THE EFFECT OF SEAWATER EXPOSURE ON THE FATIGUE DELAMINATION GROWTH OF A POLYMERIC COMPOSITE

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ABSTRACT

The effect of seawater exposure on the fatigue delamination growth of a graphite/epoxy composite has been investigated using edge delamination tests to determine the suitability of such material in offshore applications under the combined effect of wave loading and seawater exposure. With dry and pre–conditioned samples, the growth of fatigue delamination and the resulting reduction in stiffness have been monitored and compared. The effect of seawater exposure on the damage growth mechanisms has been established by periodically interrupting the fatigue experiment to measure the growth of delamination and to examine polished edges of the sample. The strain energy release rate associated with the delamination growth has been estimated. The effect of moisture on strain energy release rate is also discussed.

KEYWORDS

graphite/epoxy composite, moisture, seawater, delamination, strain energy release rate

INTRODUCTION

The use of fiber-reinforced polymeric composites on offshore structures could strongly enhance the ability to recover oil in deep water [Williams, 1990]. Fiber–reinforced composites are generally considered to have superior fatigue performance [Reifsnider, 1991]. Coupled with good corrosion resistance, the high specific stiffness and strength of the composite materials offer potential advantages such as substantial weight and cost reduction of the recovery structure for deep water.

The long–term durability of composites however, must be characterized before their full potential can be realized in the aggressive environment of seawater, in which the composite is subjected to fatigue wave loading and moisture absorption. Fatigue and damage development in composites have been the subjects of many investigations in recent years [Reifsnider, 1991]. Of the several forms of damage, delamination has been identified as the most dominant in the fatigue life of a fiber–reinforced composite.

The effect of moisture on the delamination is quite complex. It can be beneficial due to the relief of residual thermal curing stresses and matrix plasticization. It can also be detrimental because of the induced chemical and/or physical degradation [Garg, 1986; Marom, 1989; Hooper, et al., 1991]. Several investigations have examined the fatigue behavior of composites in seawater environment [Sumsion, 1976; 1979; Sandifer, 1982], but few have investigated the combined effect of fatigue wave loading and seawater exposure on the mechanisms and rate of damage growth.

In this paper, results in the effect of seawater exposure on the fatigue delamination growth of a graphite/epoxy composite will be presented. In particular, the delamination growth and the resulting stiffness reduction have been characterized. The difference between the damage development of the dry and pre–conditioned samples can be used to gage the effect of moisture on fatigue damage. In addition, the interlaminar strain energy release rate of the composite laminate has been estimated to illustrate the stress–relieving effect of the moisture absorption.

EXPERIMENTAL PROCEDURES

Materials. The composite used in this investigation was the TACTIX 556 epoxy novolac resin (Dow Chemical USA) reinforced with IM–7 (Hercules, Inc.) graphite fibers. The TACTIX 556 resin is a low moisture absorption hydrocarbon epoxy novolac resin that has a dicyclopentadiene backbone. The material was supplied by Dow Chemical in the form of cured quasi–isotropic laminates with a stacking sequence of $[45, 0, -45, 90]_S$. The average ply thickness is 0.16 mm (0.00625 inch) and the nominal fiber volume fraction is 50%.

The laminate was cut with a water–cooled diamond blade into samples of 228.6 mm by 12.7 mm (9 inch by 0.5 inch). The average moisture content of the laminate after the cutting operation is approximately 0.43 wt.%, as determined by the weight loss after drying at 100°C in a vacuum oven for 20 hours. No additional weight loss can be detected for longer times. All the samples used in this investigation, however, were used in the as–cut condition. Sample edges were polished on a Struér Abramin polisher. Initial examination of the polished sample edges revealed occasional occurrence of manufacturing flaws that often exist between plies.

Moisture Conditioning. Substitute seawater mixed from distilled water and a synthetic sea salt, Instant Ocean, was used for moisture conditioning. The Instant Ocean meets the ASTM standard for substitute seawater. The specific gravity of the substitute seawater was controlled to 1.027±0.001. Some of the samples were conditioned in the seawater prior to testing. A silicone gel coating, which was later removed prior to microscope examination, was applied to the edges of these samples to minimize the diffusion and possible wicking through the edges.

The results of the sorption experiment will not be presented here because the weight gain data was inaccurate due to the growth of a thin film, which was possibly organic, on the sample surface. Two presoaked samples with estimated weight gains of 0.35% and 0.80% (near saturation) were used in fatigue experiments. These weight gains were based on the as–cut laminate weight, excluding the film weight that was estimated from the extrapolation of the initial linear region of the sorption curve.

Testing Procedures. An MTS 810 servohydraulic testing machine was used in all tests. Quasi–static tension tests were performed to determine the laminate modulus. The test was performed under displacement–controlled mode at 0.25 mm/min (0.01 in/min). T–type strain gages were used to measure the strains.

Edge–delamination tests [O'Brien, 1982] in fatigue were performed under tension–tension load–controlled mode. A tubular composite structure, such as the riser, typically is subjected to tension–tension fatigue [Sparks, 1991]. Although the behavior of the flat specimens is not representative of the behavior of tubular specimens, interlaminar normal stresses exist in both cases [Foral and Gilbreath, 1989]. The maximum fatigue stress applied was 275.8 MPa (40 ksi), which was approximately 40% of the ultimate tensile strength of the laminate. The stress ratio was 0.25; the frequency was 0.1 Hz. The low frequency, which corresponds to the peak width of a typical wave loading power spectrum [Hartt and Lin, 1986], was selected so that the synergistic effect of fatigue and seawater exposure can be characterized in reasonable time periods. Fatigue tests were performed up to 100,000 cycles.

An environmental cell was designed so that the sample can be tested in fatigue under the exposure of seawater. The seawater in the environmental cell was drained and refilled with fresh seawater every 5,000 cycle. Fatigue tests in the environment cell (wet fatigue) were performed on an as–cut sample (dry sample) and presoaked samples with moisture gains of 0.35% and 0.80% at the beginning of fatigue. Fatigue tests in air (dry fatigue) were also performed with dry samples.

Modulus of the damaged sample was measured periodically by interrupting the fatigue test, removing the sample from the environmental cell if needed, and testing quasi–statically in a low load range. The load and displacement, which was measured with an extensometer, were transferred to an X–Y plotter. The knife edges of the extensometer were positioned in V–notches cut into two small pieces of fiber glass–reinforced epoxy that were bonded to the sample with a silicone gel.

Delamination area was measured with an ultrasonic C–scan unit (Testek, Model LSB). The scanned results were first reproduced and enlarged on a xerox machine. The delamination was then determined by tracing the copies at least three times on a digitizing tablet. The polished edges of samples were monitored using an optical microscope (magnification 50–400X), which was also used to measure the length of delamination on the sample edges.

RESULTS AND DISCUSSION

Tensile Tests. The average undamaged laminate modulus (E_0) was determined as 52.7 GPa (7.64 Msi). Although lamina elastic properties were unavailable at this time, they were needed in later calculation. The following set of constants were used: E_L=134 GPa (19.5 Msi), E_T= 10.0 GPa (1.45 Msi), G_{LT}=5.52 GPa (0.8 Msi), ν_{LT}=0.3. These constants are similar to those of the T300/5208 system since the IM7/556 system has similar lamina properties [Barron, 1992]. Adjustments in properties of the T300/5208 system were made so that the calculated laminate modulus matched the measured laminate modulus.

Ply Crack Development. Several forms of damage developed during fatigue cycling, and the characteristics of moisture–conditioned samples are different from those of dry samples. Transverse cracks first form in the 90° plies. They usually lead to cracks in the –45° plies. These cracks are dominated by the fiber/matrix interfacial failure, suggesting a relatively weak fiber/matrix interface. They developed rapidly and reached saturation in less than 30,000 cycles. The average numbers of cracks for all samples at saturation are shown in Table 1.

Table 1. Average number of ply cracks at saturation

sample condition	fatigue test condition	cracks in 90° ply per mm (per inch)	crack in –45° ply per mm (per inch)
Dry	Dry	0.866 (22.0)	0.728 (18.5)
Dry	Wet	0.921 (23.4)	0.823 (20.9)
0.35%	Wet	0.850 (21.6)	0.583 (14.8)
0.80%	Wet	0.874 (22.2)	0.508 (12.9)

The numbers of transverse cracks in the 90° plies are similar for all cases. A reduction in the number of transverse cracks had been observed on another system even when there is a degradation of transverse tensile strength because relief of residual thermal curing stresses in the 90° plies is expected for the sample soaked to saturation [Kriz and Stinchcomb, 1982]. It is not clear whether seawater absorption degrades the fiber/matrix interface of the system studied here, but seawater exposure might not have a significant effect on the interfacial strength of the system used in this study since the cracking is of fiber/matrix interfacial failure in either dry or wet condition. In a recent study conducted at Texas A&M University [Grant, 1991], two of the three graphite/thermoset systems studied gave the same transverse tensile strength for dry specimens as those saturated with seawater. In both systems with unchanged transverse strength, failures for dry and saturated specimens were both at the interface, which was also the case for the transverse cracks observed in the fatigue tests performed here.

The number of cracks in the –45° ply, on the other hand, exhibits a decreasing trend as the moisture content of the sample increases. This observation supports the relief of thermal curing stresses caused by the moisture–induced swelling. Even for the case with the sample soaked to a nominal weight gain of 0.35%, there is a reduction in ply cracks because the moisture is non–uniformly distributed and the moisture content is higher than nominal value in –45° plies.

Edge Delamination Development. The edge delamination, which was also dominated by the fiber/matrix interfacial failure, forms at the –45°/90° interface, in the 90° ply and mid–plane 90°/90° interface, or at the 0°/–45° interface. The delamination grew rapidly along the length of the specimen, and more slowly across the width. The characteristics of the edge delamination growth is different between dry and moisture–conditioned samples. For the fatigue tests with dry samples, the dominant mode of delamination is at the –45°/90° ply interface. These cracks are long and straight, occasionally jump to the opposite –45°/90° ply interface through 90° transverse cracks. This is illustrated in Fig. 1a. The 0°/–45° delamination, which always emanated from the –45° ply crack, is also present. The pattern of edge delamination is the same for dry test with dry sample and wet test with initially dry sample. The moisture obviously has little effect during fatigue cycling.

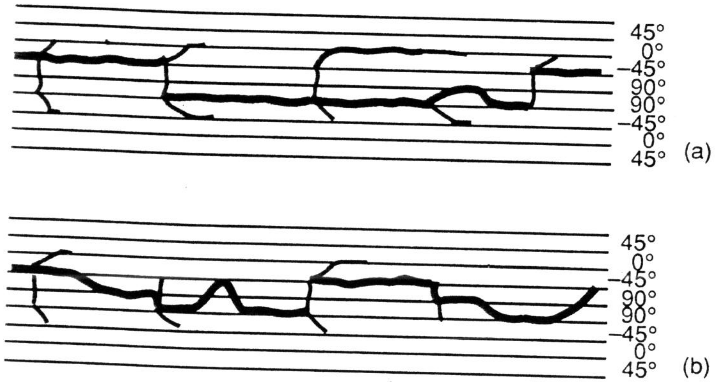

Figure 1. Illustrations of the edge delamination.

For the moisture–conditioned samples, the delamination path is irregular, and the delamination at the 90°/90° interface or within 90° plies becomes significant, as illustrated in Fig. 1b. The difference in the combination of delamination paths for all samples is shown in Table 2. The percentage of the 0°/–45° delamination is misleading because most of these cracks are small compared to the other two modes. The effect of moisture is seen to decrease the 0°/–45° and –45°/90° delamination, but to increase the delamination in the 90° plies. The reduction in the 0°/–45° delamination is expected since the –45° ply cracks are less for moisture–conditioned samples, and the 0°/–45° delamination always emanate from the –45° ply crack.

Table 2. Delamination path characteristics

sample condition	fatigue test condition	90°/90° or 90° (% of total)	–45°/90° (% of total)	0°/–45° (% of total)
Dry	Dry	20.7	41.8	37.5
Dry	Wet	15.3	44.1	40.5
0.35%	Wet	34.0	38.5	27.5
0.80%	Wet	43.7	36.1	20.2

Closed–form solution of the strain energy release rate (SERR) associated with the edge delamination had been derived based on the classical laminate theory [O'Brien, 1982]. The SERR (G) is independent of the delamination size and is given by:

$$G = 0.5\,(E - E^*)\,\varepsilon^2 t \tag{1}$$

where E is the laminate modulus, E^* is the modulus of the delaminated sublaminates, ε is the strain, and t is the laminate thickness. This was later expanded to include the effects of residual thermal curing stresses and moisture absorption using ply–by–ply analysis [O'Brien et al., 1985; Hooper et al., 1991], which was the procedure used here. Various hygrothermal constants are needed in the calculation. Only the temperature difference resulting from the cure cycle is available at ΔT=–132°C (–270°F). The following values are assummed; coefficients of thermal expansion: $\alpha_L=-3.6\times10^{-7}$ mm/mm/°C (-2×10^{-7} in/in/°F), $\alpha_T=2.7\times10^{-5}$ mm/mm/°C (1.5×10^{-5} in/in/°F); diffusion coefficient: $D=3.875\times10^{-12}$ mm^2/s (1.5×10^{-7} in^2/hr); maximum moisture content: M_m=0.81%; and coefficients of moisture expansion: $\beta_L=0$, $\beta_T=2.5\times10^{-3}$ mm/mm/% (2.5×10^{-3} in/in/%). The results of the calculation for delamination at –45°/90° and 90°/90° interfaces are shown in Table 3, in which the SERR was calculated with and without the consideration of residual thermal curing stresses from cure cycle and hygroscopic stresses from 0.80% moisture absorption. Since load–controlled fatigue tests were used, the strain increases as the fatigue cycle increases due to the modulus reduction. The strain was calculated from the maximum stress level and undamaged laminate modulus. The SERR is thus the initial SERR at the beginning of fatigue.

Table 3. Strain energy release rate calculation

delamination location	dry J/m^2 (in–lb/in^2)	dry+thermal J/m^2 (in–lb/in^2)	dry+thermal+0.80% J/m^2 (in–lb/in^2)
–45°/90°	117 (0.669)	164 (0.935)	142 (0.809)
90°/90°	33.1 (0.189)	63.0 (0.360)	34.8 (0.199)

For the fatigue tests with dry samples, the delamination in the 90° plies is small compared to the delamination at –45°/90° interface because the SERR available is less than that for –45°/90° delaminations. The effect of thermal cool–down stress from cure cycle is to raise the SERR, while the moisture tends to reduce the SERR. In the table presented here, however, the reduction in SERR due to the moisture absorption is relatively small because the TACTIX 556 resin absorbs relatively less moisture, which should lead to less moisture–induced swelling.

Although the effect of moisture on the SERR is larger for delamination at 90°/90° interface, it is conceivable the increase in the 90° delamination for pre–conditioned samples is caused by the seawater degradation. The delamination at the –45°/90° interface requires a relatively high SERR. The effect of moisture–induced reduction in SERR can be higher than the effect of the moisture–induced degradation, leading to reduction in the –45°/90° delamination. The 90°/90°

delamination, on the other hand, requires relatively small SERR [Lee, 1990]. The effect of moisture–induced degradation can be larger than the effect of moisture–induced reduction in SERR, leading to increase in that mode of delamination.

The SERR calculation shown above however, can only be used for the purpose of comparison because actual hygrothermal data is unavailable. Such information is currently being developed for the system used in this study. It should also be noted that all modes of delaminations are presented in one sample, and the calculation is not strically valid. In addition, the 90° delamination is often quite irregular, not following the 90°/90° interface.

The delamination growth obtained from C–scan results are shown in Fig. 2 as a function of fatigue cycles. The delaminated area (A), which was measured in the gage section only, is normalized against the entire area (A_0) in the gage section. The C–scan image is actually a through–thickness representation of all modes of delaminations. However, since the –45°/90° and 90° delamination are always larger than the 0°/–45° delamination and they overlap, the C–scan image is a representation of –45°/90° and/or 90° delaminations. It can be seen that the case of the wet fatigue with 0.80% moisture sample has the smallest delamination growth. Although a significant portion of the delamination is the 90° delamination that requires less energy, the available SERR for 90° delamination is also less. There is also the moisture–induced reduction in SERR, and the resulting overall delamination growth is less.

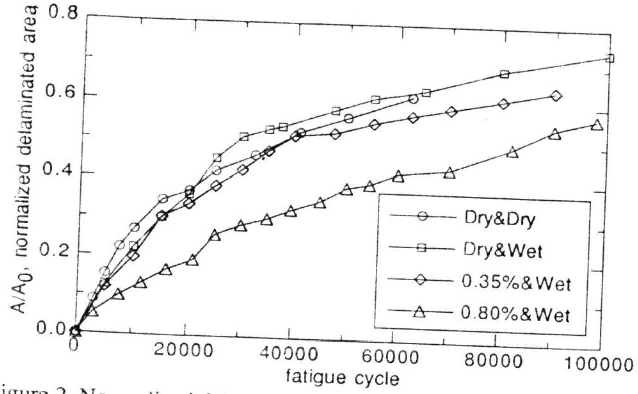

Figure 2. Normalized delaminated area as a function of fatigue cycles.

Stiffness Reduction and Delamination. The modulus reduction as a function of fatigue cycle is shown in Figure 3. Scattering of data is obvious since it was impossible to position and align the extensometer and the sample to exact locations. The reduction of modulus is smaller for the case of wet fatigue with 0.80% moisture sample. This is expected since the delamination growth is smallest for this case. For other cases, the trend of modulus reduction is similar.

It is useful to plot the modulus reduction as a function of delamination growth, and the result is shown in Figure 4. Linear relationship based on simple rule of mixture was suggested to relate the modulus reduction to delamination [O'Brien, 1982]:

$$E = E_0 - (E_0 - E^*)\,(A/A_0) \tag{2}$$

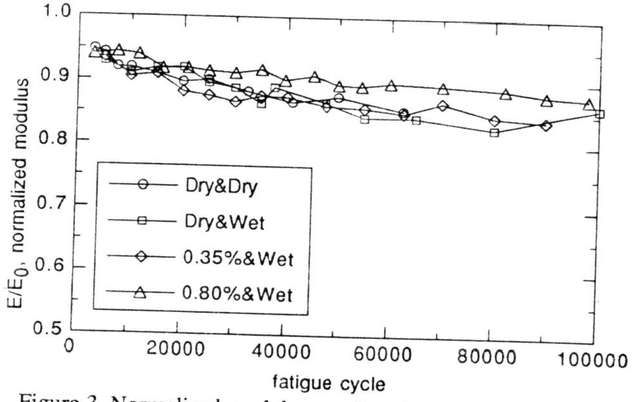

Figure 3. Normalized modulus as a function of fatigue cycles.

The data in Fig. 4 does not show significant difference in trend, hence Eq. (2) was applied for all the data, and the curve–fitting result is:

$$E = 0.95\,E_0 - (E_0 - 0.847\,E_0)\,(A/A_0) \tag{3}$$

The initial reduction of 5% is due to ply crackings that is not accounted for in Eq. (2). It is possible to calculate the value of E^* from lamina properties, and E^* was estimated to be $0.877E_0$ based on the elastic constants listed previously for –45°/90° delamination.

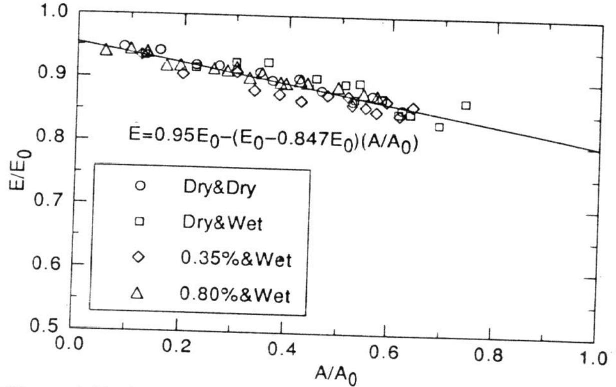

Figure 4. Reduction in modulus as a function of delaminated area.

SUMMARY AND CONCLUSION

For the graphite/epoxy composite laminate studied, the seawater exposure has no adverse effect on the fatigue edge delamination growth. Seawater exposure has the effects of switching delamination mode and reducing available strain energy release rate. The delamination growth resistance of pre–conditioned sample is enhanced by the seawater exposure due to a combination of moisture–induced stress relief and delamination mode change.

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