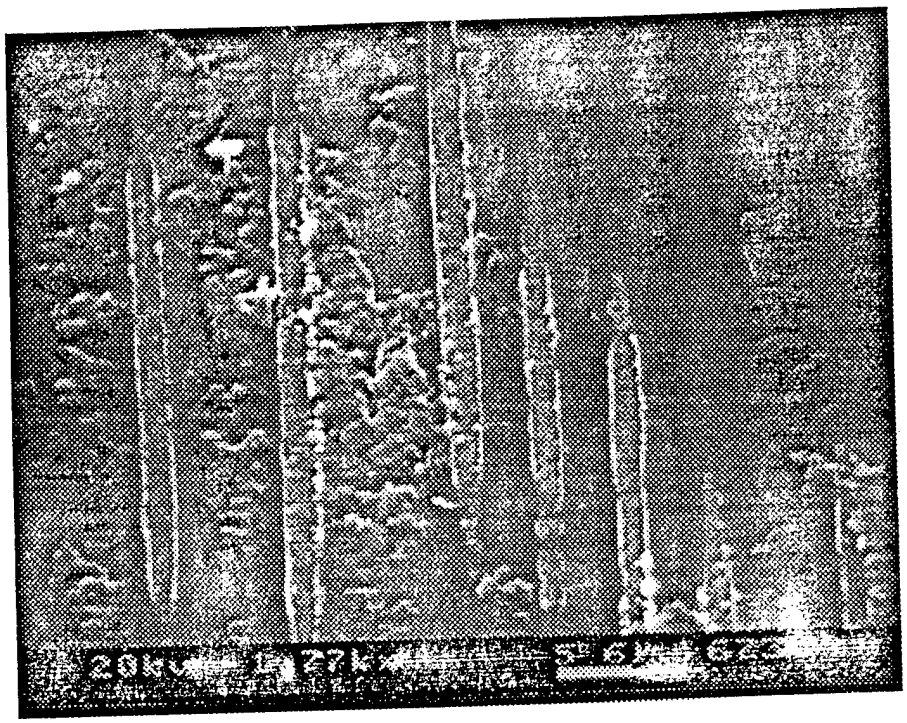

Figure 11. Exposed Surface of IM6 Composite at -650mV for 30 Days

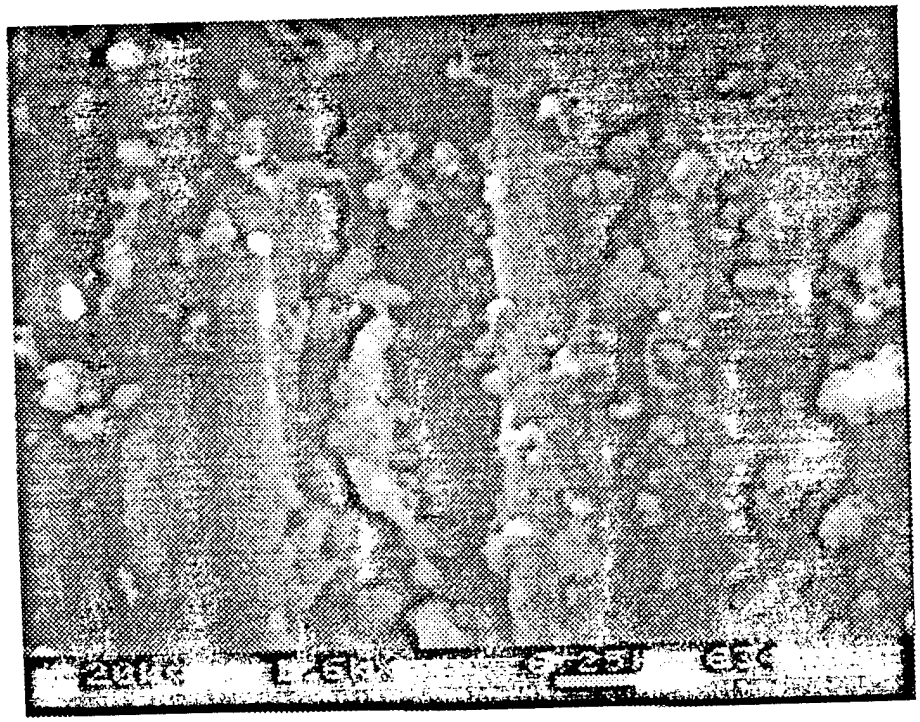

Figure 12. Exposed Surface of AS4 Composite at -650mV for 30 Days

The decrease in impedance upon initial application of potentials indicated that the cathodic reaction occurred at the carbon fiber/polymer interface immediately with no time delay. This implies that defects exist on the surface and permit the cathodic reaction to occur. The initial decrease in impedance is therefore a measure of the pre-existing defect content of the composites. Recent data indicated no difference in initial impedance response between open circuit and cathodic polarization conditions for a defect free specimen [11]. In the range of diffusion controlled potentials, the potential should not influence the initial impedance behavior.

The high pH of the solution indicated that the reduction of oxygen reaction occurred to produce hydroxyl ions $(OH)^-$ under the applied potential conditions. The mechanism of this reaction can be represented by the following equation

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

This confirms the results from several previous studies that the increase of dissolved oxygen concentration in solution decreased the time of initiating blisters in a vinyl ester composites [3]. A typical diffusion limited curve for oxygen was reported for T-300 fiber reinforced composites tested in 3.0% NaCl solutions at cathodic potentials. Similar features were also found on other composite systems such as a carbon fiber vinyl ester composite at -650mV applied potential or coupled to steel after six months in sea water.

In addition, with increasingly cathodic potentials applied the impedance decreased. The impedance variation appeared to be dependent on a reaction occurring at the cathodic site and polymer thickness.

Surface Features and Impedance

Cracks and polymer separation were found on all exposed specimen surfaces. This damage permitted easier access of solution to the carbon fiber. The surface features confirmed the reasons for decreasing in impedance and polymer resistance in the EIS studies. There are several available mechanisms. One possible mechanism is that the osmotic pressure increased as the hydroxyl ions were formed at carbon fiber/polymer interface by cathodic reduction of oxygen. As a result of the osmotic pressure, the local osmotic stress at the carbon fiber interface increased. The rate of damage accumulation in this mechanism depends on the mechanical properties and the thickness of the polymer film. For a thick polymer layer (over 100μm), when the osmotic stress

overcomes the yield stress of polymer or the interfacial bonding stress, it resulted in localized plastic deformation or creeping of polymer and eventually caused blister burst or delamination, as schematically shown in fig. 13. The galvanic blistering processes were found in previous studies of vinyl ester polymer composites [2-4]. However, in this study, the polymer film separating fibers from the exposed surface is relatively thin. The thin film could not resist the higher stresses as the osmotic rate increased due to the decreased transport distance. The increased pressure overcomes the polymer rupture strength and the blisters burst, see fig. 14. These broken blisters opened up free path and allowed more electrolyte to cathodic site. The third possibility is that the cathodic reaction products react with components of composite to either dissolve the components or the polymer matrix [9]. This process will enlarge pores and permit more electrolyte down to the cathodic site.

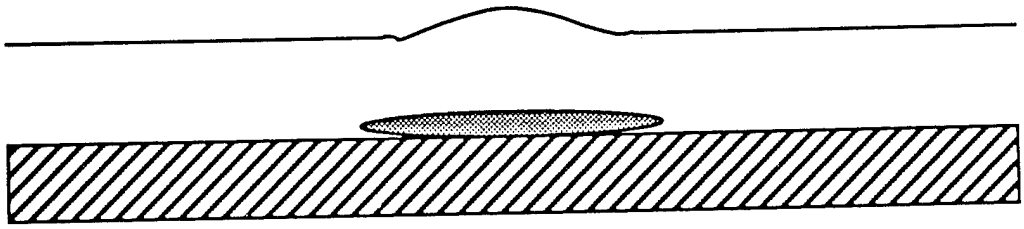

Figure 13. Schematic Diagram of Fluid Filled Blister From Osmotic Pressure

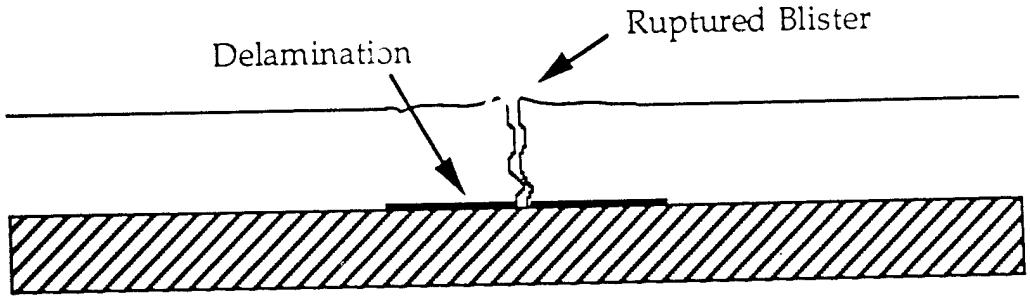

Figure 14. Rupture of Blister and Collapse Leaves Interfacial Delamination and Tortuous Path for Solution Down to Carbon Fibers

The difference in impedance behavior between the composites at -650mV applied potentials may imply that the sizing process used on IM6/3501-6 (fig. 5) but not on AS4/3501-6 (fig. 4) influenced the rate of damage. SEM examination showed different damage features for these two materials. It was found that a large portion of polymer was removed for IM6/3501-6 material, as shown in fig. 11 while narrow matrix cracking along the fibers was observed for AS4/3501-6 composite, see fig. 12. One explanation is that the sizing at the interface has a poor chemical bonding and mechanical properties in comparison with the bulk matrix material properties. The material of the sizing interface can rupture rapidly and in turn accelerate the damage process and open up a free path to the cathodic site in this case. On the other hand, the bulk matrix polymer for AS4/3501-6 may retard the blister rupture and cause the increase in impedance at low frequency because of a reaction product in the carbon/polymer matrix interface, as shown in fig. 4 for AS4/3501-6 composite. The polymer resistance Rp of IM6/3501-6 material at -650mV applied potential was slightly lower than that of AS4/3501-6 composite, fig. 7 and fig. 8. However, the damage rate at -900mV applied potential condition showed no difference between both materials, see figs. 4-5 and figs. 7-8.

Differences and Similarities in Composite Behavior

Some differences were found between the composites with same polymer matrix but different fibers in the present study. The parameters those control the damage processes are the polymer type, fiber type, fiber surface treatment, the manufacturing processes and the interfacial behavior between the fibers and polymer matrix. The polymer type, fiber surface treatment and manufacturing processes will control the permeation rate of oxygen and solution to the cathodic site and the content of initial defects. The fiber surface treatment and the interfacial behavior between the fibers and polymer significantly influences the rate of damage formation. Detailed study of the parameters which control the interface strength properties in carbon epoxy system was given in the reference [10]. As discussed in the previous section, the polymer thickness is another factor which affects the degree of damage. It is noted that the fiber type did not significantly influence the degradation mechanisms of the composites under cathodically polarized conditions. This suggests that the polymer condition and interface behavior between fibers and polymer matrix are the more important parameters. A good fiber surface treatment and interfacial strength between fibers and polymer matrix are necessary. Pre-existing defects can be avoided by good manufacturing processes.

CONCLUSIONS

1. The fiber type did not significantly influence the degradation mechanisms of the composites under galvanic exposure conditions. The polymer conditions, fiber surface treatment and interface behavior between fibers and polymer matrix are the more important control parameters.

2. The parameters from modeling provided an important degradation mechanisms of composites.

3. The decreasing in polymer resistance, Rp, with increasing time of exposure indicated that dynamic degradation processes were occurring due to the cathodic reaction at the fiber surface. The value of Rp also decreased with increasingly negative applied potentials.

4. The observed damage on exposed specimen provided an evidence of decreasing of impedance behavior of composites.

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