GRAPHITE/EPOXY COMPOSITES FOR OFFSHORE APPLICATIONS

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SUMMARY: The transverse fatigue crack growth rates of a graphite/epoxy composite (AS4C/E719LT) were investigated using a high pressure test system. Compact tension specimens of the as-received and conditioned composite were fatigued in ambient air, ambient seawater, 13.8 MPa (2000 psi) seawater and 27.6 MPa (4000 psi) seawater. The crack growth rates of the specimens tested in ambient and high pressure seawater were found to be approximately ten times higher than the growth rates of the specimens tested in ambient air. This was true for the as-received as well as the conditioned specimens, however, rates for the conditoned specimens were lower for all test conditions. Three possible mechanisms have been described for this change in growth rates. The first mechanism is the weakening of the fiber/matrix bond resulting in a reduced fracture toughness of the composite. Alternately, a change in the local stress field at the crack tip resulting from the presence of the incompressible seawater may be the controlling factor. A third possibility seems to result from competition between crack propagation through the matrix or along the fiber/matrix interface. If the composite is dry, as it would be in the as-received condition, both options are possible, and equally as likely, and crack propagation is accelerated in ambient or high pressure seawater. If the composite is saturated, however, the behavior is dominated by the properties of the toughened matrix, through which crack propagation becomes more difficult. These findings have ramifications for graphite/epoxy composites which would be used in offshore applications where they would be exposed to high pressure seawater.

KEYWORDS: corrosion fatigue, seawater, environmental test chamber, high hydrostatic pressure, graphite/epoxy

INTRODUCTION

The quest for oil in deep waters has resulted in a search for materials which can withstand the rigors of offshore environments. Depths approaching 3,000 meters and hydrostatic pressures of approximately 30 MPa will certainly test the materials used for deep water structures. Polymer composites are particularly attractive for deep water applications because of their light weight and high strength to weight ratios. However, many of the previous uses have focused on aerospace applications in which long term exposure to marine environments has not been a major factor.

The work of previous investigators indicates that the behavior of polymer composites exposed to high hydrostatic pressures and seawater environments is very dependent on the particular

polymer-reinforcement system as well as the reinforcement orientation, the processing and the mode of deformation. The hydrostatic pressure could act to close voids and pores and thus inhibit the uptake of saltwater [1]. In other cases, however, there may be increased moisture uptake due to high pressure [2]. The large hydrostatic pressure can suppress the longitudinal splitting of fibers or the debonding of fiber bundles and subsequent delamination [3] or close flaws and microcracks that initiate catastrophic cracking [4]. In addition, the reduced free volume of the polymer matrix brought about by the hydrostatic load may increase interlaminar strength by restricting polymer chain motion [5] or decrease transverse tensile strength and interfacial strength [6]. It has been reported that the increased matrix plasticization that results from moisture absorption degrades the mechanical performance of graphite/epoxy composites and can contribute to accelerated fatigue crack propagation [7]. The results of another study show increases of 15% in the Mode I fracture toughness and decreases of 15% in the Mode II fracture toughness at saturation for a carbon fiber composite with toughness-modified epoxy matrix [8]. The dry Mode I test specimens experienced brittle matrix failure and had good fiber/matrix adhesion, while the saturated specimens experienced ductile matrix failure and had poor fiber/matrix adhesion. The decrease in Mode II fracture toughness values was primarily due to poor fiber/matrix bonding.

Weakening of the fiber/matrix interface by moisture absorption allows increased fiber debonding and a corresponding rise in the interlaminar fracture resistance of graphite/epoxy composites [9]. Such fiber debonding causes crack bridging that reduces the stress intensity in the region of the crack tip and therefore slows crack propagation. Other studies reveal that increased matrix plasticity coupled with accelerated fiber/matrix interface degradation lowers the Mode I transverse fracture toughness of graphite/epoxy composites [10]. This behavior is attributed to the crack propagating more via the weakened interface than through the tougher matrix in wet specimens.

This paper describes an examination of a particular graphite/epoxy composite exposed to high pressure seawater environments. This composite is one which was under consideration for offshore applications. The particular concern is corrosion fatigue that could result from wave forces and hydrostatic presures that would develop at very large depths. The following section describes the use of compact tension specimens to study the transverse fatigue crack growth in unidirectional composites subjected to axial loading and hydrostatic pressure. The main objectives were to determine the effect that pressurized seawater has on the fatigue crack growth rate in as-received and conditioned (soaked in seawater to saturation) specimens and to investigate the factors which control failure for each of the test conditions. Tests were conducted in a pressure chamber designed for studying the corrosion fatigue behavior of composite materials subjected to high hydrostatic pressure seawater. While this research is being carried out as a function of frequency, this paper will focus on the behavior at a single frequency.

EXPERIMENTAL PROCEDURES

Materials and Specimens

Compact tension (CT) specimens (25.4 mm wide) were machined from 12 ply thick panels of AS4C/E719LT graphite/epoxy unidirectional plates according to ASTM E647 [11] for metallic materials. The flat panels were fabricated using a filament winding and autoclave cure process by R-Cubed Composites from prepreg manufactured by Fiberite. The E719LT

matrix material is a thermosetting solution-based resin with two proprietary elastomer additives for increased matrix toughness.

Specimens were notched parallel to the fiber direction using a 0.51 mm wide slitting saw blade. Fig. 1 shows the geometry of the CT specimens as well as the orientation of fibers and plies relative to the machined notch. All specimens were stored in a sealed container with desiccant to prevent moisture uptake prior to testing. The elastic properties of the test materials were determined by tension and shear tests on coupon specimens and are given in Table 1 [12].

Table 1. Material properties of AS4C/E719LT.

E_1 (GPa)	E_2 (GPa)	G_{12} (GPa)	ν_{12}	V_f (%)
128.2	8.48	5.31	0.35	60

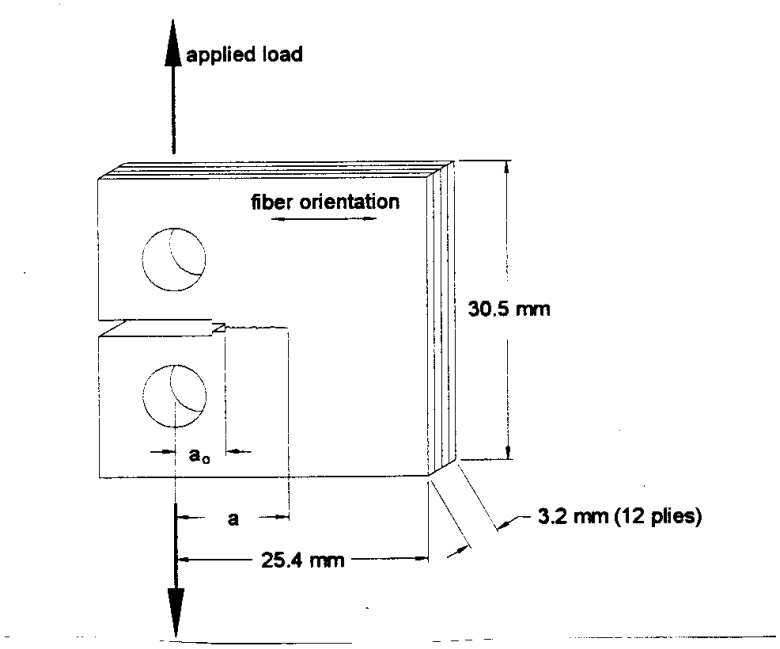

Fig. 1: Compact tension specimen geometry showing orientation of fibers and plies relative to the machined notch.

Hydrostatic Pressure Test System

The experimental test system (Fig. 2) consists of an Inconel 600 hydrostatic pressure test chamber designed by Fowkes [13] in conjunction with Autoclave Engineers. The dimensions of the test chamber accommodate a 25.4 mm wide CT specimen as well as associated grips and instrumentation. The 3.8 liter capacity chamber was also designed to maximize the environment volume to specimen area ratio and minimize the chamber surface area. The test vessel is mounted in a 100 kN MTS servohydraulic fatigue test frame, which provides control of applied loads and displacements. Data are obtained via a PC-based digital acquisition program. Pressure is monitored using an optical sensor transducer with an operating range of 0-38 MPa and an accuracy of ±0.1% in that range. The test system also contains a load

sensing clevis pin which was designed in conjunction with and manufactured by the StrainSert Company. This pin has the capability of accurately monitoring loads of less than 4.5 N and a maximum load capacity of 1560 N at 38 MPa.. The pin has an offset load due to the hydrostatic pressure of less than 9 N at 28 MPa, minimizing errors due to pressure fluctuations resulting from ram motion or pumping of the pressurizing fluid. The remainder of the test loop consists of the system pump, fluid reservoir, fluid filter, and high pressure fittings, tubes and control valves.

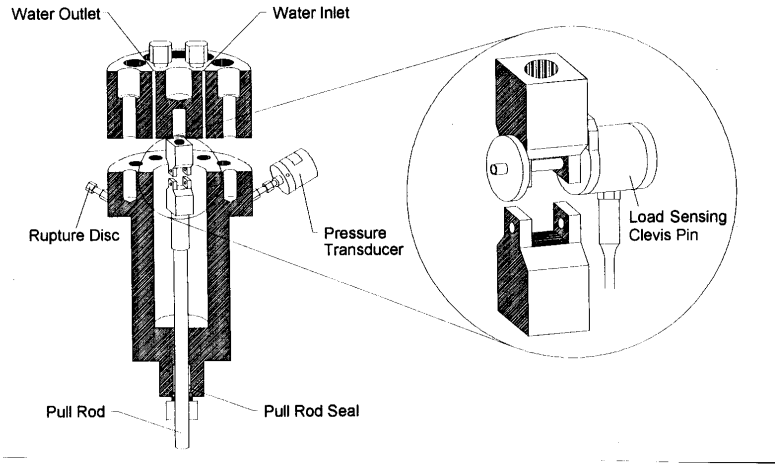

Fig. 2: Schematic of high pressure chamber and load sensing clevis pen.

Test Methods

Crack length in the enclosed chamber was monitored using the crack compliance method and the specimen compliance calibration was performed in load and displacement control. The details of the procedure have been described elsewhere [14,15]. In addition, the fracture toughness of the composite, K_{IC}, was determined from these tests according to ASTM E399 [16] for metallic materials.

Specimens were precracked in ambient air (21°C and 40-50% RH) prior to fatigue testing using the K_{max} decreasing method followed by additional precracking at the test loads. The final length of the precrack was measured under an optical microscope and was then compared with the value from the compliance calibration to ensure agreement between the actual and calculated crack lengths.
Load control tension-tension fatigue testing was performed in air, ambient seawater, 13.8 MPa (2000 psi) and 27.6 MPa (4000 psi) seawater. The mean load was 68 N with a ±45 N cyclic load (R=0.2). Waveform was 2 Hz sinusoidal. The seawater solution used in all tests consisted of synthetic sea salt in distilled water. The pH and dissolved oxygen of the seawater were monitored prior to and after testing. Specimens were also weighed before and after testing to determine any possible weight gain or loss from exposure to the seawater environment. After the specimen was precracked, it was placed in the chamber, the chamber was sealed, and the seawater was allowed to circulate though the chamber for ten minutes. Next, the chamber was taken up to the test pressure and held for two minutes to allow for pressure stabilization and to check for leaks in the system.

During testing, the load and load line displacement of the specimen were monitored using a LabVIEW® based data acquisition routine. Compliance was determined by obtaining the

slope of the load-displacement curves during load-increasing cycles. The top and bottom ten percent of the data points for each curve were excluded to eliminate crack-closure and incipient plasticity effects as suggested in the *Metals Handbook* [17]. Compliance vs. number of cycles data were converted into crack length (a) vs. cycles (N) data using the compliance calibration curve. The seven-point incremental polynomial method outlined in ASTM E647 [11] was then used to generate da/dN vs. ΔK data from the a vs. N data.

After testing, specimens were removed from the system, dried, and then stored in a vacuum desiccator for subsequent failure analysis. Specimen fracture surfaces were examined using both optical and scanning electron microscopy (SEM). To prevent surface charging, specimens were coated with a 250-350• layer of Au-Pd prior to examination in a JEOL JSM-35C scanning electron microscope. Micrographs were made of the representative fracture surface features.

EXPERIMENTAL RESULTS

Compliance curves for the as-received and conditioned composites were plotted versus crack length . A fifth order polynomial fit [18], was used to fit the data points to the curves which were identical [14]. Fracture toughness of the AS4C/E719LT composite was determined from the load displacement curves generated during the calibration process. The average K_{IC} for the as-received composite was 3.3 MPa-√m.

The results of the fatigue crack growth rate tests of the as-received AS4C/E719LT are given in Fig. 3. The plots represent three tests for each condition. There was no change in the pH or dissolved oxygen content of the water during any of the seawater tests, nor was there any measurable weight gain or loss of the specimens. Crack growth rates for tests in ambient, 13.8 and 27.6 MPa (2000 and 4000 psi) seawater were almost ten times higher than those conducted in ambient air. Two mechanisms may be responsible for the increased crack growth rate in the specimens exposed to both ambient and the high pressure seawater.

The first mechanism involves a change in fiber-matrix debonding due to the presence of the seawater. The presence of the seawater may weaken the fiber/matrix bond resulting in a decrease in the composite fracture toughness. This decrease in toughness would then result in an increase in crack growth rates for specimens tested in ambient or high pressure seawater as compared to those tested in ambient air [10]. The second model involves the presence of the nearly incompressible seawater in the fatigue-induced damage zone at the fatigue crack tip. This water cannot be expelled during the relatively short down-loading time interval during the fatigue cycle. The entrapped seawater exerts pressure on the crack faces, switching a global tension/tension fatigue test into localized tension/compression cyclic stress fields in the vicinities of the cracks [19].

Both of the proposed mechanisms are rate limited by the flow of water to the crack tip either by bulk diffusion or diffusion along fiber-matrix interfaces. At crack growth rates above $2.5x10^{-03}$ mm/cycle, there is a possible deviation to slightly lower crack growth rates of the specimens tested in ambient seawater versus those of the specimens tested at 13.8 and 27.6 MPa (2000 and 4000 psi). This may be an indication of a slight influence of pressure on the crack growth rates at higher crack growth rates.

The results of the fatigue crack growth rates of the conditioned AS4C/E719LT are given in Fig. 4. The plots represent two tests for each condition. Again, crack growth rates for tests

conducted in ambient seawater and 27.6 MPa (4000 psi) seawater are almost 10 times higher than those conducted in ambient air. Comparison of Figures 3 and 4, however, shows that all the plots are shifted to lower rates than those for the as-received specimens in Fig. 3. This seems to support the idea that there is a competition between bulk diffusion and diffusion along fiber-matrix interfaces as well as a competition between crack propagation through the matrix and along the fiber/matrix interface. If the presence of seawater weakened the fiber-matrix bond, resulting in a decrease in composite toughness and an increase in crack growth rates, one would presume that the conditioned specimens tested in air would show higher crack growth rates than the as-received specimens tested in air. However, they did not. The rates were lower, suggesting that the saturated composite is tougher or that the saturated matrix is tougher and that crack propagation in the conditioned specimens tested in air is dominated by crack propagation through the matrix. When the conditoned specimens were tested in ambient or high pressure seawater, their rates were greater than those for the conditioned specimens tested in air because the cracks could propagate more easily though the weakened interface than the already saturated matrix.

Figures 5(a-b) and 6(a-b) show micrographs of the representative fracture surfaces for as-received and conditioned specimens, respectively. One would anticipate that the most dramatic differences would occur for the conditioned specimens tested in air and the conditioned specimens tested in seawater. However, if crack propagation in the as-received specimens takes place predominantly (but not exclusively) along the interface and if crack propagation in the conditioned specimens takes place predominantly (but not exclusively) through the matrix, then differences may be difficult to observe. Evidently this is the case. The fracture surfaces of specimens for the two cases showed no noticeable morphological differences due to either ambient or pressurized seawater. Each case showed surface features resulting from the transverse cracking, which is controlled by both fiber-matrix interface failure and matrix fracture [20]. These features include broken fibers free of matrix material, indicating a weak fiber/matrix interfacial bond, and matrix failure indicated by cleavage and river markings. Also present were manufacturing flaws such as particle inclusions and porosity.

CONCLUSIONS

The transverse fatigue crack growth rates of a graphite/epoxy composite (AS4C/E719LT) were investigated using a high pressure test system. Compact tension specimens of the as-received and conditioned composite were fatigued in ambient air, ambient seawater, 13.8 MPa (2000 psi) seawater and 27.6 MPa (4000 psi) seawater. The crack growth rates of the specimens tested in ambient and high pressure seawater were found to be approximately ten times higher than the growth rates of the specimens tested in ambient air. This was true for the as-received as well as the conditioned specimens, however, rates for the conditoned specimens were lower for all test conditions. Three possible mechanisms have been described for this change in growth rates. The first mechanism is the weakening of the fiber-matrix bond resulting in a reduced fracture toughness of the composite. Alternately, a change in the local stress field at the crack tip resulting from the presence of the incompressible seawater may be the controlling factor. A third possibility seems to be a competition between crack propagation through the matrix or along the fiber/matrix interface. If the composite is dry, as it would be in the as-received condition, both options are possible as equally as likely and crack propagation is accelerated in ambient or high pressure seawater, If the composite is saturated, however, the behavior is dominated by the properties of the toughend matrix, through which crack propagation becomes more difficult.

Post-failure optical and scanning electron microscopy did not indicate significant differences between the fracture surfaces of the specimens tested in ambient air versus those tested in ambient and high pressure seawater. This is understandable if it is assumed that crack propagation through the matrix and along the fiber/matrix interface are both possible and microscopy of selected regions of the fracture surfaces may not reveal noticeable differences. Typical fracture surface morphologies included clean broken fibers, matrix fracture, broken fibers with adhered matrix materials, and surface voids and inclusions. A more detailed statistical analysis of the fracture surfaces is needed to confirm the third possibility.

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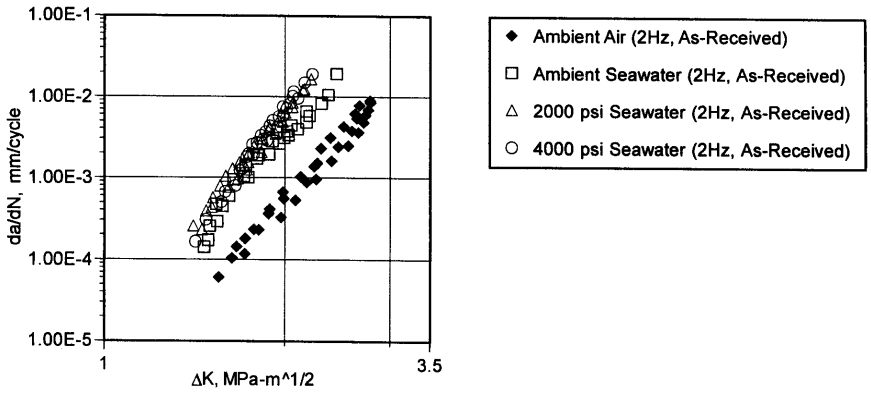


Fig. 3: Fatigue crack growth rate data for transverse cracking of as-received graphite/epoxy composites.

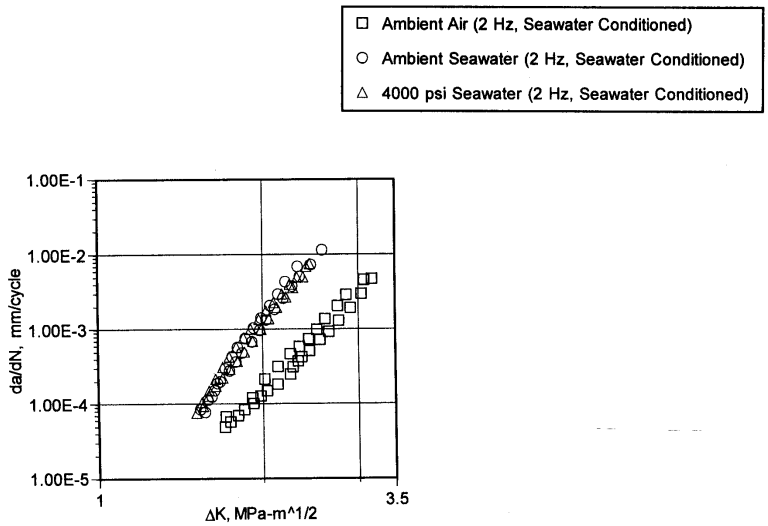
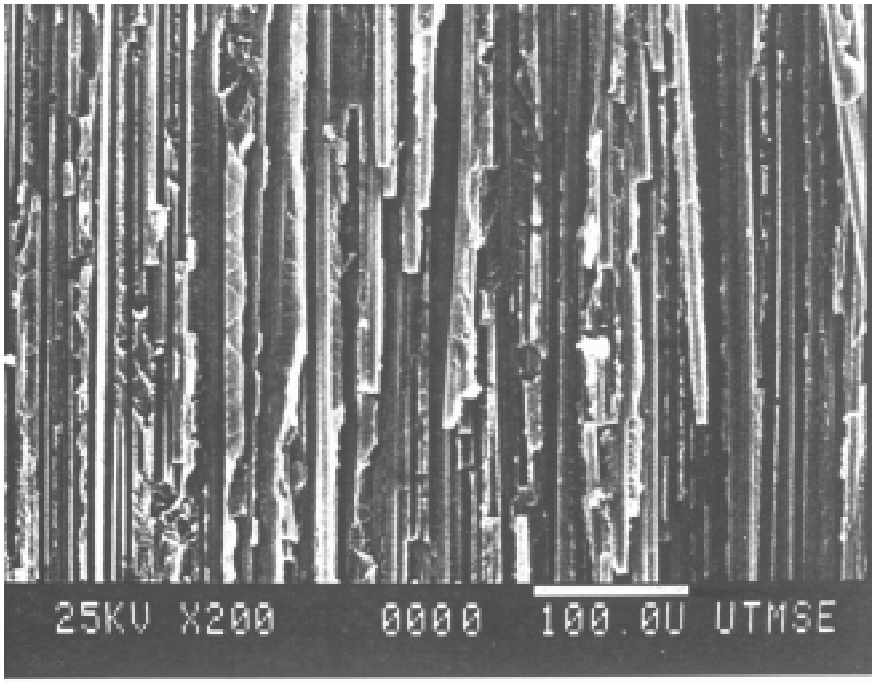
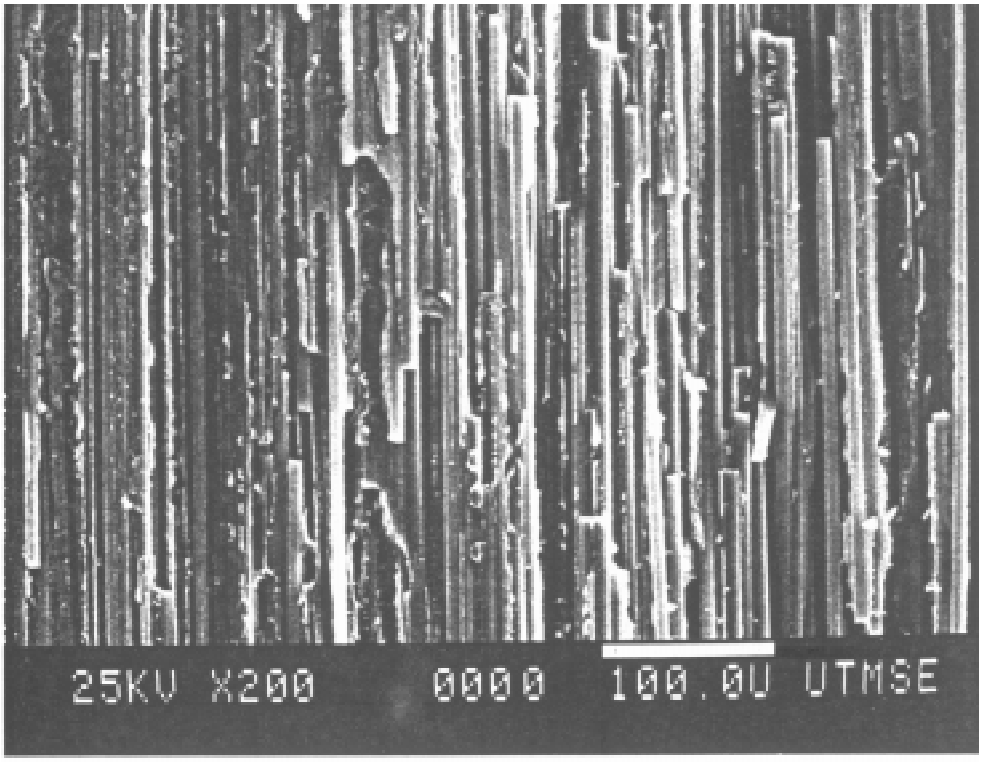


Fig. 4: Fatigue crack growth rate data for transverse cracking of conditioned graphite/epoxy composites.

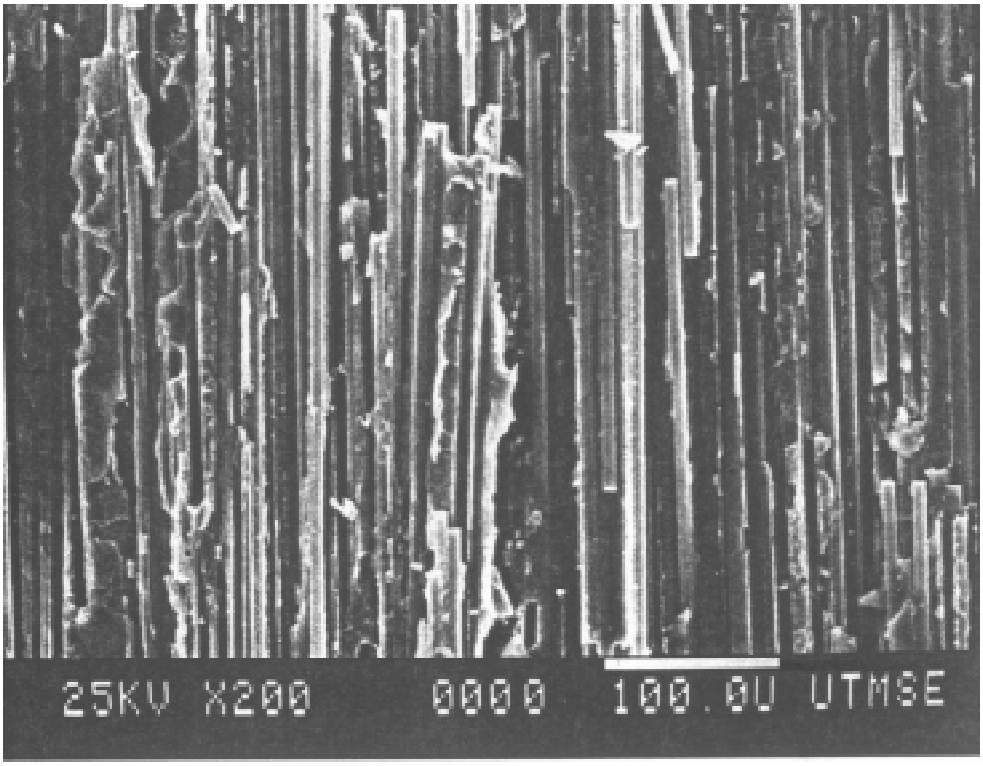


(a)

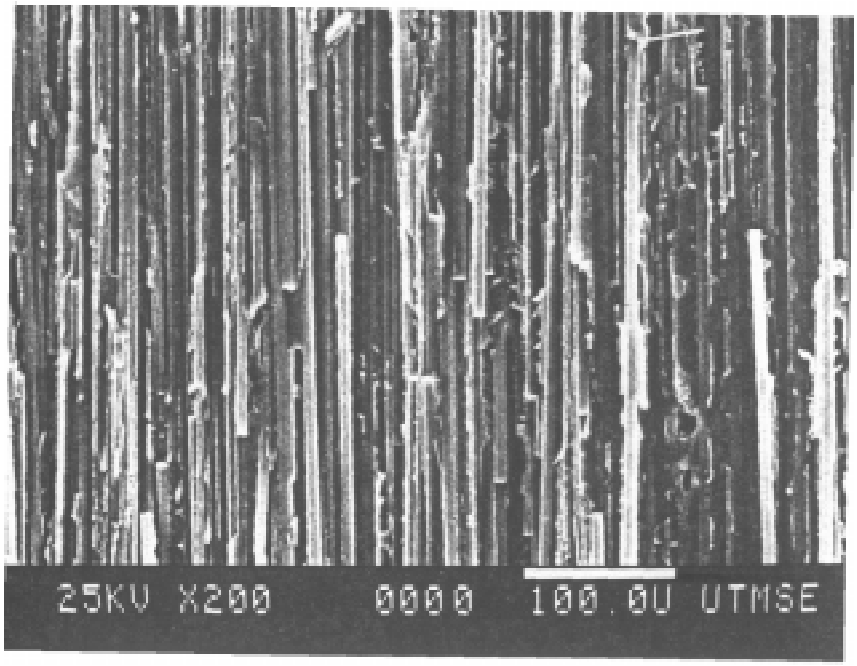


(b)

Fig. 5: Fracture surfaces from as-received graphite/epoxy composites
a.tested in ambient air
b. tested in 4000 psi seawater



(a)



(b)

Fig. 6: Fracture surfaces from conditioned graphite/epoxy composites
a.tested in ambient air
b. tested in 4000 psi seawater

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