JOURNAL OF MATERIALS SCIENCE **30** (1995) 5537–5542

The effect of the moisture absorption on the interfacial strength of polymeric matrix composites

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Seven composite material systems have been studied to determine their potential suitability for structural applications for continuous immersion in sea water. The matrices of these composites have been found to absorb moisture with saturation occurring at 0.6%–2% of the matrix weight of additional moisture over approximately 1% present after fabrication, when soaked at ambient temperature in simulated sea water, with 20.7 MPa (3000 p.s.i.) hydrostatic pressure giving a very minor increase in moisture absorption. Pure water absorption gave a slightly higher saturation level than did simulated sea water. With the exception of the graphite/vinylester composites, the degradation in transverse tensile strength and interfacial shear strength due to moisture absorption has been found to vary from 0%–22%, with the thermoset/graphite systems and the vinylester/glass systems both showing sufficient promise to justify further study. The observed correlation in the decrease in interfacial shear strength due to moisture absorption with decreases in transverse tensile strength supports the hypothesis that the moisture-induced degradation is associated with a decrease in the interfacial strength rather than the degradation of matrix mechanical properties. *In situ* fracture observations in the scanning electron microscope further support this hypothesis.

1. Introduction

Considerable oil reserves are found off the continental United States at ocean depths of 1800 m (6000 ft) or deeper. However, current technology will not allow these reserves to be recovered (drilled and produced) economically. New production systems, such as floating platforms and tension leg platforms, are being developed to facilitate the production of oil at these depths where conventional platforms are impractical. The use of high-strength, light weight polymeric composite materials in these new systems as risers and/or tendon legs offers great potential to reduce the weight supported by the surface structure, and thus, greatly reduce the size and cost of the entire production system. Tamarelle and Sparks [1] have shown that even with the much higher cost of graphite/epoxy risers compared to steel risers, the overall production system cost is reduced when steel risers are replaced by graphite/epoxy risers for production at 3000 ft ocean depth, with the cost savings increasing at greater depths.

Several questions must be addressed, however, before such a materials substitution can be made. First, the long-term durability of polymeric composite materials in sea water must be determined. While polymeric composite materials are not subject to galvanic corrosion as are metals, the polymeric matrix can absorb 1%–2% water at ambient temperature (with the equilibrium level of moisture content increasing with increasing temperature), which may degrade the mechanical properties of either the matrix itself or the fibre/matrix interface. Second, the susceptibility of polymeric composites to biofouling needs to be determined. The use of vinylester/glass composites in mine-sweeping ships for more than 10 years without biofouling problems gives some basis for optimism in this regard [2]. Third, composites material risers cannot simply be screwed together as is done with metal risers. Thus, appropriate couplers for composite material risers need to be developed. The results to be presented in this paper address the concern regarding moisture uptake and its effect on matrix and fibre/matrix mechanical properties. Work which addresses the other two questions will be presented at a later date.

2. Summary of previous work

The effect of moisture on aerospace composites is well documented [3]. In a hot, humid environment, polymeric composites are known to absorb moisture. This moisture reduces the glass transition temperature of the polymeric matrix and reduces the strength of

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the fibre/matrix interface. The most significant loss of mechanical properties is found in the hot, wet compressive strength of polymeric composite materials. However, much less work has been done to document the effect of polymeric composite materials subjected to continuous, long-term immersion in sea water. Moisture absorption can be by Fickian diffusion through the matrix [4], an accelerated non-Fickian diffusion through voids or cracks in the matrix [5], or through wicking, which is accelerated diffusion along the fibre/matrix interface [6]. The moisture absorption is usually limited to the matrix. While little moisture is absorbed by glass or graphite fibres, glass fibres have been found to be susceptible to stress corrosion cracking, especially in pure water [7].

The effect of moisture at the fibre/matrix interface may be two-fold. First, the moisture can directly reduce the chemical bonding strength at the interface. Second, the matrix swelling that accompanies moisture absorption can change the residual stresses that develop due to curing-related shrinkage of the matrix and during cooling down from T_g due to the greater coefficient of thermal expansion in the polymer matrix than in the fibres [8]. Because the residual stresses that develop in the matrix during cool-down are tensile parallel to the fibres and compressive at the fibre/matrix interface, moisture absorption and the associated swelling will reduce the tensile stress parallel to the fibres and will also reduce the compressive stresses present at the fibre matrix interface. To the extent that the interfacial shear strength is due to mechanical as well as chemical interaction at the interface, this relaxation of residual compressive stresses at the interface will reduce the interfacial shear strength [9]. Results of moisture absorption and resultant mechanical property degradation have been reported in the literature by a number of investigators [10–15]. Generally, the tensile strength of unidirectional composites is unaffected by moisture absorption. However, reductions in compressive strength of unidirection composites loaded parallel to the fibre direction or transverse tensile strength have indicated strength reductions that range from 10%–50%.

The sensitivity of a composite system to sea-water absorption may also depend on processing, which can affect both the void content and the interfacial strength. Thus, results in the literature on the same system are sometimes inconsistent. Minimizing void content would seem to be important in achieving good durability for composites subjected to sea-water immersion [16].

It is envisioned that risers would be made of filament wound tubular goods and would be subjected to static axial tension and hydrostatic pressure with some axial and bending fatigue. Thus, the effect of sea-water immersion on the corrosion fatigue behaviour of multi-axial laminates would seem to be the primary driver from a design point of view. Whether such corrosion fatigue tests need to be performed under hydrostatic pressure is uncertain. The approach taken in this research programme has been to carry out an initial screening of various candidate composite material systems using unidirectional composite laminates with the degradation measured using transverse tension tests prior to initiating corrosion fatigue testing. This approach has one advantage and one disadvantage. The advantage is that the transverse tension test is very sensitive to changes in the mechanical properties of both the matrix and the fibre/matrix interface. The disadvantage is that the transverse tension test is also quite sensitive to incipient flaws. Some scatter in the results is expected, with low transverse tensile strength results giving an indication of the stress to propagate incipient flaws rather than an actual indication of the matrix or interfacial cohesive strength. Thus each specimen must be examined after the test to try to identify whether the observed behaviour was dominated by an incipient flaw.

It has also been the objective of the preliminary phase of this investigation to determine what, if any, effect hydrostatic pressure has on the kinetics of moisture absorption as well as the equilibrium level of moisture absorption. Similarly, a determination of the relative absorption and degradation produced by pure (distilled) water and sea water has been made to try to determine what, if any, effect the salt and other trace minerals in sea water might have on the degradation process. Future work will address the corrosion fatigue behaviour of multi-axial laminates.

3. Experimental procedure and composite material systems studied

The experimental programme consisted in (1) periodic measurements of weight gain for immersion in simulated sea water at ambient pressure, sea water at 20.7 MPa (3000 p.s.i.) hydrostatic pressure, and pure (distilled) water at ambient pressure, all over a period of 3 months, (2) the measurement of transverse tensile strength for composite materials that are nominally dry and after immersion for 3 months, which allowed moisture saturation to be achieved, and (3) the measurement of interfacial shear strength for nominally dry and moisture-saturated specimens using microindentation testing.

3.1. Material systems studied

Seven composite materials systems were studied, all with thermosetting resin matrices, five with graphite fibres and two with glass fibres. Hexcel's T2C145/F263 is a standard tetraglycidcyl 4,4′-diamino diphenylmethane (TGDDM) system cross-linked with diaminodiphenyl (DDS) and reinforced with graphite fibres (T2C145). ICI's IM7/977-2 is a hybrid TGDDM and aramid polymer network cross-linked with DDS and reinforced with IM7 graphite fibres. 3M Corporation's IM7/SP500-2 has a backbone made from the tricyclic hydrocarbon fluorene with graphite fibre reinforcement. Because the fluorene is hydrophobic and requires less cross-linking with the highly polar DDS than do most epoxy systems, it absorbs much less moisture, making it an interesting candidate for sea-water applications. Vinylester resin systems, one with a brominated back bone for fire retardation (Dow Derakane 510) and one without (Dow Derakane 411) were reinforced with E-glass and graphite fibres. All laminates were fabricated by the materials suppliers and all were unidirectional layups. Specimens referred to as "dry" in this paper have not been artificially dried by heating but contain the level of residual moisture (approximately 1%) that is typical for standard processing of these systems. Thus, "dry" actually means not soaked rather than absolutely dry.

3.2. Weight gain measurements

Unidirectional laminates that were four plies thick were used both for the weight gain and the transverse tensile strength tests. By using four ply thick specimens (approximately 0.76 mm (0.03 in.) total ply thickness), approximately 75% of the saturation weight gain was achieved after 1 week. Simulated sea water was produced using "Instant Ocean" from a pet store and advertised as having salt and trace minerals in concentrations similar to that of true sea water. Specimen weight was measured periodically using an electronic balance after the specimen was removed from immersion in the pressure vessels containing pure (distilled) water or simulated sea water, respectively. The weight of the respective specimens was measured very quickly after wiping the surface dry to minimize weight loss due to evaporation. The weight gain is reported as a percentage of the matrix weight rather than the entire composite weight because the fibres do not absorb moisture. The volume per cent fibre in the systems studied ranged from 55%–65%, as measured from photomicrographs using the point count method.

3.3. Transverse tensile strength

Transverse tensile strength specimens were cut from the same laminates that were used for the weight gain experiments. These specimens were 1.5 in long by 0.4 in wide (~ 3.8 cm × 1.0 cm) with a gauge section that was 0.5 in long by 0.2 in wide (~ 1.27 cm × 0.50 cm). The specimens were approximately 0.03 in (~ 0.08 cm) thick (four plies, but ply thickness varied from system to system). To minimize the volume of material loaded to the highest stress level, and thus, avoid the scatter associated with failure by propagation of incipient flaws, a 0.25 in (~ 0.64 cm) radius notch was introduced into the gauge section, parallel to the fibre direction (the axis of the notch ran across the specimen, perpendicular to the axis of the specimen gauge section), which effectively reduced the thickness from 0.03 in (0.08 cm) to 0.015 in (0.04 cm). Because the radius of curvature was large relative to the thickness of the specimen, it was assumed that the stress concentration factor was essentially 1.0. If a larger stress concentration factor were used, it would change the absolute values of the transverse tensile strengths calculated but would not change the relative values or the conclusions based on these relative values. At least five specimens were tested for each condition, with the average values reported. For tests which gave substantially lower values of transverse tensile strength than others in their set of five, the fracture surface was examined to determine if this failure was initiated by an incipient flaw. Where this was found to be the case, such values were not used in determining the average transverse tensile strength.

3.4. Interfacial shear strength

The interfacial shear strength in several of the systems has been measured on both dry and water-saturated specimens using an interfacial testing system (ITS) developed at Massachusetts Institute, DuPont and Dow Chemical [17]. This approach, sometimes called the microindentation technique, applies a monotonically increasing load to a single fibre end on a polished edge of the unidirectional composite laminate and determines the critical load at which fibre debonding occurs. This load, in conjunction with finite element analysis, is used to estimate the interfacial shear strength for the composite. Because this analysis is linear elastic, it may give somewhat high estimates of the actual interfacial shear strength [18]. Nevertheless, the relative values of interfacial shear strength measured in this way should be very useful to indicate loss of interfacial shear strength due to moisture absorption.

3.5. *In situ* observations of fracture in the SEM

Three-point bending has been used to develop the necessary tensile stresses to initiate transverse tensile failures in the outermost element of specimens loaded in the scanning electron microscope. Polished edges of the laminate which show fibre ends as well as the matrix are observed in the SEM during loading to see the micromechanisms which lead to transverse cracking and failure in the three-point bend specimens. Because the specimens are sputter-coated with a gold–palladium film, water-saturated specimens may also be observed without loss of moisture due to the vacuum in the SEM.

4. Results and discussion

4.1. Saturation level of moisture absorption

The results of the moist absorption at saturation in the seven composite systems studied, measured in weight gain as a percentage of matrix weight, are presented in Fig. 1 for immersion in sea water at

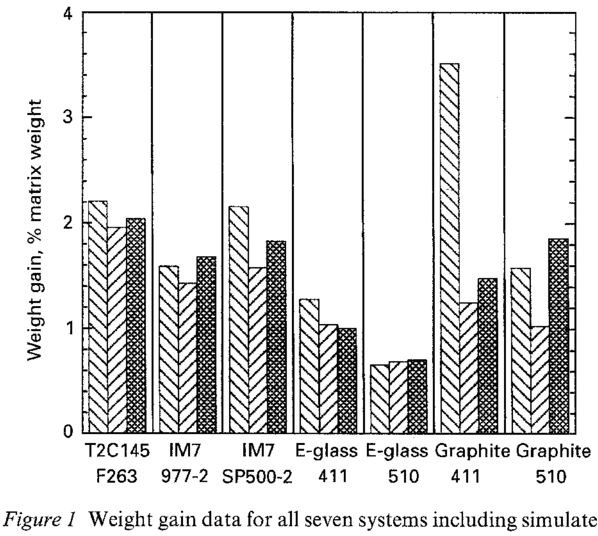

Figure 1 Weight gain data for all seven systems including simulated sea water, sea water at 20.7 MPa, and distilled water. ▧ Distilled; ▨ sea water; ▩ sea water at 20.7 MPa.

atmospheric pressure, for sea water at 20.7 MPa hydrostatic pressure, and for pure water, all at ambient temperature. Because our purpose was to study additional water absorption over and above the usual residual moisture present after fabrication, the reported values understate the absolute moisture content by approximately 1%, based on a few artificial drying experiments. System A (T2C145/F263) with a generic epoxy matrix is seen to absorb the most moisture due to the high density of polar molecules in this system. The hybrid epoxy composite (System B: IM7/977-2) and the fluorene composite (System C: IM7/SP500-2) with a much lower degree of polarity in their molecular structures, are seen to have a much smaller saturation level of moisture absorption. The results for immersion in sea water 20.7 MPa (3000 p.s.i.) indicated slightly more moisture absorption than the results at ambient pressure, as seen in Fig. 1. It appears that the greater driving force for moisture absorption at higher pressure is almost cancelled by the reduction in free volume; the hydrostatic pressure also gives a relative small change in the equilibrium moisture saturation level at this pressure.

At atmospheric pressure, from 5%–25% more distilled water than sea water was found to be absorbed in the various systems studied, the flame-resistant vinylester being the exception in this regard, as seen in Fig. 1. One possible explanation is that the salt and/or trace elements are absorbed into the composite less readily than the water. This would result in an accumulation of salt and/or trace elements at the surface of the composite which could inhibit further water absorption, effectively creating an osmotic pressure.

4.2. Effect of sea-water absorption on transverse tensile strength

The degree of degradation of the transverse tensile strength due to sea water absorption in the various composite materials systems is seen in Fig. 2. The dry and wet transverse tensile strength of the graphite/vinylester systems are seen to be poor due to poor interfacial bonding. The two systems which showed the least degradation are the IM7/977-2 and the IM7/SP500-2, each of which has graphite fibres and a somewhat lower moisture absorption than the graphite/epoxy system (T2C145/F263). The vinylester/glass systems which showed the lowest degree of moisture absorption nevertheless had approximately 20% reduction in the transverse tensile strength, which is similar to the graphite/epoxy system T2C145/F263. This greater degree of degradation of the transverse tensile strength, despite the lower moisture absorption for these systems, as seen in Fig. 1, is undoubtedly the result of a greater sensitivity of the thermoset/E-glass interface to moisture than the thermoset/graphite interface. If the observed degree of degradation of the transverse tensile strength seen in Fig. 2 is indicative of the degradation of other mechanical properties over longer immersion times, then it should be possible to use some of these composite material systems for structural application requiring long-term immersion in sea water. It is also worth noting that moisture-induced degradation of the transverse tensile strength at 20.7 MPa hydrostatic pressure in sea water or in pure water at ambient pressure were essentially the same as for sea water at ambient pressure, as seen in Fig. 2.

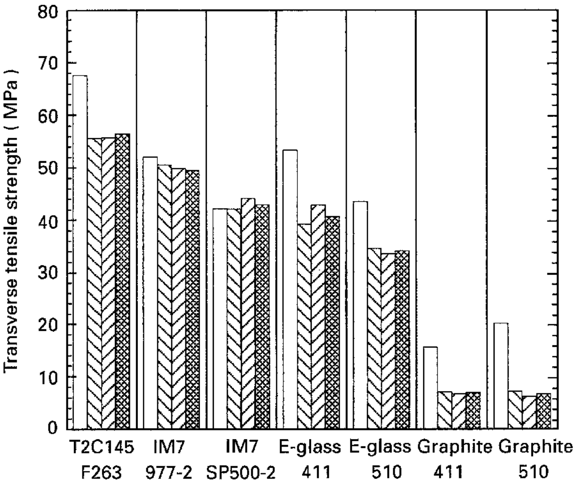

Figure 2 Transverse tensile strength results for all seven systems with all three conditions of soak. ☐ Dry; ▧ distilled water; ▨ sea water; ▩ sea water at 20.7 MPa.

The graphite/vinylester composites had low transverse tensile strength, both dry and wet, indicating poor adhesion between the graphite fibres and the vinylester matrix. These systems have been eliminated from further consideration at this time.

It should be emphasized that the behaviour of systems subjected to cyclic or static loading while immersed in sea water may be quite different than that indicated in Fig. 2. The combined effect of stress and "corrosive environment" resulting in environmental stress cracking can sometimes be much more severe than the effects separately. Because our specimens were saturated by immersion in sea water in an unstressed condition, a more severe degradation may be found in phase II of this programme, where corrosion fatigue behaviour of multi-axial specimens will be explored. Also, the effect of biofouling needs to be determined before long-term structural application of composites requiring continuous immersion in sea water can be recommended. Such an investigation is already underway.

4.3. Interfacial shear strength measurements

The results of the interfacial shear strength measurements are presented in Fig. 3. A comparison of Figs 2 and 3 indicates that the reduction in transverse tensile strength comparing dry and water-saturated composite material specimens is similar to the observed change in the interfacial shear strength for T2C145/F263 and for IM7/977-2. This provides direct support for the hypothesis that the degradation of the composite systems is primarily interfacial rather than in the matrix. For IM7/SP500-2, the interfacial shear strength reduction due to absorbed moisture indicated in Fig. 3 is not consistent with the small increase in transverse tensile strength in the wet specimens seen in

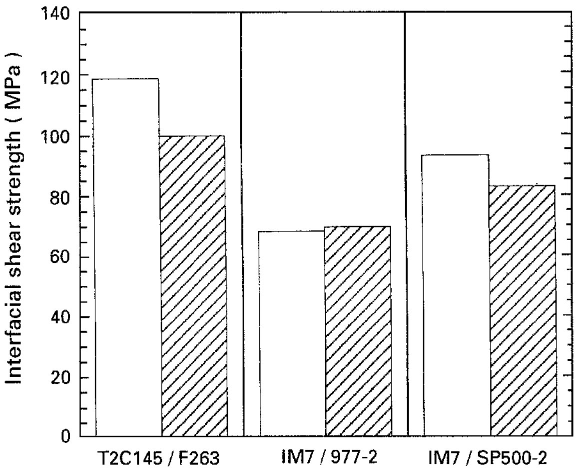

Figure 3 Interfacial shear strength determined using a microindentation test for nominally dry and moisture-saturated specimens soaked in simulated sea water. □ Dry; ▨ sea water.

Fig. 2. However, *in situ* observations of the fracture process in the SEM to be published elsewhere [19] confirm a change from primarily matrix failure dry to primarily interfacial failure wet in the T2C145/F263, (as seen in Fig. 4), interfacial failure wet and dry in the IM7/977-2, and matrix-dominated failure both wet and dry for the IM7/SP500-2. This is why the moisture-induced reduction in interfacial shear strength was not reflected in the transverse tensile strength in this system. In fact, the moisture-induced plasticizing of the matrix, making it more resistant to the propagation of incipient flaws, accounts for the small increase in transverse tensile strength. Whether the matrix-dominated failure IM7/SP500-2 is due to its stronger interface (it was the second strongest of three graphite/epoxy systems), a more brittle resin, or larger incipient flaws developed in processing, is unclear.

5. Conclusion

Seven composite materials systems have been studied to determine their potential suitability for structural application in sea water. The matrices of these composites have been found to saturate in moisture absorption at a level of 0.6%–2% of their weight when soaked at room temperature, with the saturation level being slightly higher, in general, for distilled water than for sea water and approximately the same for sea water at ambient pressure and sea water at 20.7 MPa (3000 p.s.i.) of hydrostatic pressure. With the exception of graphite/vinylester composites, the degradation in transverse tensile strength and interfacial shear strength due to moisture absorption has been found to vary from 0%–22%, with the epoxy/graphite systems (including IM7/SP500-2) and the vinylester (410)/E-glass systems giving the most promise for further study. The graphite/vinylester systems had weak interfaces, both dry and wet. The correlation of decrease in the interfacial shear strength degradation with moisture absorption to the transverse tensile strength

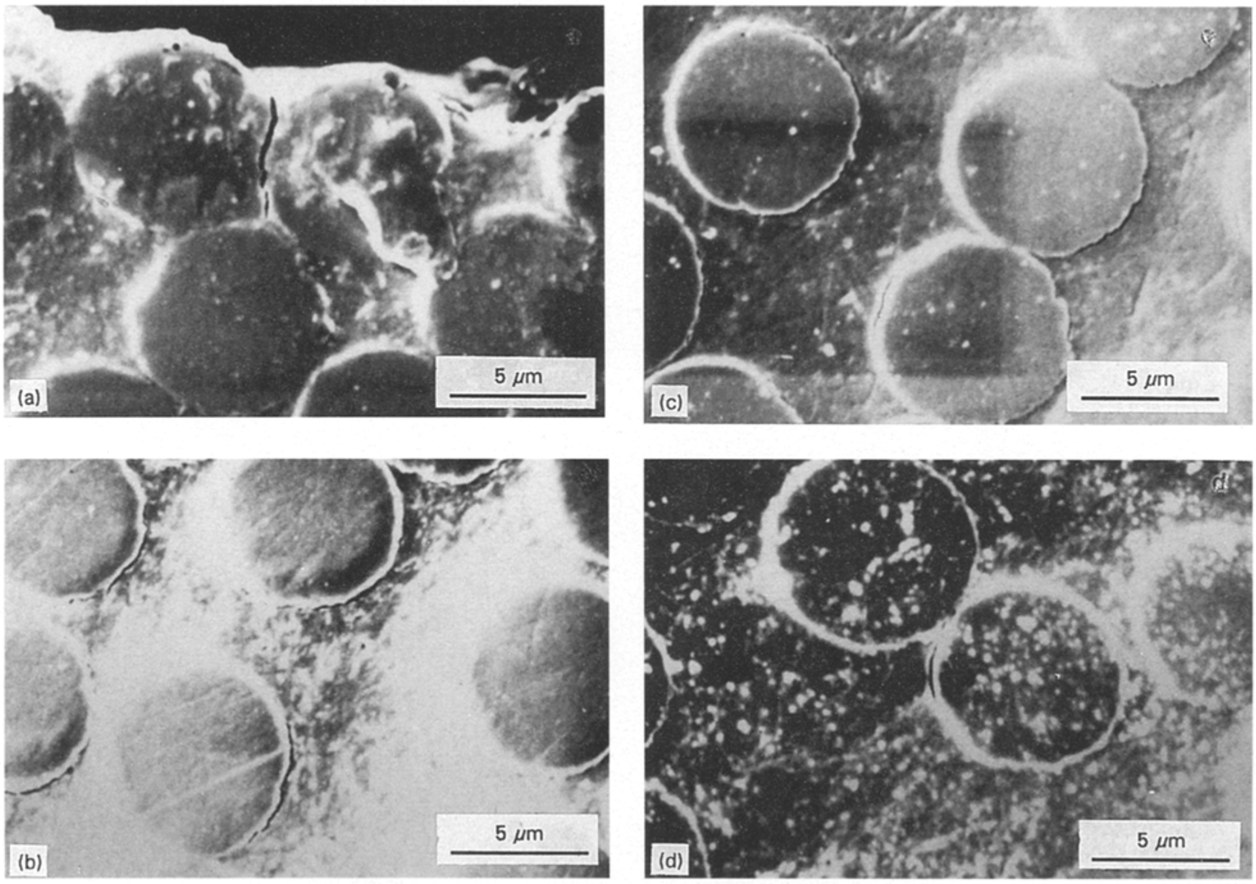

Figure 4 In situ observations in SEM of fracture of IM7/SP500-2 composite specimen after soaking to saturation in (a) pure water, (b) simulated sea water, and (c, d) simulated sea water at 20.7 MPa hydrostatic pressure. Note the absence of semicircular debonding cracks, with matrix cracking beginning at the surface of the specimen (top of each micrograph) but not initiating with interfacial debonding.

supports the hypothesis that the degradation of the T2C145/F263 is associated with a decrease in the interfacial strength rather than the matrix mechanical properties. *In situ* fracture observations in the scanning electron microscope further support this hypothesis.

6. Postscript

While these results are encouraging, we have recently been made aware of reports of more significant reductions in interfacial strength (or mechanical properties which are sensitive to interfacial shear strength) in both graphite/epoxy composites soaked at ambient temperature [15] and glass/epoxy composites soaked at temperatures of 65–75 °C [7]. We are currently collaborating with these researchers to understand better the implications of these results for our work and for the prospects of commercial applications of composites in marine environments.

Acknowledgement

The staff of the Electron Microscope Center at Texas A and M University are thanked for their assistance and the use of their equipment. The support of the National Science Foundation through the Offshore Technology Research Center is gratefully acknowledged. The donation of composite materials by ICI, 3M and Hexcel is also acknowledged.

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Received 15 April 1994
and accepted 11 April 1995