

Aging of Polymeric Composites: A Literature Review

by

Margie N. Treviño-Garrido

Submitted to the
Department of Mechanical Engineering
in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Mechanical Engineering

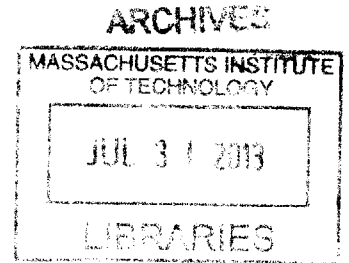
at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 2013

© 2013 Margie N. Treviño-Garrido. All rights reserved.

The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part in any medium now known or hereafter created.



Signature of Author: _____
Margie N. Treviño-Garrido

Department of Mechanical Engineering
January 31, 2013

Certified by: _____
James H. Williams, Jr.
Professor of Mechanical Engineering and Writing and Humanistic Studies
Thesis Supervisor

Accepted by: _____

Anette Hosoi
Associate Professor of Mechanical Engineering
Undergraduate Officer

Aging of Polymeric Composites: A Literature Review

by

Margie N. Treviño-Garrido

Submitted to the Department of Mechanical Engineering on January 31, 2013
in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Mechanical Engineering

Abstract

Due to their increased use in today's society, an extensive survey was undertaken in this report to condense what's been, thus far, discovered as to the effects of aging on polymeric composites. Special emphasis was placed on composites with vinyl ester as the matrix reinforced with glass or carbon fibers. Moisture exposure, thermal conditioning, and cyclic loading were the aging mechanisms used to mimic environmental effects. Fatigue, flexural, tensile tests, and scanning electron microscopy were among the many methods used in studies to determine the effects of aging on composites. The deleterious effect of moisture on composite performance was undeniable, with the drop in flexural strength being as high as 48%. Studies found no difference between salt and distilled water aging, although salt water was reported as being more slowly absorbed. Composite materials were observed to experience no further loss of strength beyond the point of saturation. Findings showed that, after aging, composites retained some of their strength, with flexural strength retention reported as high as 66%. Frequently, the glass transition temperatures of the materials changed depending on the aging process. In most cases, Fick's law of diffusion was confirmed as an accurate model for moisture absorption. Temperature fluctuations were always deemed as damaging to composite structures. Due to the haziness still present in current research coupled with the importance of composite applications, the need for additional investigation in this topic is urgently obvious. All in all, future studies are encouraged to tabulate test procedures and results in an effort to minimize the current ambiguities in the aging information accumulated thus far.

Thesis Supervisor: James H. Williams, Jr.

Title: Professor of Mechanical Engineering and Writing and Humanistic Studies

Acknowledgments

I would like to thank Professor James H. Williams Jr. (who is supported by the DDG-1000 Program Manager/NAV SEA PMS 500 and the DDG-1000 Ship Design Manager/NAVSEA 05D) for his time and guidance throughout the development of this thesis.

Table of Contents

Abstract	3
Acknowledgments.....	5
1. Introduction.....	8
2. Applications of Composites Today.....	10
3. Process of Extensive Article Searching	16
4. Data Compilation and Comparison.....	17
4.1 Polymeric Composite Materials.....	17
4.2 Environmental Testing.....	18
5. Discussion.....	19
6. Recommendations.....	91
7. Conclusions.....	92
References.....	97

List of Tables

Table 1. Summary of Literature Survey.....26

1. Introduction

Polymeric composites are an unavoidable topic in scientific research today. Due to the remarkable properties they exhibit, they are now present in numerous applications ranging from small sporting goods to large aircraft. In particular, their applications in the outdoor environment are steadily increasing. Composite materials are now used in ships, offshore drilling platforms and bridges. Some estimate that more than half of the annual tonnage of polymers is employed outdoors where useful life is inevitably shortened by weathering. Weather and radiation factors that contribute to degradation in plastics include temperature variations, moisture, sunlight, oxidation, microbiological attack, and other environmental elements. One of the most important requirements of a structural polymer is its ability to retain a significant proportion of its load-bearing capability for long periods of time under diverse environmental conditions. Therefore, there is an understandable urgency to better understand the effects of aging on composite polymers. This investigation is an extensive survey of the available literature on the topic of aging in composites.

Section 2 reviews some background information for this investigation. Different applications of polymeric composites are further discussed, and the importance of relevant research is stressed. Section 3 explains the overall process of accumulating the journal articles that are discussed. Section 4 gives an overview of the many different materials and testing procedures investigated in the articles. Section 5 draws attention to some meaningful patterns found amongst the literature. Section 6 attempts to give some recommendations for future research on the topic, and meaningful conclusions are drawn in Section 7.

2. Applications of Composites Today

The importance of studying the effects of aging on composite materials has become increasingly evident in recent years. More and more, composites are being used in all sorts of applications. Due to the unique set of properties that synthetic polymers offer, their applications in the outdoor environment are steadily increasing. Polymers have substituted, in many instances, and particularly in the building industry, traditional materials such as wood, metal, ceramic, and glass. The utilization of polymers in concrete admixtures has become much more prevalent in the last two decades. Consider the materials present in composite pipes; they exhibit high corrosion and heat resistance, and high strength properties. It is no surprise they are extensively used for underwater and underground transportation of fluids such as natural gas, oil, thermal water, wastewater, and drinking water. Composites also have prevalent use in marine applications. Polyester resins have been employed for pleasure boat construction since the 1950s. Glass-fiber reinforced polymer (GRP) composites are often used in marine craft such as canoes, fishing trawlers, patrol boats and naval mine-hunting ships and in the non-pressure hull casing, sonar dome and masts of submarines. Marine composite structures requiring high stiffness are often built using carbon fiber composite. Carbon/epoxy laminate is occasionally used, but the high cost of epoxy resin has led to increased use of carbon/polyester and carbon/vinyl ester composites in racing yachts, naval patrol vessels, offshore drilling components, and civil infrastructure for strengthening bridge pylons. Glass counterpart carbon fiber has very high modulus, which can replace glass in marine applications especially for unmanned underwater applications. There has also been a growing interest in using fiber-reinforced polymeric composites in offshore applications. Composite materials are used in ships, offshore drilling platforms and bridges. Fiberglass composites are used in offshore drilling

platforms for deck grates, low-pressure pipes and storage tanks, and in civil infrastructure for the repair, strengthening and rehabilitation of aging pylons to bridges and piers.

Take for instance the Hutton Field oil field located in the East Shetland Basin in the UK North Sea on the western side of the Viking Graben. It was the location for the first ever production Tension Leg Platform (TLP). Its platform was the first to be permanently moored to the seafloor via tethers or tendons at each of the structure's corners. These tension legs are massive structures comprised of a series of pipes made of a glass fiber/vinyl ester composite. In fact, there are many other marine structures today that use this same composite. Composites are even being used in aircraft. Approximately fifty percent of the 787 Boeing airplane is made up of composite material.

It is estimated that more than half of the annual tonnage of polymers is employed outdoors where useful life is inevitably shortened by weathering. The outdoor environment comprises several influencing factors such as solar radiation, temperature, rainfall, humidity, wind, and various pollutants. The degradation of a material depends on the mechanism and extent of its interaction with its surroundings. Weather and radiation factors that contribute to degradation in plastics include temperature variations, moisture, sunlight, oxidation, microbiological attack, and other environmental elements. Weathering examples such as the hydrolytic reversion of polyurethanes, the ozone-induced stress cracking of rubbers, the discoloration of polymers by sunlight and their crazing and the dimensional variability of nylons demonstrate the interaction between the environment and polymers. A large number of engineering polymers such as polyamides, polyacetals, polycarbonate, polyphenylene oxide, polysulphone, and thermoplastic polyesters have been studied extensively from the viewpoint of degradation and polymer stabilization. Investigations into the weathering of polymers have

shown photo-oxidation to play a major part in the degradation of several materials including polyamides, s-R polyacetals, polycarbonate, polystyrene, and polyurethanes. The negative influence of water absorption in exposed samples of polyamides, polycarbonate based on bisphenol A and polyurethanes is clearly evident. Attempts to improve the outdoor performance of polymers by the use of selected additives, UV stabilizers, copolymerization, and suitable fillers are reported to be effective. One of the most important requirements of a structural polymer is its ability to retain a significant proportion of its load-bearing capability for long periods of time under diverse environmental conditions. Composite pipes used for underwater and underground transportation of fluid materials may be subjected to impact loads, during establishing or in service. These loads may cause the potential damaged zones in the composite pipes which are sometimes not realized by visual inspection. In addition, the boundary conditions, dimensions, impact velocity, and environmental effects (seawater, acidity, humidity, thermal effects, etc.) may change the response of the composite pipe. As far as impact loading is concerned, the fatigue performance of composite pipes under internal pressure is an important research topic that deserves investigation. So far, studies have generally focused on plate and beam structures. Most experimental data on the influence of the environment on composites are based on tests on uncracked specimens, and the influence of moisture on crack propagation in resins and composites has received much less attention. Resistance to delamination propagation is essential in the reliability estimation of many composite structures.

The structural integrity and lifetime performance of fibrous polymeric composites are strongly dependent on the stability of the fiber/polymer interfacial region. One of the main drawbacks of thermoset plastics in seawater is that the polymer matrix and fiber/matrix interface can be degraded by a hydrolysis reaction of unsaturated groups within the resin. Seawater

degradation can cause swelling and plasticization of the polyester matrix and debonding at the fiber/matrix interface that may reduce the mechanical properties. When used in marine applications, the glass/vinyl ester composites retain their mechanical properties and do not degrade when immersed in seawater even for many years. Marine applications of composites require the characterization of the long term influence of water on diffusivity and thermomechanical properties. Much work has been published on the diffusion kinetics of water vapor in resins and composites and the effect of absorbed moisture on the mechanical properties. When used in marine applications it is essential that glass/polyester and glass/vinyl ester composites retain their mechanical properties and do not degrade when immersed in seawater for many years. A disadvantage of using polyester-based composites in seawater is that the polymer matrix and fiber/matrix interphase can be degraded by a hydrolysis reaction of unsaturated groups within the resin. Seawater degradation can cause swelling and plasticization of the polyester matrix and debonding at the fiber/matrix interface that may reduce the mechanical properties. Another disadvantage of using GRP composites in marine structures is their relatively low Young's modulus. The modulus is typically below 40 GPa because of the low stiffness of glass fibers, and this makes it difficult to build ultra-light marine structures with adequate stiffness. A concern with using carbon fiber composites in marine structures is the limited understanding and small database of information of their long-term durability in seawater. Composite marine structures can be immersed continuously in seawater for 30–40 years. In the seawater environment, a composite structure is subjected to moisture absorption and fatigue wave loading. Composite materials are known to exhibit some degree of degradation due to moisture absorption. Several studies have examined the fatigue performance of polymeric composites in seawater. Some studies have concluded seawater exposure gives degradation in

performance, while others observed very little degradation. Few have, however, studied the effect of seawater exposure on damage development and failure mechanisms which may change, even when there is no significant seawater induced degradation of fatigue strength. The effect of moisture on delamination cracking resistance is crucial to the durability of composite materials in a seawater environment because delamination crack growth has been identified as the most dominant failure mechanism in the fatigue life of fiber-reinforced composites. Due to the complexity of the effect of moisture on long-term durability, however, a variety of results have been reported on the effect of moisture on delamination cracking resistance of composite materials. Both beneficial and detrimental effects of moisture have been reported with distilled water being the most often used medium. No change in fracture toughness has been observed when moisture does not cause any change in fracture surface morphology; however, an increase in fracture toughness or a decrease in crack growth rate has also been observed and attributed to matrix plasticization.

Long-term durability in a marine environment is essential. Durability is defined as the ability of a composite material to retain its original physical, chemical and mechanical properties when immersed in seawater. To realize the full potential of polymeric composites in marine applications, it is important to develop a better understanding of the magnitude and mechanisms of seawater degradation. There are few studies on the effects of long term immersion of composites in water. On account of the time-consuming nature of such tests, and the previous lack of a standard test method for mode II testing, few long term data are available. While a large amount of information is available on the seawater durability of glass/polyester and glass/vinyl ester composites because of their use in marine structures over many years, much less is known about the seawater durability of carbon fiber composites. As a result, safety factors in

design for long-term loading remain high, reflecting a lack of confidence in predictive methods for composite behavior in the presence of water. Regardless of the field of application, there is often understandable concern with respect to the durability of polymeric materials, partly because their application as engineering materials is still in a stage of development. If the useful lifetime of these materials could be predicted, the maintenance and replacements of these materials could be better planned. Outdoor weathering of all composites is a subject likely to remain active for the foreseeable future. Despite the tremendous progress that has been made in the sector of infrastructure composite materials and engineering within the past few years, there still remain technological challenges. These challenges include the development of reliable test methods, less expensive yet sophisticated and specialized materials, viable and robust life prediction tools, as well as consideration of the environmental and mechanical response of these materials. Other significant hurdles include the absence of comprehensive data characterizing the long-term durability of glass-fiber-reinforced polymeric composites coupled with the absence of adequate established standards for repair, design and maintenance. These attempts seek to facilitate an understanding of the response of fiber-reinforced composite systems to the applied environment, and also to serve as a precursor to the development of reliable analytical and life prediction tools. Fiber-reinforced composite data currently available are industry-specific, with most of the current data belonging to the aerospace and petrochemical industries where years of experience with composites have resulted in a database, while little data are available for the marine and infrastructure sectors. The absence of data on glass-fiber-reinforced composites for marine and infrastructure applications, where longevity is of interest, has been in part responsible for their slow acceptance. Although much research has been done on seawater degradation of polymer-matrix composite laminates, less work has been done on carbon/vinyl ester composites.

Moreover, there have been concerns in recent years over volatile emissions during fabrication of polyester resins, and these concerns have resulted in new environmental legislation on styrene emissions and resin suppliers have proposed new formulations. These are of three types: low styrene content, low styrene emission resins, and mixed resins. Many published studies provide data on aged glass reinforced composites, but very few results allow a comparison to be made between the aging of standard and low styrene materials. Hence, it is important to study the aging behavior of low styrene resin.

3. Process of Extensive Article Searching

This was a study conducted using the resources offered by the MIT libraries to its undergraduate student population. MIT offers many research resources to its students. The key journal database services available are Compendex, INSPEC, Web of Science, Scopus, and SciFinder. Vera is another extremely useful search engine that allows you to browse specific journals owned by MIT. Full text papers, reports, and proceedings can be found at AIP Online Conference Proceedings, ASME Digital Library, and SAE Digital Library. Dissertations and theses were found on ProQuest. Different handbooks and encyclopedia articles were found on Knovel. Some popular journals cited were Composites Part A (Applied Science and Manufacturing), Composites Part B: Engineering, Composites, and Polymer. Additionally, through use of MIT's ILLiad interlibrary borrowing system, literature material not owned by MIT was obtained.

4. Data Compilation and Comparison

It was difficult to focus on a clearly-defined set of conditions, but this paper will attempt to draw as much comparison amongst them as possible.

4.1 Polymeric Composite Materials

Over the course of this survey, many materials were looked at. Numerous different matrix-fiber combinations were considered. The matrices and fibers looked at included, but were not limited to, FRP-wood composites, isophthalic polyesters, epoxy resins, and aramid fibers. However, special emphasis was placed on thermosetting plastics and polymeric fiber-reinforced composites. Of particular interest were composites with vinyl ester as the matrix reinforced with glass or carbon fibers. Different specimen preparations were encountered. Narasimha Murthy and McBagonluri used panels in their experimentation,^{78,72} whereas other studies, such as Banna and Gasem, used glass fiber reinforced pipe specimens.^{9,34} McBagonluri used five main layers: three layers of unidirectional glass sandwiched between two substantially thicker layers of continuous strand mat for a total thickness of 3.175 mm. Narasimha Murthy did something similar by opting for flat panels measuring 250mm by 250mm with a thickness of 3 mm.⁷⁸ However, the curing methods were different between both. McBagonluri opted for curing at a higher temperature (65°C). Narasimha Murthy decided to cure the composite panels at room temperature since this is the temperature at which most marine composite structures are cured.⁷⁸

The level of specification of material preparation varied greatly amongst different studies. One study,¹⁴ for instance, listed the stacking sequences of their panels as being $[0/90/\pm 45]_{2s}$, $[0/90/\pm 45]_{3s}$, and $[0/90]_{2s}$. Fiber volume fractions were also frequently mentioned. In the case of Buck's work, the panels produced had fiber volume fractions in the range of forty-eight percent

to fifty-seven percent.¹⁴ Throughout the various studies, coupons were often cut out using water jets. Test specimens were not always flat panels. In other cases, such as with Banna and Gasem, they were glass fiber reinforced pipes.^{9,34} In the case of pipes, pipe thickness or pipe diameters were often cited. In the case of Gasem, the fiber helix angle of the pipe³⁴ was given to be 55°.

4.2 Environmental Testing

The aging mechanism that samples were exposed to before testing was another point of variance. The focal point in test conditions will aging consisting of immersion in a liquid for long periods of time. The liquid was not always water as illustrated in the case of Banna where the panels were immersed in solution of H₂SO₄. The water varied from distilled to saline. Of the articles that analyzed seawater exposure, salinity content ranged from 2.9 to 3.5%. McBagonluri used 20-gallon tanks to immerse the panels in water and 3.5% by weight salt solution;⁷² Narasimha used a salinity content of about 2.9%.⁷⁸ In some cases, such as Gasem, the salinity of the simulated seawater was not mentioned³⁴. Salinity was often monitored by using salimeters and by adding fresh solution when necessary. Some studies also performed cyclic moisture absorption-desorption using month-long cycles. In this case, ovens were used to facilitate specimen desorption. Some studies, like McBagonluri, tried to separate temperature effects from that of moisture;⁷² others did not. Immersion times ranged from 300 hours³⁴ with Gasem to over 2 years⁶³ with Kootsookos. Water uptake was generally measured by weighing the specimens upon retrieval from tanks.¹¹²

Diverse testing procedures and parameters were explored. Some specimens were tested underwater; others were tested in air. Tests in air were at times conducted at different temperatures. Fatigue tests were common, often being conducted at a minimum-to-maximum load ratio of R=0.1 at frequencies of 2 Hz and 10 Hz. Fatigue tests were sometimes conducted

in salt water. Flexural strength was often determined using the three-point bend test. Narasimha Murthy, Yu et al., and Gellert were a few of the many studies that conducted three-point bend tests according to the standard set by ASTM-D790.^{78,112,36} The three-point flexural test is advantageous in that it facilitates the preparation of specimens. The downside is that the testing method is very sensitive to specimen and loading geometry and strain rate. Tensile tests were oftentimes performed at strain rates in the neighborhood of 10^{-5} s^{-1} . The tensile fracture surfaces were examined for seawater degradation effect using scanning electron microscopy (SEM). The loss factor, $\tan\delta$, was often obtained from DMTA testing.

5. Discussion

The results for the different studies, again, varied depending on the types of tests that were conducted, what things were measured, the matrix/fiber combination, and the material preparation that was looked at. It was clear that the data on the effects of the environment on the mechanical properties of composites strongly depend on the specific formulation of the resin and the processing techniques employed. Comparison amongst results was also made difficult by the usage of different unit systems. Some studies employed the SI unit system whilst others used the English unit system. Regardless, several correlations proved worthy of discussion.

There's no question that water immersion has significant aging effects on a polymeric composite. Overwhelmingly, evidence suggested that the material properties of composites subjected to water immersion decline over time. One of the earliest articles in the collection reported that the fatigue life of a chopped glass mat/polyester composite decreased with exposure to water. In this case, the resin debonded from the fiber after a short 40-day exposure to water at 51°C. Roy Xu reported the maximum CAI strength reduction is around 10% after a 29-month

seawater exposure.⁹³ This is much smaller than the 42% CAI strength reduction that was reported by Imielińska.⁵⁰ Similar observations made by McBagonluri.⁷²

Overall, flexural strength of composite specimens was observed to decrease with increasing time of immersion. For Gellert, flexural strength losses were between 15% and 21%.³⁶ Decreases in flexural strength were reported as great as 48%.⁷⁸

There was also an undeniable reduction in tensile strength. Tang et al. reported 25 and 32% reduction of ultimate strength in freshwater and saltwater conditions, respectively, as compared to the dry air environment.¹⁰² Wu found that maximum reduction in tensile strength after 12 months of exposure was in seawater at a level of 13.5%, whereas the minimum, 8.26%, was recorded for the case of cycling,¹¹¹ and Narasimha reported that the ultimate tensile strength fell as far as 34%.⁷⁸ Haque reported the maximum degradation of failure stress and failure strains due to moisture absorption were approximately 8 and 12%, respectively for samples loaded in the fiber direction and thickness direction.⁴⁵

Upon moisture absorption, there was also a marked decrease in the material's modulus. Tang et al. reported 15 and 11% reductions in tensile modulus, respectively, for fresh and salt water.¹⁰² The elastic modulus in wet specimens was found to decrease in Haque's findings.⁴⁵ Wu reported that the specimens in their investigation demonstrated a rapid decrease in the modulus in the first month, followed by an increase, due to residual curing, until the 6-month level, followed by a decrease again, indicating the dominance of moisture-related degradation over residual cure effects.¹¹¹

Water aging was also characterized by a drop in the interlaminar shear strength of materials (ILSS). In Gellert's findings, interlaminar shear strengths fell by between 12 and 21% after 485 days immersion.³⁶ In the case of Wu, shortbeam shear strength is seen to decrease over

the 12-month period of exposure for all conditions considered, with the maximum overall decrease at the 12-month level being 19.3% for samples in deionized water and the minimum being 10.9% for samples subject to the cycling regime in seawater. In terms of creep, Gellert documented significantly higher for the immersed than for the atmospherically aged laminates where aging had been accompanied by flexure loading at set deflections.³⁶

Typically, water uptake weakens the fiber-matrix interface, exposing the fibers. Subsequently, there are chemical interactions that occur due to hydrolysis and leaching. Some authors theorize that water breaks down the ester chain and diffuses into the matrix materials, leading to further degradation. SEM observations by Yu et al. revealed that water absorption caused heavy debonding of the matrix from fiber, resulting in degradation in flexural and interlaminar shear strengths.¹¹² It was also found that, in cyclic exposure to moisture, most of the reduction in strength is observed after the first cycle. Sample properties do not change much after that.

Cyclic loading was another prevalent topic of discussion amongst investigations. Cyclic loading was found to be much more damaging to polymer composites than static loading. Shan found that cyclic loading in distilled water significantly shortens the fatigue life of both unidirectional glass and glass-carbon hybrid fiber reinforced epoxy matrix composites compared to their fatigue lives in air, at lower stress levels.⁹⁶ Gellert, when looking at four glass-fiber reinforced polymer (GRP) materials, found that loading while aging affected the strength of only the phenolic GRP with strength loss advancing from 25 to 36% loss from the initial strength.³⁶ In Buck's study, the addition of a sustained load typically caused a more rapid reduction in the durability of E-glass/vinyl ester composite.¹⁴ According to Wu, however, the process of cycling resulted in the lowest overall loss in strength.¹¹¹

A common theme was also that composite materials experienced no further loss of strength beyond the point of saturation. This was supported in Gellert when the unloaded phenolic lost 25% of initial strength at saturation, with no further loss as immersion continued from 200 to 800 days.³⁶ In Yu et al., the transverse flexural strength and ILSS of the pultruded CF/VE composite decreased rapidly during initial immersion and then leveled off to constant values up to saturation¹¹².

The permanent detrimental effects of aging remain inevitable. Yet, some composite materials, after aging, recover part of their strength. Findings in Yu et. al confirm that the ultimate retentions of the flexural strength and ILSS were of the order of 49 and 54% in distilled water, and 63 and 66% in salt solution, respectively.¹¹² Wu confirmed that, after drying the specimens, there is a partial regain of performance.¹¹¹ Haque, after temperature aging, reported that load bearing structures exposed to temperatures up to 400° F still retain up to 70% of their original flexural properties.⁴⁵

Moisture absorption is also seen to change the glass transition temperature of composites. When re-dried, the glass transition temperature of the composites in distilled water, 3% NaCl, and 5% H₂SO₄ aqueous solutions nearly recovers to the same as that before immersion, but is higher in 10% NaOH aqueous solution due to hydrolysis.¹¹⁴ Haque reported that physical interaction of moisture with the vinyl ester resin reduces the glass transition temperature from 121 to 118°C via plasticization and swelling.⁴⁵ Wu also observed that moisture absorption results in a consequent decrease in the T_g.¹¹¹ The maximum decrease in T_g, 14%, was seen after immersion in seawater for 18 months, whereas the minimum, 11.4%, was recorded for deionized water over the same period of time. Initially, until the 6-month level, there is very little change in the T_g for specimens immersed in seawater and synthetic seawater.

It was also found that distilled and salt water affect composites similarly. No clear difference between their aging effects was observed. Tang reports that the difference of mechanical properties between salt and distilled water immersion is not statistically significant, and McBagonluri claims that fatigue curves for fresh-water and salt-water aged samples were nearly identical.⁷² In contrast, salt water was reported by some to be more slowly absorbed, and Narasimha correlated higher levels of saturation with decreased strength.⁷⁸ Moreover, Wu noticed that, after immersion in seawater, the surfaces of all the specimens showed discoloration with the initiation of blistering at areas where fibers were close to the surface. This demonstrated both effects of salts on the fiber-matrix integrity and the existence of osmotic processes. Conversely, specimens immersed in deionized water and synthetic seawater did not show discoloration and blistering. There is a discernible difference in response between samples immersed in seawater and deionized water, with the former causing a greater level of fiber-matrix debonding and outer-layer degradation, resulting in increased degradation of the tensile performance, and the latter causing faster diffusion up to the mid-plane, resulting in more severe drops in the interlaminar shear strength.¹¹¹

Most papers agreed that the physical mechanism for moisture absorption is generally observed to be a mass diffusion process followed by Fick's law of diffusion. The Fickian model was used to describe moisture absorption for pultruded carbon fiber/vinyl ester in the investigation led by Yu et al. In this same study, it was noted that temperature did not change the Fickian behavior of the composite.¹¹² On the other hand, according to Gellert, the weight uptake plots indicate deviations from classical Fickian diffusion uptake for the polyester and vinyl ester GRPs with continuing uptake rather than a plateau at long immersion times.³⁶

For the most part, it was observed that increasing temperature lowered the strength of composites, regardless of whether the sample was subjected to a sustained load during conditioning. Results from Haque show that the average strength degradation at temperatures close to the glass transition temperature is in the range of 9-13% for specimens loaded in the thickness direction and 20-25% for specimens loaded in the fiber direction, respectively.⁴⁵ As stated in Sorathia's findings, between the temperatures of 150°F and 400°F, glass/vinyl ester samples begin to exhibit thermal damage.⁹⁸ Buck, Yu et al., and Lee further indicate that higher temperatures increase moisture absorption, which, as has already been stated, is degrading to a composite.^{14,112,66} Vauthier further highlights that even with a low moisture content in the test environment, a temperature rise has deleterious effects on the material's lifetime.

Also a part of the results have been several attempts to model composite fatigue behavior. Tang et al. created a model that can be used to predict the fatigue life of a vinyl ester/E-glass polymer composite at an applied load and predict the residual strength modulus after a number of cycles at a given load in various civil engineering and offshore environments.¹⁰² Mahfuz attempted to predict the fatigue life of S2-glass/vinyl-ester composites.⁶⁹

There were also some seemingly contradictory results. The extent of the effects of thermal aging was a point of contention. Failure modes were another topic of contention. McBagonluri suggested that the properties of the thermally aged material did not appear to differ from those of the as-delivered material.⁷² However, there are other studies, such as Sorathia, that claim that E' decreases significantly at high temperatures beyond 150°F.⁹⁸ Some studies, like Buck, reported there being no change in mass of the specimens after water conditioning.¹⁴ This was explained by Buck as being due to opposing factors of resin loss due to the conditioning and water absorption by the material. There were numerous others, though, that did. Salt water was

reported by some to be more slowly absorbed. Narasimha correlated higher levels of saturation with decreased strength.⁷⁸

Table 1. Summary of Literature Survey

Material(s)	Test Condition(s)	Testing Method(s)	Aging Results	Relevant Article Figure(s) and/or Table(s)	Ref. No.
Glassy polymers	None	None (Review of Literature)	The increase of the yield stress of glassy polymers with aging time can be understood in terms of the reduction of molecular mobility during aging. Such increases have been observed for example in PVC, PC, and PS, and are typically of the order of $5\pm 10\%$ of the yield stress per decade of aging time for aging temperatures of 20 ± 30 °C below the glass transition temperature.	Fig. 1 - Torsional creep curves of compliance as a function of logarithmic creep time for an epoxy resin quenched from equilibrium at 120 °C to the aging temperature of 105°C, and then measured after 0.5, 1, 2, 4, 8, 24, 48, 96, 195, 383, and 767 h.	1
E-glass/epoxy (G/E)	Specimens were submerged in distilled water at various temperatures and durations. Samples were conditioned at room temperature and at 65C, and tested after time durations of 500, 1000, and 3000 h.	Five G/E specimens were tested dry in tension along the fiber direction at room temperature to obtain the control tensile properties which include tensile strength, tensile modulus and tensile strain to failure.	At shorter durations of conditioning at room temperature, a slight increase in strength and a slight decrease in modulus were observed. At longer durations, 3000 h, a noticeable reduction in strength and strain-to-failure was observed. Specimens conditioned under stress, in water at 65 °C for 1000 h exhibited higher loss in modulus. Constant stress may have a positive effect in short-term. Extended exposure to moisture at room temperature leads to brittle failure. Exposure at high temperatures may lead to ductile failure of E-glass/epoxy composites.		2

<p>Recycled cellulose fiber (RCF) reinforced epoxy/clay nanocomposites</p>	<p>Water absorption test carried out by immersing samples with dimensions 10 mm x 10 mm x 3.5 mm in a water bath at room temperature</p>	<p>Flexural strength, flexural modulus and fracture toughness were determined by using three-point bend tests</p>	<p>Water absorption decreased as the clay content increased. Flexural strength, flexural modulus and fracture toughness decreased significantly due to water absorption. Impact strength and impact toughness increased after water exposure. The addition of nanoclay slightly minimized the effect of moisture on mechanical properties. SEM images showed water absorption severely damaged the cellulose fibers and the bonding at fibers-matrix interfaces in wet composites.</p>	<p>Table 2 - Maximum water uptake and diffusion coefficient (D) of nanoclay filled RCF/epoxy composites.</p>	<p>3</p>
<p>Nano-filler reinforced epoxy nanocomposites</p>	<p>Specimens with dimensions 10 mm x 10 mm x 3.5 mm were cut from the fabricated composites and placed in water bath at room temperature for about 130 days.</p>	<p>Charpy impact tests and three-point bending tests</p>	<p>Nano-filler in epoxy matrix led to significant reduction in both water uptake and diffusion coefficients. Flexural strength and modulus of all types of nanocomposites decreased due to the plasticization effect of the water uptake. Fracture toughness and impact strength increased due to water absorption. Water treatment increased the mobility of the epoxy chain, which led to increase the ductility of the epoxy matrix resulting in enhancing the toughness of the composites. Addition of nanoclay, HNT and n-SiC particles improved the mechanical properties of the nanocomposites after exposing to water compared to neat epoxy in same condition. Reinforcement with 1 wt. % nano-filler showed better mechanical properties than other filler content. Enhancement in barrier and mechanical properties of nanocomposites were more pronounced for nanocomposites filled with n-SiC than those filled with nanoclay platelet and halloysite</p>		<p>4</p>

			nanotubes.	
Ureaformaldehyde/sand composite	Aging at room temperature and at 5°C for about 1000 days	Mechanical testing, optical microscopy, and gravimetric techniques	Aging at room temperature and a -5C for about 1000 days does not affect strength. Solar exposure causes degradation of mechanical properties. Water immersion tests indicate that freshly cured specimens outperform samples which are exposed to solar radiation prior to immersion in water.	5
Four glass fiber laminated polyester resins (isophthalic, vinyl ester and bisphenol A and B)	Immersion in water kept at a constant temperature (20°C or 90°C)	The ten seconds shear modulus was measured for unfilled resins as a function of temperature, using a Clash-Berg torsional stiffness tester. Tensile tests were carried out with an Instron machine equipped with a thermostatic chamber and strain gauge extensometers.	Isophthalic resins demonstrated lowest hydrolytic stability. They underwent significant weight losses and embrittlement after conditioning in water. Both isophthalic and bisphenol B resins showed the formation of randomly distributed disc shaped fractures of size ranging from 0.1 to 1.0 mm, decreasing mechanical strength. The bisphenol modification significantly improved the hygrothermal stability. Vinyl ester resin showed highest stability on aging, slightly higher than bisphenol A polyester. Although these systems were also embrittled by the long term conditioning in water, the effect was less evident. Heat resistance in the presence of sorbed water may be related both to the chemical structure and to the cross-linking homogeneity of the thermosets. The less homogeneous isophthalic system, which shows a glass transition widely spread over the temperature scale, is also the less stable one. Chemical structure is equally responsible for the low heat resistance due to the possible hydrolysis of the ester groups. Systems with lower ester content possessed higher hygrothermal	6

			stability. Isophthalic resin contained the highest ester content and the lowest hydrolytic stability while the vinyl ester, which has the lowest ester content, was the most stable resin.	
Matrix was medium viscosity epoxy resin (LAPOX L-12)	Normal condition and sea water environments	critical stress intensity factor, interlaminar shear strength and impact toughness have been evaluated, both in interlaminar and translaminar directions	ILSS is found to be decreased as the duration of immersion increased in the seawater environment. The characterizing parameters have shown changes in their magnitudes with the variation in immersion time. SEM analysis has shown that the fibers pull out, matrix cracking and also the nature of crack growth is different in seawater environment.	7
Unidirectionally reinforced pultruded rods containing E-glass fibers in polyester and vinylester matrices	Specimens were conditioned at standard laboratory conditions (21C, 65% relative humidity) or submerged in aqueous solutions (tap water) at 80C for durations of 14 and 84 days.	Observations of the surfaces and cross-sections of the rods by optical microscopy and SEM	Embedded hygrothermally conditioned rods developed surface blisters of different sizes and depths. SEM studies of the surface revealed degradation of the polymer matrix material and exposure and degradation of the fibers close to the surface of the rods. Rods with the vinylester resin matrix showed less extensive degradation than those with the polyester resin matrix. The degradation characteristics of the two types of rods appear to be similar.	8
Bisphenol A epoxy vinyl ester pipe (H150) and bisphenol A epoxy novolac vinyl ester pipe (P150)	Glassfiber reinforced pipe sections were exposed to different acidic solutions at different temperatures (25C and 75C) and exposure durations (1 and 4 weeks)	Tensile testing on laterally loaded pipe sections. Compression testing on axially loaded pipe sections. Three-point bending test and microstructure analysis (optical microscopy, scanning electron microscopy, and energy dispersive spectroscopy)	P150 resulted in modulus and stress at 5% strain decreasing with duration of exposure. H150 was little changed by the bending test and sometimes increased in value.	9

<p>PEI, PEEK, PES, PC, PA 12, and PA 6 polymers</p>	<p>Immersion in water for more than 6 days at ambient temperatures. Dry specimens were conditioned under vacuum in an oven for 24 h at 100°C.</p>	<p>Damping spectra and shear moduli were measured in a torsion pendulum. Young's modulus was determined in a tensile test machine by stress-strain diagrams. For measuring thermal expansion, an inductive dilatometer was applied.</p>	<p>Even at very low temperatures, absorbed water influences the mechanical performance in an unexpected way. The results at low temperatures might be a tool for a better understanding of the features of the hydrogen bonded water, which itself could be a sensor for analyzing molecular mobilities. The interpretation of results is generally not yet clear and some cryogenic results are in contradiction to well established correlations for dry polymers.</p>		<p>10</p>
<p>Carbon fiber/epoxy laminates</p>	<p>Specimens from the first set were placed at room temperature in constant humidity environments of approximately 0%, 33%, 65% and 95% relative humidity (RH). Specimens from the second set (with the reduced level of fiber surface treatment) were either stored at 21°C and 65% RH or for some levels, dried in vacuum at room temperature. All specimens were left for several months until new equilibrium values of moisture content were obtained.</p>	<p>Plain and notched specimens were loaded in tension parallel to the 0° direction until failure occurred. Toughnesses were evaluated and cracking mechanisms in failed specimens were examined.</p>	<p>When moisture is absorbed by (0°, +45°) carbon fiber/ epoxy laminates, swelling of the matrix relieves residual internal stresses. In notched laminates, this reduces interlaminar stresses at the notch tip. The effect on tensile notch sensitivity depends on the failure mechanisms at the notch tip which are determined by the ply stacking sequence and the shear strength. In laminates, with 45° layers orientated in the same direction either side of 0° layers, failure generally occurred with no delamination between 0° and 45° layers and absorbed moisture had no effect. However, in laminates with 45° layers at right angles to each other either side of 0° layers, there was significant delamination between the 0° layers and the 45° layers, and moisture reduced the toughness by approximately 10%. The decrease in interlaminar stresses reduced the extent of the delamination and thus there was less reduction in the stress</p>	<p>Fig - 1 Effect of moisture on the toughness of two (0°, ±45°) carbon fiber/epoxy laminates with different ply stacking sequences and the standard level of fiber surface treatment</p>	<p>11</p>

			concentration effects on the 0° fibers. For short beam interlaminar shear tests, notch sensitivity tests showed no evidence of a reduction in shear strength on absorption of moisture.		
Brominated vinyl ester resin (Ashland Derakane 510A-40) reinforced with a 24 oz. woven roving E-glass (Vetrotex 324)	One-sided heating simulating fire exposure	Quasi-static tension strength tests were conducted on shear coupons to 180C. Isothermal compression creep rupture data was taken over a temperature range of 90-130C within a test window of 0.1-10,000 min. One-sided heat flux compression creep rupture tests.	The dominant relaxation mechanism, elevated temperature through the glass transition of the matrix, is controlling the viscoelastic behavior and the failure time predictions. Temperature, not stress, is dominating the viscoelastic relaxation. Delaminations are suspected of causing an insulating effect that propagates through thickness and decreases temperatures in each layer toward the back side of the test coupon, increasing the residual average compression strength and the predicted lifetime of the test coupon.	Figure 9 - Creep rupture stress vs. reduced time for temperatures 90-130C.	12
None	None	None	It was found that the aging shift rate parameter is the most critical parameter in determining magnitude of aging effect on long term response. Compliance of IM7-8320 composite changes by 8-12% over a 10 year period. It was also discovered that even for fiber dominated lay-ups, physical aging is extraordinarily important in calculating the long term response of laminates accurately.	Fig. 15 - Long term transverse and shear compliance of IM7/8320 lamina (shift rate modified). Fig. 16 - Change in compliance of quasi-isotropic laminate of IM7/8320.	13

Glass/vinyl ester composite with CM5005 and QM6408 fabric reinforcements	Samples were conditioned with some combination of moisture, elevated temperature, and sustained load	Ultimate tensile strength	Exposure to moisture at elevated temperature reduces the composite durability for the lay-ups studied. The addition of a sustained load typically causes a more rapid reduction in the durability. Conditioning also generally increases the material stiffness in the direction of the applied load. There may be significant consequences resulting from the use of polymeric composites for outdoor applications if the proper precautions are not taken.		14
Glass fiber/carbon fiber hybrid polymer matrix composite	Specimens were placed in an atmospheric oven and the temperature was ramped from room temperature to the aging temperature of 180±2C at 5 C/min for 3, 6, and 12 months	Static flexure testing and fatigue testing. A four point loading configuration was used to test all specimens; the test was developed based upon ASTM standard D4476.	Physical aging was the dominant aging mechanism of the bulk composite (away from the oxidation layer). Exposure to 180C in air for 3 months resulted in improved fatigue performance of the composite, with mildly diminished static flexure strength. Aging for 6 months resulted in moderately degraded fatigue performance and a further reduction in flexure strength, while severely reduced performance (both static and fatigue) for 12 months aging time was discovered. At 12 months aging time, dimensional relaxation caused a significant amount of microstructure damage to both the GFC and the CFC, hindering load transfer between fibers. The drastic reduction in properties for the 12 month aging condition was largely attributed to thermal aging.		15

<p>Matrix was a two-part, cold-curing epoxy resin. Three variants of Twaron 1055 aramid fibers: HM, HMA, HMF.</p>	<p>Microcomposites were immersed in distilled water kept at ambient temperature (22±2C) for periods of time up to 1.63 years</p>	<p>Raman spectra were obtained using the 632.8-nm red line of a 15-mW He-Ne laser</p>	<p>Diffusion characteristics for the matrix were in line with data reported in the literature. Fiber diffusion coefficient is estimated to exceed that for the matrix. Moisture transport is governed by Fickian diffusion associated with a matrix diffusion coefficient of $3 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ and an equilibrium water uptake of 5.6% (both values for the matrix). Water ingress in the composite is responsible for de-bonding near the fiber ends for fibers which had received surface treatment. Debonding of fibers which had received a surface treatment indicates a vulnerability of the interfaces in aramid/epoxy composites to hygrothermal effects.</p>	<p>Fig. 2 - Development of the axial fiber strain, determined from Raman band shifts, with time of exposure to water for the HMA320 DS-type specimen Fig. 4 - Development of the axial fiber strain, determined from Raman band shifts, with time of exposure to water for the DFPO specimens: (a) HM; (b) HMA; and (c) HMF fibers</p>	<p>16</p>
<p>Carbon fiber (IMV, Hercules) reinforced epoxy resin (TACTIX 556, Dew Chemical) composite</p>	<p>Simulated seawater, which was mixed from distilled water and a synthetic sea salt (Instant Ocean, Aquarium Systems), was used for immersion. [45/0/-45/90]_s and [06] specimens were used in weight gain measurements. Specimens from [45/0/-45/90]_s laminates were also presoaked to moisture gains of 0.25, 0.40 and 0.44% of the weight of the composite prior to testing. Saturation moisture absorption is</p>	<p>Axial and transverse coefficients of thermal expansion were measured. Edge delamination tests in fatigue were performed in a tension-tension, load-controlled mode.</p>	<p>Seawater absorption does not significantly reduce the maximum available strain energy release rate or accelerate the growth of edge cracking in fatigue. There is probably a moisture induced degradation of the interfacial strength, and this degradation leads to a change in the dominant edge-cracking mode from -45/90 interply delamination cracking to intraply crack- ing in 90° plies. The resistance of fatigue edge-crack growth of seawater presoaked specimens is similar to that of dry specimens due to a combination of the change in the dominant edge-cracking mode and lower available strain energy release rate.</p>		<p>17</p>

	0.44 wt%. All immersions were performed at room temperature.			
Sisal fiber reinforced polypropylene (SF/PP) composites	Specimens were immersed in hot water bath at 90C for different durations before removal	Tensile tests, Izod impact tests, and fracture surfaces of the tested specimens were examined by a scanning electron microscope	From the apparent weight gain measurement, the rate and the maximum value of moisture absorption increases with increasing sisal fiber content. In the water immersion experiments, an induction period (dIP) was observed for the individual SF/PP composites within which no significant weight loss (WL) can be detected . At the end of dIP for the individual composites, WL increased sharply with increasing immersion time. The higher the SF content, the higher the WL value was found at any given immersion time. The weight loss was mainly related to the dissolution of the lignaceous material and waxy substances on the sisal fiber surface. Due to the weight loss characteristics of the SF/PP composites, the moisture absorption is non-Fickian. While the tensile modulus and tensile strength decreased continuously with increasing immersion time, the impact strength was improved initially with increasing immersion time until reaching the maximum. These seemingly contradictory behaviors are due to the plasticization of the SF/PP interface and swelling of the sisal fibers.	18

<p>(1) PEEK developed for wire covering(2) Injection molding grade PEEK</p>	<p>(1.1) 322 days at 100C in water(1.2) 420 days at 200C in air(2.1) 33 days in water at 80C(2.2) 30 min at 288C in water pressurized at 180 MPa(2.3) Environmental stress cracking at 0.9% strain at 23C in: acetone, trichloroethylene, ethyl acetate, isopropyl alcohol, n-hexane, JPS (jet fuel), and Avtur 2494 (jet fuel)(2.4) Exposure for 7 days at 23C in: acetone, methyl ethyl ketone, kerosene, gasoline 7 days in concentrated sulphuric acid at 23C (2.6) 30 days in 50% sulphuric acid at 100C(2.7) 7 days in concentrated ammonium hydroxide at 23C</p>	<p>Comprehensive testing.Specimens were uniaxially orientated and were tested both along and across the fiber axis, and in shear using the short beam shear test.</p>	<p>(1.1) Tensile strength decreased by 5%(1.2) No cracking when flexed and no loss of dielectric resistance(2.1) Tensile strength increased by 5%(2.2) No change in dimensions or obvious signs of degradation(2.3) No cracks after 20 minutes exposure(2.4) No change in weight was detected, and tensile strength and tensile elongation were at least 95% of the original value(2.5) Sample dissolved(2.6) Less than 1% increase in weight and greater than 95% retention of original tensile elongation(2.7) Less than 1% increase in weight and greater than 95% retention of tensile strength and elongation</p>		<p>19</p>
<p>0°90° carbon fiber-reinforced epoxy laminate (XAS/91 4 fiber/resin system).</p>	<p>Three laminates were exposed to different humidity environments at 60C until reaching equilibrium level for that particular environment: 60°C, 59% RH</p>	<p>Residual strain and moisture expansion coefficient measurements</p>	<p>The progressive uptake of moisture steadily reduces the transverse residual strain until reaching an equilibrium moisture content of 1.72%, there is almost total relief of the thermally induced strains.</p>		<p>20</p>

	<p>equilibrium level 60°C, 75% RH</p> <p>equilibrium level 60°C, 90% RH</p> <p>equilibrium level</p>				
Poly(vinyl acetate) (PVAc)		Shear stress relaxation at three temperatures below the glass transition	The mechanical properties of PVAc reach equilibrium before either the volume or enthalpy.		21
Courtauld's XAS carbon fibers in Uba-Geigy's BSL914C epoxy resin	<p>The moisture absorption behavior of the materials was studied by exposing coupons to a hot/wet environment at 70°C/95% RH and monitoring their weight change as a function of time. Some coupons were also exposed to a 70°C/0% RH environment to determine the moisture content of the as-received specimens. Batches of test specimens were exposed to the same environment for varying times so that they absorbed either 50, 75 or 100% of the saturated moisture content.</p>	Tensile and compressive static and fatigue tests	<p>Exposure to a hot/wet environment (75°C/95% RH) had no significant effect on the room temperature static properties, but increasing the test temperature to 100°C (with a moisture content of 50% of saturation) reduced the static strengths by 9 to 19%. No observed decrease in fatigue life and only a slight decrease in residual strength compared with the as-received material, perhaps because the tests were performed at room temperature. After exposure to the hot/wet environment, fiber micro-buckling was observed in the 0° plies of coupons tested in compressive fatigue. This did not precipitate catastrophic failure. The microscopic evidence suggested that compressive failure occurred by macro-buckling of the outer 0° plies due to the reduction in the support offered by the inner plies which became damaged during fatigue. There was no change in the moisture absorption characteristics after compressive fatigue up to half the fatigue life.</p>		22

<p>Fiberglass pipes manufactured using the "Drostholm" procedure of filament winding, where chopped fibers are dispersed over the filament wound layers. A vinyl-ester resin, with proprietary formulation, was used as matrix.</p>	<p>Immersion times of the aged specimens were selected according to the water absorption characteristic of the composite. The times of immersion ranged from 25 to 270 days, and the specimens were removed from the immersion bath just before the test.</p>	<p>The kinetics of water absorption was followed using the procedures recommended by ASTM D-570 standard. The specimens for the ring test were machined from the pipes with a constant width of 18 mm. The ring tests were performed on mechanically driven test equipment, with 100 kN capacity. After the test, the fracture of the specimens was analyzed by visual inspection to identify the failure mode pattern.</p>	<p>Water absorption caused plasticization of the resin, reducing the stiffness of the pipes. Tensile strength, and the associated pressure class of the pipes, was not affected. Failure of these pipes after being exposed to water is more probable by mechanical constraints due to large dimensional changes caused by water plasticization and swelling than by the loss of mechanical strength.</p>	<p>Table 1 - Water absorption parameters</p>	<p>23</p>
<p>Aramid fiber-reinforced epoxy composite</p>	<p>Specimens immersed in distilled and salt water. Saline solution was prepared according to ASTM Standard D-1141, using the standard solution without heavy metals. Ten specimens were tested in the as-fabricated condition and after 500, 1000 and 2000 h immersion.</p>	<p>Tests were performed according to ASTM Standard D-2344</p>	<p>The aramid/epoxy composites are affected by a similar degradation mechanism when immersed in saline solution and distilled water. A greater absorption rate was measured for the specimens immersed in distilled water, resulting in a faster decrease in the interlaminar shear strength (ILSS) values.</p>		<p>24</p>

<p>Matrix resins were orthophthalic polyester, isophthalic polyester, vinyl ester, and epoxy</p>	<p>Resins and composites were aged for 18 months, under three immersion conditions: 20C seawater, 50C seawater and 50C distilled water.</p>	<p>Tensile tests, on resins and at 45° to fiber direction of composites, both before and after aging</p>	<p>Distilled water aging differs significantly from seawater aging in terms of weight gain but in terms of the shear property changes measured here the former is only slightly more severe. While permanent damage is induced in the polyester composites after 18 months, the epoxy and vinyl ester shear properties are much less affected by aging, and property losses for these two materials are largely recovered after drying. A simplified two parameter damage mechanics model has been applied to characterize the stress-strain behavior based on load-unload cycles. Such models have rarely been applied to this type of marine composite previously, much less to follow aging effects. Such an approach provides useful information which complements the more traditional modulus and strength parameters used to characterize material behavior and evaluate aging effects. This offers the potential for a more complete characterization of mechanical behavior and subsequent integration into complex structural models.</p>	<p>Fig. 10 - Percentage changes in mean apparent shear strength after aging.</p>	<p>25</p>
--	---	--	---	--	-----------

Glass/epoxy composite	Composites were immersed in water for up to eight months at temperatures up to 70C. Composite specimens of dimensions 50.8 mm x 50.8 mm x 1.6 mm were immersed in distilled water at 20, 50 and 70C and in seawater at room temperature (20C). Unreinforced matrix resin samples were also immersed for periods up to 2 years.	Tension tests on unreinforced resins were performed using Type I dogbone specimens (ASTM D638). Fracture toughness tests on unreinforced resins were performed according to the ESIS protocol using single edge notch bend specimens with a crack length to specimen height ratio of 0.5.	Seawater was absorbed less rapidly than distilled water. Weight gains below 1% did not influence the shear strength while higher weight gains reduced shear strength up to 25%. The loss in apparent interlaminar shear strength was uniquely related to specimen weight gain. Mode II fracture toughness also decreased with increasing immersion time after an initial incubation period, but the accelerated tests were found to reduce it less than the room temperature tests at comparable weight gains.		26
Matrix used was vinyl-ester. Different arrangements of glass fibers were used to reinforce vinyl-ester matrix: mat, unidirectional, and bidirectional cloth.	Samples were immersed in distilled water at 80C	Flexural modulus was measured as a function of immersion time	There was a decrease of the modulus and the interfacial resistance in relation to the time of immersion. The loss of interfacial resistance is less than the loss of the modulus.		27
Glass-epoxy composite pipes	The pipes were immersed in artificial seawater having a salinity of about 3.5% for 3, 6, 9, and 12 months in laboratory conditions	At the end of the conditioning period, the specimens were impacted at three distinct energy levels as 15 J, 20 J, and 25 J at ambient temperature of 20C	Moisture absorption, salt in seawater, diameter of specimen and residual stresses produced by manufacturing process of the composite pipe have significant effect on maximum contact force, maximum deflection, absorbed energy and failure of composite pipes according to exposure time to seawater.		28

<p>Glass-epoxy composite pipes</p>	<p>Specimens immersed for 3, 6, and 9 months in the barrels filled with artificial seawater having a salinity of about 3.5% in laboratory conditions.</p>	<p>Impact tests carried out at three different energy levels (5, 7.5, and 10 J), fatigue tests, and image analysis by scanning electron microscope (SEM)</p>	<p>At the end of a short seawater immersion time, residual stresses resulting from manufacturing process of composite pipe decrease or vanish by absorption of seawater. Composite pipe shows more elastic behavior than dry condition because of moisture absorption, the salt of the seawater, and absence of or decrease in residual stresses. Matrix cracking due to bending tensile stress and delamination at lower interface because of shear stresses and transverse normal stresses occur in the specimens subjected to impact loading. Micro-cracks and following matrix damage and debonding between fiber and matrix interfaces at the points crossing of the fiber bundles due to swell specimen diameter occur in non-impacted specimens and additional delaminations also occur in the impacted specimens under fatigue loading. Delamination expands, and matrix damage and debonding between fiber and matrix interfaces increase by increase in the number of cycle. Combining of these loads and seawater effect, fatigue life increases in the impacted specimens up to 3 months and reaches generally maximum value. After that, they decrease with the increase in seawater immersion time. Fatigue life of non-impacted specimen is greater than that of impacted one. Matrix failure increases with increase in seawater immersion time in the inner and outer surfaces of the specimens. De-bonding between fiber and matrix interfaces also</p>	<p>29</p>
------------------------------------	---	--	---	-----------

			occurs in the inner surface of the specimens. Leakage and eruption damage of non-impacted composite specimens are usually observed at the end regions of the specimens. However, leakage and eruption damages are seen around the impact zone for the impacted specimens.	
Polyester resins and a CSM polyester laminate	Immersed in distilled water at 51C	Static tensile tests and zero-tension fatigue tests	The general results under fatigue loading of dry and soaked specimens follow known trends. Residual and the static strengths have similar trends, namely that the soaked specimens have higher measured failure strengths than the dry specimens. For the soaked specimens, immersion in water at a temperature of 51C causes a significant redistribution of the complex internal stress system which supresses the onset of further damage after the initial debonding which occurs due to water sorption, so that there is an increasing residual strength with increasing number of fatigue stress cycles. The problem of the effects of water sorption on the properties of GRP laminates is complex.	30

<p>Unidirectional E-glass fiber reinforced epoxy resin (E-GFRE) composites</p>	<p>Case A, the pins were rubbed against a steel cylinder surface under dry contact condition. Case B, the pins were always rubbed against a clean fresh steel surface under dry contact condition. Case C, the pins were rubbed against the steel surface under water lubricated contact conditions.</p>	<p>Friction and wear experiments were conducted in the normal direction of the fiber orientation against a cylindrical counterface using a pin-on-ring technique for different sliding surface conditions. Friction coefficient and wear rate at various normal loads and sliding velocities were determined.</p>	<p>The highest friction coefficient and wear rate were observed when sliding took place against steel surface with remaining wear debris, (case A). The sliding against dry clean steel surface, (case B), improves the friction and wear properties, i.e. decreases friction coefficient by about 33-62% and wear rate by about 30-75%, depending on the value of normal load or speed. When sliding took place against a steel surface under water lubricated contact condition, (case C), the lowest friction coefficient and wear rate were observed. Reductions of about 62-88% in friction and 30-75% in wear rate were achieved, again depending on the value of applied normal load and speed.</p>		<p>31</p>
<p>Glass reinforced iso-polyester and vinylester structural plates</p>	<p>Plate specimens were kept at room temperature and were cyclically exposed to temperatures ranging from 0-70F under three different treatments, namely (i) untreated (as received), (ii) water and (iii) 4% salt solution</p>	<p>Ultimate tensile strength and stiffness were evaluated utilizing tension test results at temperatures ranging from 74 to 200F</p>	<p>Considering the available real time tests and the limited number of test results, the life expectancy of the composite material can only be estimated up to 18 months. For all design purposes, the strength of the material due to aging does not go below 50% of the initial ultimate strength.</p>		<p>32</p>

<p>50vol% 2 inch random nonwoven mat kenaf fiber vinyl ester composites</p>	<p>24 h at 25C moisture uptake</p>	<p>Tensile stiffness and flexural stiffness</p>	<p>The 2wt% addition of n-undecanoyl chloride or 10-undecenoyl chloride to the styrene-based resin prior to molding of the kenaf composites was observed to decrease the moisture uptake of the molded panels by more than 50%. The tensile stiffness and flexural stiffness of the soaked panels containing these additives were seen to increase by more than 30% and 70%, respectively, relative to panels made with no additives. While dry panel (50% relative humidity at 25°C) strengths did not significantly change in the presence of the additives, tensile strength was observed to increase by more than 40% and flexural strength more than doubled for the soaked panels.</p>		<p>33</p>
<p>Glass/vinyl ester filament wound pipes</p>	<p>Specimens were exposed for 300, 1000, and 3000 h in the environment of interest before testing at room temperature. The exposure conditions presented in this paper include: dry heat at 40C, dry heat at 70C, 65% and 100% relative humidity at room temperature; and salt spray and seawater environments at room temperature.</p>	<p>Three point bending tests. Fracture resistance was assessed using pre-cracked notched ring specimens.</p>	<p>No significant degradation in the flexural strength and stiffness and fracture resistance of glass/vinyl ester GFRP pipe specimens has been observed as a result of exposure to artificial exposure to dry heat (at a constant temperature for up to 70C) and high humidity environment (up to 100%). Flexural ductility exhibits noticeable degradation due to exposure in high humidity environments. Exposure of glass/vinyl ester to salt spray environment and full immersion in seawater at room temperature do not show rapid degradation effects on either the flexural or the fracture properties of the tested GFRP pipe material.</p>		<p>34</p>

IM7/K3B Composite	Isothermal aging involving temperatures ranging from 200-230C.	Short-term (96 h) tests and long term (1500+ h) tests. Tension/compression tests.	<p>Results from the short term behavior indicated that although trends in the data with respect to aging time and aging temperature are similar, differences exist due to load direction and mode. Temperature has a similar effect on tension and compression loading with the compression loading producing more exponential long-term behavior as compared to the tension cases. The differences in the material parameters associated with tension induced shear versus compression induced shear may be due to experimental procedures or the relationships between physical aging mechanisms and stress. Further development of experimental techniques or analytical models may be required to resolve this issue. The long-term (1500+ hour) predictions compared favorably to the long-term test data with the model demonstrating more accuracy in the shear mode as compared to the transverse mode. The sensitivity of the long-term predictions to aging shift rate imply that the predictive model must account for both loading mode and loading direction.</p>	35
-------------------	--	---	--	----

<p>Laminating resins were (i) Cellobond A 2785 CV, an isophthalic polyester (thixotropic), (ii) CL 1723, a developmental resol phenolic, (iii) Hetron 922-6, a vinylester and (iv) Norpol 92-20, a vinylester</p>	<p>Immersion in 30C seawater (salinity of about 29% (parts per thousand))</p>	<p>Flexural testing for flexural modulus, strength and strain to failure followed Method I, Procedure A of ASTM D790M-84. For interlaminar shear strength a 4-point shear test was used.</p>	<p>Phenolic GRP displayed anomalous uptake behavior considered to relate to both interface and matrix absorption. Water uptake by the polyester and vinylester laminates appeared to be affected initially by suppression from fiber barrier effects then later by enhancement from interface effects. Flexural strength fell by 15–21% for the water saturated polyester and vinylester GRPs, and by 25% for the phenolic GRP. Loading at 20% of ultimate strain while under immersion exacerbated only the phenolic laminate degradation, advancing the loss in strength to 36%. Interlaminar shear strengths fell by between 12 and 21% for the GRPs at close to saturation.</p>	<p>36</p>
<p>Resins were polyester and vinylester. Fibers were E-glass, carbon, and aramid.</p>	<p>Environments considered were air, deionized water, acetic acid at two concentrations, and ammonia at two concentrations. Temperatures considered were room temperature, 50C, and 80C.</p>	<p>Mechanical testing included tension, flexure, and short beam shear tests. Weight loss, thermogravimetric, and calorimetric measurements were made.</p>	<p>A combination of weight loss and thermogravimetric measurements are useful in determining whether degradation in the composite is due to fiber or matrix degradation. Trends in weight loss closely parallel loss of mechanical properties in polyester/glass rods.</p>	<p>37</p>

<p>Epoxy, epoxy/glass, and glass/epoxy/wood hybrid composites</p>	<p>Composite specimens were aged in the following media: water, HCl, and NaOH solution at room temperature and at elevated temperatures. Some of the samples were aged under sustained flexural stress (39% of ultimate strength) while immersed in the above liquid environments. Each cycle of the six-cycle aging procedure consisted of the following four steps: vacuum soaking in room-temperature water for 30 min, pressure soaking in room-temperature water 30 min, freezing for 2.5 h, and oven drying at 668C for 1 h.</p>	<p>A sinusoidal strain was imposed on the sample, and the resulting sinusoidal stress was measured</p>	<p>Immersion in aging media lowered the glass transition temperature (T_g) and enhanced apparent phase separation in the samples because of polymer plasticization. In water immersion, the T_g and the stiffness increased with time owing to continued resin curing. At ambient temperature, sustained load had little effect on the mechanical behavior of the aged samples. The extent of degradation was the least for samples aged in salt solution. Soaking in room-temperature acid solution was most damaging to pure red oak wood samples. Six-cycle aging did not damage the neat resin or the hybrid samples, but it damaged pure wood specimens. The composite wrapping around the wood core of the hybrid sample protected it sufficiently, thereby preventing damage to the hybrid specimen during the aging process.</p>	<p>38</p>
---	--	--	--	-----------

Matrices were polyester and vinylester. Reinforcements were E glass fibers for the polyester resin and ECR glass fibers for the vinylester resin. GRP Pipes

Soaked in water at 60°C for up to 4000 h

Sample pipes were internally pressurized with closed end testing procedure. Internal pressure was increased at the rate of 0.5 MPa per second. The pressurizing liquid was soluble oil at 23°C, and the tests were stopped when weepage was detected by the escape of oil from the outer pipes.

The degradation induced by hygrothermal aging is measured by the decrease of the mechanical properties. Such aging damage parameter is expressed as a function of the exposure duration. The axial modulus was not changed by such degradation. The most affected mechanical property was P_w for vinylester pipes and P_{NL} for polyester pipes. The damage parameter can be related to the failure stress for ductile composites and to the elastic threshold stress for brittle composites. The preconditioning of pipes before making tests leads to chemical degradation of matrix and introduces defects. Hence, the matrix cannot transmit forces. These actions are emphasized when the matrix is more ductile. The failure will occur by bursting when the tensile stress in the pipe reaches the fibers' failure strength. Increasing both the matrix ductility and the soaking duration drastically modify the degradation mechanisms and the failure mode. The cracks' growth is not affected by water uptake while a considerable decrease of the damage threshold pressure is observed. Variables representing damage by immersion in hot water and damage by loading are not coupled. The parameter representing soaking damage is related to the failure stress or the elastic threshold stress, the parameter representing mechanical damage is related to the axial modulus.

<p>Pure and Glass Fiber Reinforced Polyester and Vinylester Resins</p>	<p>Immersion in water at 60°C for various times</p>	<p>Differential Scanning Calorimeter Analysis Infrared Spectroscopy Compression-compression tests were run at a frequency of 5 Hz and at a heating rate of 5°C/min. Before loading a pre-deformation of about 3 µm was applied with an oscillation amplitude of 2.6 µm. The samples were tested in a temperature range of -120°C to 220°C.</p>	<p>This study has shown that the water uptake and its effects on physico-chemical and mechanical properties depend strongly on the chemical structure and the morphology of the material studied. The presence of fiber enhances the plasticization and the hydrolysis of the matrix. On the other hand, during aging, debonding and cracks in the composites are observed. Plasticization and hydrolysis predominate during the hydrothermal aging of the resins and composites. A post-curing reaction can be observed when the polymerization of the untreated material is not achieved. In the first case a decrease in the T_g is shown and the storage modulus at the glassy and rubbery states remains constant. In the second case an increase of the storage modulus at the glassy state is observed, while the T_g decreases drastically for an aging duration below 550 h and increases after this duration. The secondary relaxations associated with the small molecular movements are not affected. It is important to note the great similarity observed between the results obtained by DSC and DMA. The decrease of the styrene content for composite A and the dehydration reaction for composite B do not affect the dynamic mechanical behavior of the composites.</p>	<p>40</p>
--	---	--	--	-----------

<p>(1) E-glass fiber/epoxy laminates with fiber volume fraction 0.40 (2) carbon fiber/epoxy laminates with fiber volume fraction 0.55</p>	<p>None</p>	<p>Tensile tests in low-temperature chamber at 77 K and 296K</p>	<p>(1) The stress–strain relations of two kinds of composites, except for the glass fiber/epoxy [0/90/90/0]s, display near linearity at room and low temperatures until failure. Its failure characteristics are brittleness or brittleness like. (2) For each tested case, the strength of laminates at 77K is higher than those at 296K, about 15–20% for the carbon fiber/epoxy laminates and 30-40% for the glass fiber/epoxy laminates. The properties of laminates are improved at low temperature. (3) The damage areas around notch tips in the laminates at 77K are larger than those at 296K. The larger the damage area, the more micro-rupture events, which means that the energy dissipation is higher during tension at 77 K. (4) The energy dissipation density at 77 K is larger than those at 296 K for all test cases. The rate of rising is different by the difference between the notch and the lay-up angle of laminates. The rate of rising of the energy dissipation density at 77 K reaches 50% and over for unnotched unidirectional composites.</p>	<p>Fig. 12 - The dependences of the tensile strength on notch length for edge-notched carbon fiber unidirectional composites at different temperatures. Fig. 13 - The dependences of the tensile strength on notch length for central-notched carbon fiber unidirectional composites at different temperatures.</p>	<p>41</p>
---	-------------	--	---	---	-----------

<p>Cylindrical specimens were prepared from two diglycidyl ether of bisphenol A (DGEBA) amine-terminated poly(propylene oxide) (PPO) networks of different crosslink density</p>	<p>Specimens were quenched in water baths maintained at the desired aging temperature with a precision of $\pm 0.2^\circ\text{C}$ and were left at this temperature for an aging time, in the range from 10 min to 42 days (0.17-1000 h)</p>	<p>Compression tests run at the aging temperature</p>	<p>There is a considerable increase of the upper yield stress (up to 1.8 times) on aging from 0.1 to 1000 h. The aging rate of the upper yield stress is initially rapid before a transition time, at which it slows down sharply before tending to an asymptotic limit at very long aging times. The transition time is shifted to higher values as the aging temperature is decreased. The aging of the yield behavior seems to be closely related to the evolution of the specific volume as the network evolves towards thermodynamic equilibrium. The yield behavior is influenced by the viscoelastic response. The physical aging seems to affect the viscoelastic response differently than the yield response. Both transition time values occur at times shorter than those required to reach equilibrium in volume recovery experiments. The lower yield stress is not influenced as much by aging time, suggesting that microscopic mechanisms controlling the plastic flow processes are somewhat independent of the prior thermomechanical history.</p>	<p>Fig. 4 - Typical compression curves obtained at $T_e = T_{ref} - 15^\circ\text{C} = 27.4^\circ\text{C}$ for different aging times in the case of the DGEBA/PPO D400 resin</p>	<p>42</p>
<p>Polycarbonate and poly(methyl methacrylate)</p>	<p>Various temperatures and aging times</p>	<p>Dynamic mechanical experiments at different temperatures</p>	<p>Results show that the horizontal shift proposed by Struik (1978) to superpose the experimental curves for different aging times is only a first approximation. Results also indicate that the McCrum (1964) analysis can be used in the α region but cannot be applied between the α and β relaxations.</p>		<p>43</p>

Pultruded carbon fiber composite rods	None	Tensile and fatigue testing starting at the basic building block up to full scale testing. Eight strands were tested in cyclic fatigue with up to 1 million cycles.	<p>There is a lower fatigue strength associated with the strand compared to that of the single rod due to the way the load is transferred from the rods to the steel termination.</p> <p>The failure mechanism was always shear failure inside the end-fitting. Characteristic static and fatigue strength was established for the strand. Performance of the strand with its end-fitting is slightly lower than the performance of the individual rods, showing that this was the critical failure mechanism that had to be qualified for the demonstration of system performance.</p>		44
S2-glass–vinyl ester woven composites	None	Compressive properties and micro-structural damage progression under high strain rate loading have been investigated using the Split Hopkinson Pressure Bar technique	Moisture and temperature degrade the compressive failure strength under high strain rate loading. The level of such degradation is seen to vary with strain rates and loading direction.		45

FRP-wood composite materials with creosote or copper naphthenate preservatives	Resistance to Delamination During Accelerated Exposure (ASTM 2000): - Cycle 1: Vacuum submersion in water (18C to 27C) for 5 min. Pressure submersion (517 kPa) for 1 h. Repeat vacuum/pressure soak. Oven-dry (65.5C) for 21 to 22 h. - Cycle 2: Steam at 100C for 1.5 h. Pressure submersion (517 kPa) for 40 min. Oven-dry (65.5°C) for 21 to 22 h. - Repeat Cycle 1	Shear tests, measurements of the percentage of wood failure experienced in shear, and measurements of the delamination of the FRP-wood interface when subjected to an accelerated-aging test	When tested in a wet condition (following a vacuum/pressure soak), creosote-treatment adversely affected the wood failure values associated with specimens fabricated with a pultruded FRP composite sheet (E-glass fiber, bonded with urethane) during the shear testing. When these tests were conducted with samples under ambient conditions, the shear strength of this material was also adversely affected by creosote. Both creosote- and copper naphthenate-treatment adversely affected the shear strength of a SCRIMP fabricated FRP material (carbon fiber, vinyl ester matrix). Creosote-treatment promoted the delamination of the pultruded FRP composite and a continuous laminated FRP composite flat-sheet (E-glass fiber, bonded with epoxy) from glulam material when subjected to accelerated-aging tests. The delamination percentages were very large in some cases.		46
IM7/977-3 carbon/epoxy composite	Isothermal conditions at 104C in the viscoelastic range	Momentary creep tests were conducted at constant tensile loads	Physical aging effects on elastic and creep compliances are different and must be modeled separately. For predictions of long term creep behavior of the composite under continuous physical aging, it was found that the effective time approach is able to provide accurate predictions based on the momentary creep models.	Fig. 5 - Creep compliance vs. creep time curves for different aging times.	47
IM7/977-3	Isothermal aging 208C	Creep testing	Physical aging significantly affects elastic and creep compliances.		48

None	None	None	<p>There is good correlation between three broad areas for the physical aging of polymers: the changes in bulk thermodynamic properties, namely volume and enthalpy; various microstructural evidence for structural changes; and changes in mechanical properties. They may broadly be linked through the concepts of free volume and free volume distribution.</p>	<p>Fig. 6 - Effect of thermal conditioning treatment on the tensile creep of rigid PVC at 60°C under a stress of 2.0 MPa. Durations of storage at 60°C were : (A) 1 h; (B) 4 h; (C) 17.5 h; (D) 72 h; (E) 168 h; (F) 2016 h Fig. 7 - Low strain tensile creep curves for rigid PVC quenched from 90°C (about 10°C above Ts) to 40C, and aged at 40°C for a period of 4 years.</p>	49
Two different woven glass-aramid-fiber/epoxy laminates	<p>Before the test samples were conditioned in an oven at 70C for 24 h, specimens were immersed in a container with distilled water at 70C for 8 weeks</p>	<p>Impact behavior was assessed using dropping-mass tower. The front and back surfaces of the sample were examined optically. Compression-after-impact (CAI) tests evaluated the damage tolerance of the composite.</p>	<p>Maximum water absorption (4.1–4.4%) and water diffusion coefficients were found to be only slightly dependent on reinforcement configuration. The delamination threshold load and impact energy absorption were not significantly affected by the absorbed water. Due to low fiber-matrix adhesion, the prevailing failure modes at low impact energy were fiber/matrix de-bonding and interfacial cracking. The compression strength suffered significant reductions with water absorbed (28%) and impact (maximum 42%). The least sensitive to impact damage were wet samples of interlaminated composite.</p>		50

<p>Multidirectional 7300/5209 and T300/934 graphite/ epoxy laminates</p>	<p>Some of the specimens were vacuum dried at 70C and others were immersed in water at either 70C or 40C for up to 140 days. Cracked and virgin narrow specimens were also exposed to similar environmental conditions.</p>	<p>Different loading modes were chosen to establish stiffness and compressive and flexural strength characteristics.</p>	<p>Moisture delayed the onset of transverse cracking and slowed down crack propagation. Moisture-induced expansion of the laminates was less for cracked laminates than for virgin, uncracked laminates. Transverse cracks, even at levels that approached saturation crack density, reduced the stiffness and compressive and flexural strengths of the multidirectional laminates by less than 10%. Hygrothermal conditions had little influence on these effects and, in almost all cases, the residual properties of the cracked laminates were greater than 90% of that of the uncracked, virgin laminates. Matrix transverse cracking is not a crucial process in affecting the structural performance of multidirectional composite laminates.</p>	<p>Table 6 - Summary of residual flexural strengths for cracked and virgin multidirectional graphite/epoxy laminates in both the wet and dry conditions</p>	<p>51</p>
<p>Fiberglass E-980 resin</p>	<p>Specimen was aged at 80C for one day, before initiating a one-day creep test at the aging temperature. Specimen was then removed from the creep test apparatus and post-cured at 200C for 12 h. Specimen was once again quenched to room temperature, aged for one day at 80C and creep tested for one day at 80C.</p>	<p>Tensile creep and dynamic mechanical analysis (DMA) tests</p>	<p>Aging was found to have significant effects on the creep response of polyester. Thermoreversibility studies demonstrated aging to be physical and not chemical. The shift factor approached the theoretically limiting value of 1.0 as the temperature approached the glass transition temperature.</p>	<p>Fig. 10 - Tensile creep compliance for cross-linked polyester resin at 60, 80, 100 and 120°C.</p>	<p>52</p>

Unidirectional glass fiber laminates	Specimens immersed in distilled water for 2, 12, 16, and 28 days	Thermal expansion behavior Dynamic mechanical thermal analysis (DMTA)	The effective contraction on cooling from the post-curing temperature is larger for the wet material with a resultant increase in thermal strain. The ingress of water into a post-cured crossply laminate at room temperature causes a reduction of the strain in the laminate because, as the water is absorbed, the transverse ply swells at a greater rate in the axial direction than the longitudinal ply. This can be an advantage in that the laminate contains less strain, but against this must be balanced the lower glass transition temperature and increased temperature sensitivity of a wet laminate. If such a laminate is then subjected to a thermal cycle, this could lead to higher thermal strains than were present initially.		53
Cross-ply epoxy-based laminates reinforced with glass, carbon and Kevlar-49 fibers	Samples were conditioned prior to testing by exposure to three standard treatments: 1) drying at 60C for 4 weeks ('fully dried' state); 2) equilibrating at 65% relative humidity (RH) for at least three months at room temperature; and 3) boiling in water for 3 weeks, followed by storage in water at room temperature until testing.	Fatigue tests in repeated tension and in bending	The fatigue resistance of CFRP is unaffected by conditioning treatment and mode of stressing; for GRP there is no significant difference between the behavior of the dry material and that conditioned at 65% relative humidity. On the other hand, boiling in water always weakens GRP and KFRP, although the effect is small except for the case of GRP in the 0/90 orientation tested in tension. The large reduction in this case results directly from loss of fiber strength during pre-conditioning. Complete drying of KFRP laminates is more damaging even than boiling		54

Carbon fiber-reinforced epoxy resins	Unidirectional material was either immersed in boiling water or aged in a hot-humid atmosphere. The (± 45) material was aged at 70°C and 95% relative humidity to accelerate the moisture uptake and then tested at 20°C, 70°C, 110°C and 130°C.	Short-beam bending, interlaminar shear strength tests, and tensile strength tests	The values obtained were found to be independent of the mode of exposure but depended on the amount of moisture present in the composite. At test temperatures above 70°C the tensile strength decreased as the composite absorbed moisture. Plasticization, swelling and debonding were identified as the factors affecting the failure mechanisms in these laminates.		55
Cylindrical epoxy specimens with length of 40 mm and diameter of 12 mm, with an optical glass fiber of 0.125 mm in diameter centrally located, are prepared by using a mixture of DER 330, DER 732 Dow Epoxy resins and a DEH 26 curing agent	Immersion in distilled water at 50C for 2330 h	An optical low coherence reflectometry (OLCR) based method is proposed to obtain the axial strain distribution	While an average moisture concentration can be used with practically no effects on the moisture induced strains, a constant coefficient of moisture expansion may not be appropriate to use in the entire range of moisture absorption time. Moisture content is linearly related to the square root of immersion time with a slope of approximately 1/5.	Fig. 7 - Axial strain evolution along the fiber induced by moisture expansion with and without a glass fiber and for different cases of the parameters Fig. 8 - Evolution of the hygrothermal axial strain along the glass fiber induced by moisture expansion	56

Unidirectional
glass/epoxy laminates

Hygrothermal aging at
95% relative humidity
and temperatures up
to 80°C for periods of
up to 900 days.

Specimens were broken
in flexure. Four-point
bending stresses were
applied to some
specimens during
hygrothermal exposure.
Measurements of shear
strength were made,
using the short-beam,
three-point loading
method.

Initial water absorption behavior
approximately followed Fick's Laws, but
deviations occurred at higher
temperatures (around 80°C). No
classical equilibrium absorption plateau
was obtained at any temperature and
irregular changes in specimen weight
were observed after prolonged
exposure at 80°C. These changes are
explained in part by postulating a
degradation process, involving
interaction between water and the
curing agent. Four-point bending
stresses were insufficient to have much
effect on the diffusivity, but surface
damage was induced between the two
loading noses on the compressive face.
Failure occurred after prolonged
exposure to high stresses at 45°C. Pre-
stressing does not affect water uptake,
but post-loading already soaked
laminates lowers the flexural modulus

<p>Fabric-epoxy systems composed of glass, aramid and carbon fibers</p>	<p>Exposure to low cycle fatigue loading and moisture at 50°C</p>	<p>Mode II fracture toughness was measured. Strain energy release rates in shear Mode II loading were calculated using the compliance method.</p>	<p>The matrix and fiber/matrix interface dominated behavior in shear loading and was insensitive to short-term exposure to both fatigue and moisture. The carbon/epoxy material exhibited enhanced resistance to Mode II delamination after short exposure due to relaxation of the processing induced thermal stresses. Long exposure caused damage to both the matrix and the fiber-matrix interface, manifested in reduction of the strain energy release rates at failure. Fractographs supported the experimentally determined results. While unconditioned failure surfaces were typified by shear hackles, fatigued specimens indicated gradual elimination of the hackles, fiber fracture and matrix abrasion. When the composites were moisturized, examinations of the fracture surfaces revealed plasticization of the matrix following short-term conditioning with gradual disappearance of the typical shear striations and appearance of voids, following long-term exposure.</p>	<p>58</p>
<p>Filament-wound glass fiber reinforced/vinyl ester thermoset pipes</p>	<p>Exposure to salt spray and oxygenated sea water immersion for periods of up to 10,000 h</p>	<p>Fatigue testing was performed as per ASTM standard D-2290</p>	<p>The most severe degradation in fatigue resistance was observed at an exposure of 300 h under salt water spray condition and at 10,000 h of exposure under oxygenated salt water immersion condition.</p>	<p>59</p>

<p>Sisal textile fiber-reinforced composites. Epoxy and vinyl-ester matrices are used.</p>	<p>Specimens were immersed in pure water during 9 days at room temperature, and dried in 1 day at 50 °C. 9600 h (400 days) aged samples. 5 cycled specimens were immersed in water for 216 h (9 days) and then dried for 24 h (1 day) in the epoxy and vinyl-ester composites.</p>	<p>Fractured surfaces are taken to study the failure mechanism and fiber/matrix interfacial adhesion.</p>	<p>Water uptake of the epoxy composites increased with cyclic times. Mechanical properties are dramatically affected by the water absorption cycles. Water-saturated samples present poor mechanical properties such as lower values of maximum strength and extreme elongation. The KIC values demonstrate a decrease in inclination with increasing cyclic times of wetting and drying for the epoxy and vinyl-ester. The KIC values of composites aged 400 days distribute within similar region to the 4 or 5 cycles. The fibers appear seriously degraded with complete lack of resin layer and the microfibrils can be clearly observed.</p>		<p>60</p>
<p>Derakane 441-400 epoxy vinyl ester and Knytex A130A</p>	<p>None</p>	<p>Tensile and fatigue tests</p>	<p>Tensile strength was 582 MPa. At a stress of 436 MPa, composite failed at 926 cycles. At a stress of 266 MPa, composite failed at 5.66×10^5 cycles. The micro-crack density is proportional to the number of micro-cracks irrespective of stress ranges, and its single slope is found to be 304. Damage rate was found that to obey a power law.</p>		<p>61</p>
<p>Vinyl ester/glass fiber reinforced composite (vinyl ester resin used was Hetron 922)</p>	<p>Specimens were immersed in four separate environments: 5 wt% NaOH, 32 wt% HCl, 25 wt% H₂SO₄, and uncut Kerosene, each at 66°C</p>	<p>Flexural testing was performed according to ASTM D790M. Resistance to corrosive environments was assessed using the procedure outlined in ASTM C581-94.</p>	<p>The degree of cure did not affect the amount of degradation in flexural properties over time. Rubber-toughening of the resin matrix and the total volume fraction of resin in the composite affected the amount of degradation exhibited. Sodium hydroxide was the only medium, which produced degradation of the flexural properties after 3 months. For all the other media, degradation occurred within the first 3 months of exposure.</p>	<p>Fig. 4 - Effect of exposure time on the bending strength of the pooled data. Fig. 5 - Effect of exposure time on the bending stiffness of the pooled data. Table 3 - Barcol Hardness measurements after 9 months of immersion</p>	<p>62</p>

			The analysis of variance technique provided a useful method for determining significant differences in measured mechanical properties.	
Glass/polyester, carbon/polyester, glass/vinyl ester and carbon/vinyl ester composites	Composite panels were immersed in a large tank containing natural seawater with a salinity content of about 2.9% and temperature of $30 \pm 0.5^\circ\text{C}$ for more than two years. Seawater in the tank was renewed about every month.	Flexural modulus and strength of the composites were determined four-point bend test method (ASTM D790). Double cantilever beam tests were performed in air in accordance to ASTM D5528 to determine the mode I interlaminar fracture toughness properties.	<p>Polyester-based composites are less chemically stable in seawater than vinyl ester-based composites due to the susceptibility of the polyester resin to hydrolysis that resulted in the leaching out of ester species with hydroxyl end groups and other low molecular weight organic species. Some chemical degradation occurs to vinyl ester-based composites, but to a much lower extent than for polyester matrix laminates. Despite the superior chemical stability, the flexural properties of the vinyl ester-based composites were degraded to a similar extent to the properties of the polyester materials. The sizing agent on the fiber reinforcement also appears to influence the water uptake behavior of the composites. It is found that fiberglass composites absorb more moisture than carbon fiber composites, and this may be due to the emulsion size used on glass fibers facilitating greater water absorption at the fiber/matrix interphase than the silane size on carbon fibres. The mode I interlaminar fracture toughness of the composites was not affected significantly by seawater immersion, although the flexural stiffness and strength decreased with increasing amounts of water absorption.</p>	<p>Fig. 5 - Effect of seawater immersion time on the normalized: (a) flexural modulus; (b) flexural strength of the polyester-based composites.</p> <p>Fig. 6 - Effect of seawater immersion time on the normalized: (a) flexural modulus; (b) flexural strength of the vinyl ester-based composites.</p>

<p>Graphite/epoxy composite material</p>	<p>For thermal damage, specimens were inserted into an oven preheated to a desired temperature. Three temperatures, 200, 250 and 300°C, were selected for testing.</p> <p>For moisture content, two chambers with varied relative humidity were used simultaneously. The relative humidity of one chamber was set to 75%, and the other was set to 90%. For the chamber of 75% relative humidity, the maximum moisture content was 0.408%, which occurred when the moisturizing process reached equilibrium. For the chamber of 90% relative humidity, the maximum moisture content was 0.933%, which also occurred at saturation of moisture content.</p>	<p>Vibration testing was conducted by using a hammer to apply an impulse force at the middle of the specimen, and a non-contact proximity sensor was mounted vertically below the free end of the beam to measure the vibrational motion. The specimen was mounted on a material-testing machine that produced a static force to enlarge the crack until it was increased to 20 mm.</p>	<p>The fundamental mode dominates the dynamic characteristics. A delamination crack may decrease the natural frequency, but increase the damping ratio of the specimen. After the specimen was exposed to high temperatures, the stiffness and hence the natural frequency increased. The damping ratio decreased significantly after specimen was subjected to prolonged exposure to humid environment. From correlation between modal parameters and delamination cracks, the method of modal analysis was suitable for nondestructive evaluation of composite materials.</p>		<p>64</p>
--	--	---	---	--	-----------

<p>E-glass/vinyl ester curved composite panels</p>	<p>Three composite material constructions are utilized in this study: (1) 0/90 biaxial layup, (2) 0/90 biaxial layup with a glass veil between plies, and (3) 0/90 biaxial layup with a coating of polyurea</p>	<p>Underwater explosive loading</p>	<p>Performance of the baseline laminate is improved when coated with the polyurea material but is degraded by the inclusion of glass veils between plies. The polyurea reduced the center point deflection by 67%, while the inclusion of glass veils increased the deflection by 43%. In all cases, the effects of the secondary pressure waves are sufficient to continue the displacement to full plate inversion. The magnitude of the kick off velocity for all panels was the same at around 16 m/s. The polyurea panel showed the fastest decay of this peak velocity back to zero.</p>	<p>65</p>
<p>Unsaturated orthophthalic polyester resin with a 3:2 molar ratio of phthalic anhydride to maleic anhydride, an unsaturated isophthalic polyester, a vinyl ester of the ester-linked bisphenol-epoxy type, and a cast acrylic sheet</p>	<p>Samples were exposed to vapor containing various water partial pressures (relative humidities) at 30°C, 40°C and 65°C. The bottom of a desiccator was filled with water or a salt solution to control the water partial pressure; the samples were placed on a rack above the liquid.</p>	<p>Water sorption as a function of temperature and water was measured. Absorption-desorption-reabsorption (ADR) testing.</p>	<p>The three ester resins underwent a weight loss during absorption. MEKP-cured resins showed a smaller weight loss than those cured with BPO. Post-curing reduced weight loss significantly. Higher temperature and relative humidity increases weight loss rate. True equilibrium water content and diffusion coefficient could not be obtained during absorption because of the weight loss. BPO-cured orthophthalic resin showed the continuous weight loss which took place during absorption, desorption and was still taking place during reabsorption. MEKP-cured orthophthalic and vinyl ester resins were much more stable, showing only slight loss during reabsorption. Isophthalic resin did not lose weight after desorption. Equilibrium water contents and diffusion coefficients were determined using absorption, desorption and</p>	<p>66</p>

			reabsorption data, and the latter are considered accurate values for these polymers.		
Cellulose acetate butyrate ester and the polyimide Kapton-H	None	Torsion and tensile creep tests	The measured shift rates were 0.75 and 0.5 for cellulose and polyimide respectively, which indicates that physical aging also occurs in polymers with stiff chains. These values, compared with those already known for most thermoplastics, suggest that physical aging is slowed down by the rigidity of the main chain.	Fig. 1 - Small strain shear creep compliance of CAB at different elapsed times, t_e , after a quench from above T_g to 20°C (maximum shear strain, 3×10^{-3})	67
Glass-epoxy (Epoxy Novolac-EPN) composite	323°K and 343°K immersion in distilled water	Moisture absorption studies, interlaminar shear strength (ILSS), in-plane shear strength (IPS)	Samples immersed at 343°K showed higher diffusivity value and lower saturation time than those of 323°K immersion while the maximum moisture content remained the same. Good Fickian correlation was observed for the composite system. The glass transition temperature of the composite decreased with increased moisture content showing a maximum drop of 30°C at full saturation, while the mechanical properties (ILSS and IPS) of saturated specimens degraded up to 26 and 33% respectively. These mechanical properties obtained at 70°C/85%RH test condition showed good correlations with those predicted by a theoretical equation.		68
S2-glass/vinyl-ester composites	None	Flexural fatigue tests	It is found that the fatigue modulus is not only a function of loading cycle but also a function of applied stress level and thickness of the specimen.	Table 1 - Fatigue modulus at n number of cycles.	69

<p>Neat resin formed from NE, MDA, and BTDE monomers. HTA7 carbon fibers.</p>	<p>Before the thermal aging tests, each sample was dried at 90°C until constant weight. After this conditioning thermal treatment, all specimens were weighed at zero time and were placed in air at 340, 360 and 380°C for the composite and at 320 and 340°C for the neat resin.</p>	<p>The gravimetric study was carried out by weighing the specimens at various times up to 600 h with an analytical microbalance of relative precision 10⁻⁴.</p>	<p>Results suggest that fibers have no effect on matrix degradation kinetics.</p>	<p>Table 1 Rate of degradation Vp for composite and neat resin</p>	<p>70</p>
<p>Standard orthophthalic polyester, low styrene content DCPD (dicyclopentadiene) orthophthalic polyester, low styrene emission orthophthalic polyester, and a vinylester</p>	<p>Accelerated aging in natural sea water for 9 months, at temperatures of 20, 40 and 60C</p>	<p>Tensile and flexure tests on specimens at a loading rate of 2 mm/min</p>	<p>The macroscopic behavior low styrene resins is very similar to that of standard orthophthalic polyesters (same mass gain and property evolution). Low styrene grades are even more brittle after aging. When these resins are employed in composites, similar initial flexural properties are obtained for all four resins. After aging the changes in properties are similar for all the materials, but the rate of strength loss varies. Low styrene resins appear to lose strength more slowly than the standard resins, but after nine months similar losses are noted. Changing from a standard polyester to a low styrene resin does not affect the aging behavior of marine composites.</p>	<p>Fig. 12. Influence of nine months' seawater aging at 20, 40 and 60 C on flexural properties of composites. Flexural stress at failure and modulus. Fig. 14. Flexural strength versus aging time (a) composite SV, (b) composite LS. Table 3 DMA results for polyesters before and after nine months in seawater at 40C</p>	<p>71</p>

Glass/vinyl ester composite	Specimens immersed in water and 3.5% by weight salt solution. Pre-conditioning consisted of tap water (45 °C), salt water (65 °C), thermal (45°C), two cycles/dry, two cycles/wet, five cycles/dry, and five cycles/wet.	Quasistatic tests were performed at a loading rate of 0.05 in. (0.127 cm) per minute. Fatigue tests were conducted at a maximum-to-minimum load ratio of R=0.1 at frequencies of 2 Hz and 10 Hz. Fatigue tests conducted in both air and salt water.	Quasistatic modulus in the dry specimens underwent a change of 11% and the strength a reduction of 32% following aging in salt water. The Poisson's ratio increased by 6%. The fresh-water-aged specimens experienced a decrease in modulus of about 11% and 32% in ultimate tensile strength, from dry to water-aged. There was no change in Poisson's ratio for this case. The results indicate little difference between the material properties of the water and salt-solution-aged materials. Quasistatic tensile strength was seen to reduce by 24% at a moisture concentration of 1% by weight. This reduction in strength was not recoverable even when the material was dried, suggesting that exposure to moisture caused permanent damage in the material system.		72
Nylon 6 films	Three kinds of films were kept dry in desiccating boxes under dynamic vacuum at RT for 3 days prior to physical or mechanical testing. Some samples were also conditioned at 92% RH for three days at RT in an environmental chamber in the presence of KNO3 saturated solutions.	Dynamic Mechanical Analysis (DMA) was carried out in tensile mode.	Modification of chain mobility in the amorphous phase via water plasticization has a determining impact on the stress-strain response. Both yield stress value and hardening behavior over a large strain domain are strikingly equivalent for samples drawn at same DT between draw temperature and main amorphous relaxation temperature. This apparent lack of thermal activation of crystal plasticity in the fibrillar transformation suggests that crystal block fragmentation proceeds via H-bond unzipping through water penetration at defective crystal interfaces		73

Plain woven glass fiber/vinyl-ester (GFRP) laminates	None	Flexure fatigue tests	<p>Flexural fatigue strengths of GFRP laminates decrease strongly with increasing time and temperature as well as the number of cycles to failure. The long term fatigue strength at any time, temperature and number of cycles to failure can be predicted using the master curves of fatigue strength obtained based on the proposed accelerated testing methodology.</p>		74
Polymeric composite materials	None	Theoretical analysis	<p>Physical aging reduces the resulting strain from the stress history since the material becomes stiffer. With the increase in initial aging time there's a corresponding reduction in strain for the same level of stress.</p> <p>The aging rate of the laminae varies slightly because the values of the shift factors are different. Their influences change depending on the orientation of the lamina.</p> <p>The unaged material undergoes significant creep deformation during loading with a value of 19% creep summed over all loading intervals. The aged laminate creeps by only 14% over the entire loading period. The effect of aging is considerable for this matrix-dominated laminate even at short time values.</p>		75

<p>Jute fiber reinforced polypropylene (PP) composites</p>	<p>Specimens were aged in hot distilled water at 80°C</p>	<p>After the fixed periods of immersion, the weight changes and the tensile properties were measured.</p>	<p>Weight gain by water absorption was significantly affected by fiber content. Specimens with jute fiber content of 30 wt% absorbed water more easily and it reached more than 10%. Significant material loss by immersion also occurred. The tensile strength after immersion decreased remarkably in the specimens with the jute fiber content of 30 wt% and more, and all the jute/PP composites showed lower strength than neat PP after immersion of 1000 h.</p>		<p>76</p>
<p>Quasi-isotropic carbon fiber-epoxy laminate</p>	<p>Exposure to ambient atmospheric conditions (20C and 50% relative humidity). Immersion in water at 20C. Immersion in water at 70C. Exposure to high temperature (70C) and high humidity (85%). Samples were loaded in through-thickness tension at the constant crack opening displacement rate of 1 mm/min until all the pins had failed.</p>	<p>Pin pull-out tests were performed to assess the influence of environmental aging on the crack bridging traction properties of the pins.</p>	<p>Fibrous composite pins accelerate the moisture absorption rate and increase the total absorbed moisture concentration when the laminate is immersed in water. The moisture absorption properties of the laminate are not affected significantly by pins when exposed to hot and humid air. Water diffusion into the z-pinned laminate is aided by interfacial cracks between the pins and laminate. The axial alignment of fibers within the composite pins in the through-thickness direction increases the water absorption rate. Water absorption reduces the mode I crack bridging traction load generated by pins by reducing the shear strength of the pin-laminate interface. The mode I delamination toughness induced by pinning is weakened by moisture absorption.</p>		<p>77</p>

<p>Marine-grade glass/epoxy, glass/vinyl ester, carbon/epoxy and carbon/vinyl ester composites</p>	<p>Composite panels were immersed in a large tank containing artificial seawater prepared according to ASTM D 1141 with salinity content of about 2.9% at room temperature for different time periods.</p>	<p>Flexural strength was determined for different immersion times using the three-point bend test as per ASTM-D790 using UTM. Tensile tests were performed on the specimens for different immersion times as per ASTM-D 638 using a strain rate of 1 mm/min. Tensile fracture surfaces were examined for seawater degradation effect using scanning electron microscopy.</p>	<p>The reduction of mechanical properties was higher in the initial stages which showed saturation in the longer durations of seawater immersion. Flexural strength and ultimate tensile strength (UTS) dropped by about 35% and 27% for glass/epoxy, 22% and 15% for glass/vinyl ester, 48% and 34% for carbon/epoxy 28%, and 21% carbon/vinyl ester composites, respectively. The water uptake behavior of epoxy-based composites was inferior to that of the vinyl system.</p>	<p>Fig. 2. Flexural strength of composite specimens vs. time of exposure to seawater. Figure 3. ILSS curve of composite specimens vs. time of exposure to seawater.</p>	<p>78</p>
<p>Glass fibers/epoxy composites</p>	<p>Specimens immersed in water were thermostated at 50C with a silicon oil bath over a heating-magnetic stirring plate. At a certain immersion time a specimen was removed from the water. The excess surface water was removed, and the specimen was analyzed with GA (weight), FT-NIR (transmission spectra) and SF (emission spectra).</p>	<p>Water absorption process was followed using three different techniques: (i) gravimetry (GA), (ii) Fourier transformed infrared spectroscopy in the near range (FT-NIR) and (iii) steady state fluorescence spectroscopy (FS).</p>	<p>The presence of silanized fibers induces changes in the process of water absorption in epoxy resin, decreasing the relative gain of mass at equilibrium. The glass fiber surface yields a change in the structure of the epoxy matrix in comparison with that of the polymer without reinforcement. The accessibility of water to the interphase is considerably delayed compared to that of the polymer matrix. Although the relative amount of water absorbed by the interface (nanometers) depends on the nature of the glass fiber surface, the differences observed do not correspond with those observed for the global absorption of water by the whole specimens. One possible explanation may be that a higher crosslinking density should yield less free volume to be occupied by water molecules during</p>	<p>Table 2 - Diffusion coefficients and mass gain at the equilibrium</p>	<p>79</p>

			the water absorption process.	
Sandwich systems which contain various core materials (wood, plywood, polyurethane, coremat)	Specimens were conditioned with steam from a 5% solution of sodium chloride (NaCl) for a 72 h period at a constant temperature of 50C in a Heraeus testing machine. Salt-treated specimens were dried in ambient temperatures until their humidity content dropped to the same value as the non-salt treated specimens.	Interfacial fracture toughness was characterized by a Mode-I CSB test configuration.	Fracture toughnesses of the systems with wood, plywood and polyurethane core materials are low. Fracture toughness of the system with coremat is higher compared to its counterparts. While fracture toughnesses of sandwich systems with wood and plywood cores are found to decrease, those of the others have been found to increase under the environmental effect of seawater.	80
Cyanate ester resin (Fiberite 954-2) and semicrystalline thermoplastic resin (Fiberite ITX) with their respective carbon-fiber composites, IM8/954-2 and IM8/ITX	Specimens were aged for periods of up to 9 months in environmental chambers at 150°C and in one of three different gas environments: nitrogen, a reduced air pressure of 13.8 kPa (2 psi air), or atmospheric ambient air (14.7 psi air).	Glass transition temperatures, T _g , of the two resin systems were monitored as a function of aging time and environment. Flexure tests were performed on 8-ply unidirectional (90°) IM8/954-2 and IM8/ITX composites, aged up to 6 months in the three gas environments at 150°C. Weight loss in the plain resin and composite samples was monitored as a function of aging time and environment.	Changes in T _g showed effects of both physical aging and chemical degradation; the latter appeared to be sensitive to the oxygen concentration in the aging environment. The samples showed a 30-40% loss in the bending strength after aging. These strength reductions were sensitive to the oxygen concentrations in the aging after aging for 6 months, possibly as a consequence of the physical aging phenomena. In both systems greatest reduction in mechanical properties occurred in the ambient air environment, while the least reduction occurred in nitrogen. All of the samples showed 1-2% weight loss after 9 months of aging at 150°C, and the composite samples lost much more weight (on a polymer basis) than unreinforced resin specimens over the same aging period. The weight loss data	81

			as well as all the above-mentioned observations suggested an oxidation process in the composites.		
IM8/954-2, a thermoplastic-toughened cyanate ester thermoset resin reinforced with graphite fibers and IM8/ITX, a semicrystalline thermoplastic resin reinforced with graphite fibers	Specimens were aged at 150°C in two different environments (ambient atmospheric air and inert nitrogen gas) for periods of up to 18 months prior to testing.	Impact tests were conducted at impact velocities (V_i) of 6.3, 10.1, 14.6, 19.8 and 254 $m*s^{-1}$ by using a gas-gun.	In both the unidirectional and cross-ply composites, damage increased progressively with aging time. Aging environment also had a significant effect on damage resistance, as shown by the fact that specimens aged in nitrogen for 18 months had equivalent damage to those aged in air for only 2 months. Tension-after-impact (TAI) strength tests were also conducted on the cross-ply composites. Strength values fell by as much as 70-75% of original tensile strength in both material systems and were dependent on variables such as aging time, aging environment and impact velocity.	Table 1 - Changes in tensile strength and elongation to failure of as-received [+45/-45], IMS/ITX and IM8/954-2 composites as a function of impacting velocity	82

<p>Glass/epoxy laminate pipe</p>	<p>The six states of the tested material are (at 60°C):</p> <ul style="list-style-type: none"> - unaged, oven-dried Mt = 0.0% - unaged Mt = 0.0% (reference state) - aged at 336 h Mt = 0.2% - aged at 1500 h Mt = 0.3% - aged at 11 300 h Mt=0.7% - aged at 11300 h Mt = 0.7%, and then oven-dried Mt = 0.0% 	<p>Tensile fatigue tests and repeated progressive loading tests under internal pressure with fixed ends</p>	<p>Young's modulus of composite and pure resin seem not to be moisture sensitive. A decrease in Tg and variations of the viscous properties and of the appearance of glass fibers at the surfaces were observed. These phenomena indicate non-negligible changes in the molecular structure of the matrix and at the fiber/matrix interface. The primary effects of water uptake result in an increase in the rate of damage during the fatigue and RFL tests. Initial fatigue properties may be recovered by removing the absorbed water. The initial number of cycles to failure may be obtained again despite the apparent degradation of the chemical and physical structure. The absorption of a damaged material and the damage of an aged material are inter-related phenomena. The absorption rate of water is a function of damage, and the rate of damage accumulation depends on water content. A coupling method is proposed for the simultaneous modeling of these two kinetic processes. The simulation of the behavior used in this model seems to be validated by experimental analysis.</p>		<p>83</p>
----------------------------------	---	---	--	--	-----------

<p>Glass fiber-reinforced polyesters (a chopped strand mat laminate in air and a mixed woven rovings/chopped strand mat laminate)</p>	<p>None</p>	<p>Data is taken from two test programs on glass fiber-reinforced polyesters (a chopped strand mat laminate in air and a mixed woven rovings/chopped strand mat laminate) in aqueous environments</p>	<p>For a particular laminate system tested in water at 40°C, the stress-rupture behavior is unaffected by specific variations in immersion conditions such as distilled water versus seawater, minor variations in resin composition or binder, total versus single-face immersion, or unsealed versus sealed edges. The load/lifetime relationship has been shown to be more complex than a linear stress/logarithm time curve. At loads above 50% UTUL, water temperature in the range investigated has little effect. Below that load level, the effect of temperature is much greater than can be accounted for by thermal activation alone. There is a clear upper limit to the loads which may be used for accelerated life testing, if the influence of a water environment is to be recorded.</p>		<p>84</p>
<p>Carbon fabric-reinforced, thermoplastic polyamide 6 (also referred to as nylon 6 and/or PA6) matrix panels</p>	<p>Fully immersed in distilled water at 100°C</p>	<p>Scanning electron microscopy (SEM) and impact resistance</p>	<p>The Bao and Yee dual diffusivity model shows good correlation with the experimental data in terms of the percentage of moisture absorption with respect to the square root of time. Scanning electron microscopy (SEM) shows that surface defects induced during processing result in matrix micro-cracks after moisture exposure, and the fiber matrix interface is compromised. The impact resistance of the material is also lowered due to water ingress. The crystallinity and melting peaks are not affected.</p>		<p>85</p>

CFRP specimens	Specimens to be tested after environmental conditioning were placed in an environmental cabinet at 60°C, 95% RH for about 18 days.	Pre-loading and loading to failure. Mechanical testing was carried out when the total moisture content in the coupons was 1.11%. Each specimen was heated to 120°C for testing.	Compressive pre-loading of RT-dry coupons to 23 kN had no significant effect on environmental degradation. This is consistent with the absence of any detectable damage due to such pre-loading. Compressive pre-loading of RT-dry or RT-wet coupons resulted in no detectable damage even at 30 kN, which corresponds to the field strain of 4000×10^{-6} associated with DUL. Compressive pre-loading would not be expected to have any effect on environmental degradation below this level. Damage caused by compressive pre-loading to any level at RT was highly localized and did not exhibit delamination in the region in which fiber buckling failure was initiated in the hot-wet coupons. Even at very high levels of pre-load, there would be no significant compressive pre-loading effect.	86
----------------	--	---	--	----

<p>Resin matrices included vinyl ester, polyester, and epoxy, and the fiber materials were silicate glass, aramid, and carbon</p>	<p>Exposure to neutral, basic, and acidic media between 23 and 80 °C over periods of 7 to 224 days</p>	<p>Thermogravimetric analysis (TGA) was used to study the effects of aqueous media on FRPs.</p>	<p>Relative weight loss upon heating the previously exposed material from 150 to 300 °C was indicative of the extent of matrix depolymerization. Indications were obtained for correlation between weight loss and the extent of degradation of various measures of mechanical strength. The measured weight change of the tested materials during exposure reflected extent of water absorption and could be related to the extent of the weight loss between 150 and 300°C. In basic environments, weight loss, rather than gain, took place as a result of fiber dissolution. FRPs with aramid fibers were especially prone to degradation due to extensive water uptake. Basic environments caused a large decrease in strength due to fiber dissolution. Acetic acid buffers caused significant matrix depolymerization. Raising the temperature to 80°C was the most effective method of enhancing the degradation effects. The trends observed at 80°C were identical with the trends observed at lower, service-like temperatures. Elevating the temperature is a promising acceleration factor. In agreement with the enhanced matrix depolymerization observed in the TGA measurements, higher temperatures also caused a decrease in glass transition temperature.</p>	<p>87</p>
---	--	---	---	-----------

<p>Carbon/epoxy and glass/epoxy laminates</p>	<p>One lot of carbon/epoxy short beam shear test specimens were exposed to 60C temperature and at 95% RH atmosphere. The other lot of the same samples were treated in 70C temperature and at 95% RH environment. They were exposed up to about 1200 h at those conditions. The one lot of glass/epoxy SBS specimens was exposed to 50C temperature and 95% RH and for another lot it was 70C temperature and 95% RH environment for about 260 h.</p>	<p>3-point bend tests were carried out to determine the ILSS values of the carbon/epoxy and glass/epoxy laminates</p>	<p>Higher temperature during hygrothermal aging not only increases the moisture uptake rate but may also modify the local stress threshold required for delamination nucleation. Higher temperature acts like an activator of the diffusion of the water molecules through the composite. The less value of ILSS for almost the same level of absorbed moisture at higher temperature could be attributed to the pronounced degradative effect of temperature. The nature of damage at the interface due to temperature is irreversible. The interfacial adhesion in the carbon/epoxy and glass/epoxy composites is more affected by hygrothermal aging at higher conditioning temperature and for more exposure time (i.e., more absorbed moisture). The reduction in ILSS values is significant in both the systems for the same level of absorbed moisture at a higher conditioning temperature. It is not only the absorbed moisture but also under what conditions it diffuses into the specimen that characterizes the interfacial degradation phenomena.</p>		<p>88</p>
---	---	---	---	--	-----------

<p>E-glass fiber woven roving (FGP, RP-10) and epoxy adhesive (Ciba-Geigy LY-556 Araldite, HY-951 hardener)</p>	<p>The composite laminates were conditioned at temperature of 60C temperature and a relative humidity (%RH) of 95% for different lengths of time. The hygrothermally conditioned specimens were kept here at a temperature of -6C for 24 h.</p>	<p>3-point bend tests at each stage of absorbed moisture level for both types of conditioned (plain moist and frozen moist) specimens</p>	<p>Hygrothermal conditioning impairs the fiber/matrix interfacial chemistry, which plays a predominantly important role in determining the mechanical properties, especially the matrix-dominated one, of a polymer composite. Interlaminar shear strength (ILSS) is found to be affected by this conditioning and the greatest degradation occurs in the frozen state. A change in loading rate results in variation of failure modes. The lower value of ILSS at lower crosshead speed is due to higher ductility or failure strain of the epoxy resin.</p>	<p>89</p>
<p>Unidirectional CFRP and GFRP laminates. Epoxy resin CIBA LY 556 with hardener HT-972 was used as the matrix.</p>	<p>Specimens were soaked in salt water and distilled water for 120 h. Specimens were soaked at 313 K, 333 K and 353 K. The salt water solution was prepared by adding 30 g of sodium chloride to one liter of the distilled water, which gave a molar concentration of 0.5128 which is approximately the concentration of NaCl in seawater.</p>	<p>Specimens were cut from the laminates and were shaped according to ASTM DD695-77 for compression, ASTM D 790-71 for flexure and ASTM D 2733-70 for interlaminar shear test.</p>	<p>The degradation in compressive, interlaminar and flexural strengths is much more severe in salt water than in distilled water. The percentage weight gain is also higher in salt water for the same temperature and duration of immersion.</p>	<p>90</p>
<p>Glass-epoxy composite patch with the dimensions, width of 100 mm and thickness of 0.5 mm</p>	<p>(1) Ambient air (2) Water at 20C for 529 days (3) Water at 46C for 529 days (4) Water at 72C for 225 days</p>	<p>Tensile testing</p>	<p>Moisture absorption has a negative effect on the repair performance. The stress intensity factor increases with an increase in the water absorption in both mode I and mixed mode of crack propagation. The fatigue life of the repaired structures decreases with the</p>	<p>91</p>

			increase in water absorption by the composite patch.		
Carbon/epoxy composite	Conditioned specimens were kept in sterile-filtered seawater (SIGMA, S-9148) over thirteen months	Compressive tests were performed at a constant strain rate of 0.25%/s at atmospheric pressure (0.1 MPa) and hydrostatic pressures of 100, 200, and 270 MPa.	Seawater absorption of carbon/epoxy composite was approximately Fickian and seawater content at saturation was about 1.2% of the specimen weight. The compressive properties of seawater-absorbed carbon/epoxy composite underwent significant changes with increasing pressure. When the hydrostatic pressure increased from 0.1 to 200 MPa, the compressive elastic modulus increased about 10%. The modulus increased 2.3% more as the pressure increased to 270 MPa. Fracture strength and fracture strain linearly increased with pressure. Fracture strength increased about 28% and fracture strain increased about 8.5% as the hydrostatic pressure increased from 0.1 to 270 MPa. End-crushing and delamination cracks were primary fracture modes at all pressure levels. The number of delamination cracks was reduced with increasing hydrostatic pressure.		92
Glass fiber reinforced vinyl ester (Glass/VE) panels	Only one surface of each composite specimen is exposed to artificial seawater with salinity content of 2.9%.	Impact damage was introduced using a drop tower setup of an Instron test machine. The impacted samples were mounted in a compression-after-impact (CAI) fixture. Strain gages were attached on the back and front faces of the specimen to monitor the	Compression-after-impact strengths of the wet specimens reduced by around 10% compared to the baseline dry specimens over 29-month seawater exposure. The fiber/matrix interfacial bonding strength will reduce on exposure. Seawater absorption reduced the fiber-matrix interfacial strengths. Since the seawater damage is limited to a few outer plies of the whole composite laminate, the CAI strength will not reduce significantly after	Table 1 - Variation of compression-after-impact (CAI) strength with seawater exposure time.	93

		variations in strain during compression.	seawater saturation.		
Kenaf/woven glass hybrid composite	Specimens were immersed distilled water, sea water and acidic rain water. The specimens were immersed in 1 day, 1 week, 2 weeks, 3 weeks and 4 weeks at room temperature.	Fracture and tensile tests	The rates of the moisture uptake by the composites increases with immersion time and exhibit non-Fickian behavior. Exposure of the natural fiber composite material to environmental conditions such as distilled water, sea water and rain water results in decreasing of fracture toughness. The reduction of fracture toughness may be due to the water absorption characteristic and depends on the content of the fiber, fiber orientation, area of exposed surface, permeability of fiber, void content and the hydrophilicity of the individual component.		94
Glass chopped strand reinforced plastics	Specimens of the composite immersed in distilled water for 10 days to 1.5 years	Fracture toughness tests (acoustic emission signals were detected during the tests). Observation of fractured surfaces by SEM and the quantitative analysis of dissolution elements from glass fibers by an atomic absorption spectrophotometer.	The fracture toughness obtained by acoustic emission method decreases as the immersion time is longer. The decrease of the fracture toughness is caused by the degradation of the bonding interface between glass fibers and resin matrix and the weakening of glass fibers due to the dissolution of the elements into the water.		95

<p>Unidirectional glass fiber reinforced and glass-carbon fiber reinforced epoxy matrix composite</p>	<p>None</p>	<p>Tension-tension fatigue in air and in distilled water at 25 °C</p>	<p>No significant change in fatigue life for both types of specimens tested in air and in water when cyclically tested at 85% of average ultimate tensile strength (UTS). The detrimental effect of water becomes apparent at lower stress levels of 65 and 45% UTS. Cyclic loading in water results in shorter fatigue lives for both glass and hybrid specimens compared to specimens tested in air. All of the glass fiber specimens did not survive to 106 cycles when cyclically loaded in water. Hybrid specimens (with 25% carbon fiber (by volume), 75% glass fiber (by volume), 30% total fiber volume fraction) showed better retention in structural integrity under environmental fatigue, for fatigue lives up to 107 cycles, a consequence of the corrosion resistant of carbon fiber. Incorporating appropriate amount of carbon fibers in glass fiber composite yields a much better performance in fatigue for glass-carbon hybrid composite. Synergistic effect of the reinforcing fibers is critical in governing the fatigue behavior of intraply hybrid composite.</p>		<p>96</p>
<p>Carbon fiber reinforced vinyl/ester facings at different orientations</p>	<p>Long-term sea water soaking</p>	<p>Mechanical properties (modulus and failure stress) subjected to tension were evaluated at target orientations corresponding to lay-up configurations of [0/90]2S, [15/75]2S, [30/60]2S, [±45]2S, and [90/0]2S</p>	<p>A novel technique to obtain seawater induced strain was developed and moisture expansion coefficients of naval composites at different orientations are included to quantify its anisotropy.</p>		<p>97</p>

Glass-reinforced vinyl ester composite	Isothermal aging for period of 8 h at 25, 66, 93, 121, 149, 204, 260, 316C	Dynamic Mechanical Thermal Analysis (DMTA)	A significant drop in E' takes place between 200 and 250F followed by a catastrophic drop between 250 and 300F. Samples aged up to 150F for 8 h do not exhibit thermal damage and recover all of original structural performance. Beyond 150F and up to 400F, glass/vinyl ester samples begin to exhibit thermal damage. Load bearing structures exposed to 400F still retain up to 70% of original flexural properties. Beyond 400F, samples suffer significant thermal damage, and there is a loss of matrix resin viscoelasticity.	98
E-glass/vinyl ester composite in the form of unidirectional ribbon	Quasistatic to dynamic conditions in load control at room temperature, 80C, and 120C	Specimens were tensile tested. Strain rates of 10 ⁻⁶ and 1.6 s ⁻¹ were achieved. Elevated temperature was obtained with a feedback-controlled forced convection chamber.	There was an increase in both the ultimate stress and ultimate strain between room temperature and 80C. The modulus is nearly constant for the three temperatures investigated, except for a slight drop at 120C.	99
Unidirectional glass fiber reinforced thermosetting resin system comprised of 30 vo1.% glass fibers and Dow Derakane 470-36 resin	Creep test sequences conducted at different temperatures	All tests were conducted in tension	The creep of the composite is dominated by the creep of the resin. The compliance in the fiber direction is found to be independent of time and aging effects. Short-term creep data cannot be used to directly estimate long-term creep behavior without introducing large overestimates. Long-term creep proceeds at a much reduced rate relative to short-term creep because of the physical aging effect. Without physical aging, many glassy polymers could not be used to make load bearing structures.	100

			<p>Long-term creep behavior of composite was predicted from momentary creep results using the 'effective time' theory. The agreement between theory and experiment is within 5% error, though after about 200 h of creep it becomes less satisfactory.</p>	
Aramid/epoxy composite	<p>Some specimens were immersed in deionized water at 80C for 4, 7, 10 or 13 weeks. Others were kept in air (RH about 35%). Specimens were referred to as 4, 7, 10, 13-week wet and dry specimens, respectively.</p>	<p>Pull-out tests were performed using an electrohydraulic servo controlled fatigue testing machine.</p>	<p>Interfacial strength of aramid/epoxy composite was decreased by 26% after 7-week immersion time in deionized water at 80C. Interfacial strength was drastically changed between 4 and 7-week immersion time and showed plateau thereafter. The change of the interfacial strength with immersion time did not correspond with that of the water gain in pullout specimens. Due to degradation of fiber/matrix interfacial strength by water absorption, 7, 10 and 13-week wet specimens were fractured by adhesive failure with interfacial crack and the fiber surface looked smooth. For dry and 4 week wet specimens the crack propagated in the matrix and much more matrix was found on the fiber, compared to the 7, 10 and 13-week wet ones. The fiber fracture load decreased by 37% for 7 week immersion time and showed almost constant thereafter. The unit friction load decreased before 4-week immersion time and showed the plateau thereafter. The smaller interfacial normal compressive stress and the smooth fiber surface contributed to the small unit friction load in wet specimens. AE signals obtained during the pull-out process were classified into</p>	101

			4 types according to fracture modes. AE signals detected at final unstable crack propagation and fiber breakage had high amplitude and long duration.	
Pultruded vinyl ester/E-glass fiber composite	Specimens were immersed in charcoal filtered tap water where chlorine and minerals were removed and in a 3.5% NaCl solution to simulate freshwater and seawater environments at 65°C for 506 and 451 h, respectively, to reach 95% of saturation.	Fatigue experiments are conducted in a tension-tension mode in the unidirectional fiber direction with a minimum stress to maximum stress ratio value of 0.1. Maximum loads applied range from 35 to 65% of ultimate tensile strength, and frequencies are set at 2 and 10 Hz.	The loss in residual tensile strength and modulus in saltwater is approximately the same as that in freshwater. The fatigue life in aqueous environments is shorter than that in air. The fatigue model agrees well with the experimental data.	102
Glass fiber-reinforced epoxy matrix composites	Two resin systems were investigated for water absorption: matrix D cured with 22 phr isophoronediamine (IPD) and matrix E cured with 27.5 phr methyldianiline (MDA). Measurements were made at 23°C and a relative humidity of 100%. The specimens were exposed only to water vapor to minimize weight loss due to leaching.	Interlaminar shear strength was measured using the short beam shear test according to ASTM D-2344. Specimens, cut from the center of the composite rods with average dimensions 12 mm × 8 mm × 2 mm, were tested in the three-point bending test at a span-to-depth ratio of 5:1 and a temperature of 23°C.	The major factor influencing water uptake in glass fiber-reinforced epoxy composites was the composite void content. The type of matrix system, i.e. the nature of the curing agent, in particular the epoxy resin/curing agent ratio, also had an important effect on water uptake. The interfacial strength and the fiber surface coating have a smaller influence. Removal of the fiber surface coating had no effect on the kinetics of water absorption, despite the large detrimental effect on the interfacial strength. The density of the matrix is lowered by the presence of glass fibers because of the formation of an interphase region. Despite the obviousness of the influence of voids on composite water absorption, these results are the first to systematically show the magnitude of the effect.	103

<p>Two carbon-fiber-reinforced epoxy composites: G30-500/R922-1 and G30-500/R6376</p>	<p>Thermo-oxidative aging (177°C in air for up to 10000 h)</p>	<p>Comprehensive mechanical tests were performed to characterize various properties including 0° unidirectional and ±45° tension (ASTM D-3039), 0° unidirectional compression, ±30°/90°/90°, edge delamination, 45°/90°/-45°/0°, compression-after-impact, and 45°/90°/-45°/0° open-hole compression. Fracture tests were performed to measure delamination fracture toughness (critical strain-energy release rate) for mode I by using double cantilever beam (DCB) specimens, and for mode II by using end-notched flexure (ENF) specimens.</p>	<p>Compression-after-impact strengths dropped sharply during initial aging and then leveled off at longer aging time as extensive delamination induced other failure modes (e.g., transverse cracking and fiber breakage) to limit the damage zone growth. Degradation regions were close to composite surfaces or edges, indicating that the oxidative diffusion mechanism dominated the degradation process. Residual stresses arising from aging-induced differential resin shrinkage and interaction between plies of different orientations were found to have a strong effect on the degradation process for plies close to the surface and, especially, near free edges. Resin fracture toughness contributed to thermo-oxidative resistance by suppressing resin cracks which would create additional paths for oxygen diffusion.</p>		<p>104</p>
<p>Jute fiber reinforced polypropylene (PP) composites</p>	<p>Composite specimens were conditioned for at least 7 days at 20C and 50% relative humidity (RH). Some specimens were subjected to 40C water absorption tests and were later cooled to 20C in demi water for 24 h prior to testing. Some specimens were UV</p>	<p>Flexural properties were measured on a Zwick 1445 according to ISO 178. Charpy unnotched impact strength was determined using a Ceast pendulum impact tester according to ISO 179/ 1fU using an impact hammer of 4 J at a speed of 2.9 m/s.</p>	<p>Mechanical performance reduces gradually upon prolonged thermal loading and immersion in water. Bacteria, fungi, and garden mold grow easily on the compound material, but only have a limited effect on mechanical properties. Mechanical properties of jute-PP composites hardly decrease during an accelerated UV aging test.</p>	<p>Fig. 6 - Mechanical properties of 50 wt % jute-PP compound versus water absorption time. Fig. 7 - Mechanical properties of pure PP and 50 wt % jute-PP compound versus UV irradiation time.</p>	<p>105</p>

<p>Three-dimensional braided carbon fiber-epoxy resin composites</p>	<p>irradiated.</p> <p>The loaded and unloaded specimens were immersed in distilled water baths at 37C. During hygrothermal aging, the unloaded and loaded specimens were withdrawn at pre-determined time durations.</p>	<p>Flexural and shear strength testing</p>	<p>Absorption diffusion of 3D composites followed Fick's second law of diffusion. The resemblance between the 3D and unidirectional composites suggested that the complex structure of the 3D fabric did not change the moisture diffusion pattern. The 3D composites showed a lower diffusion rate. Under the application of tensile and compressive stresses, moisture uptake and equilibrium moisture content changed. Tensile stresses promoted moisture absorption while compressive stresses resisted, but to a lesser extent, the moisture absorption process. The change of equilibrium weight gain with tensile stresses was more significant than with compressive ones. A similar trend was observed in the change of flexural strength with external stresses. The mechanical deterioration of the composites was directly related to the moisture uptake level and the moisture diffusion mechanism remained unchanged under external stresses. The external stresses affected the matrix free-volume, propagation of matrix cracks, and interrupted moisture absorption along fiber-matrix interfaces. Tensile stresses enhanced matrix strain and induced matrix cracks, whereas compressive stresses hindered matrix free volume and slowed down crack propagation.</p>	<p>106</p>
--	--	--	---	------------

<p>Three-dimensional (3D) braided carbon/Kevlar/epoxy hybrid composite</p>	<p>Specimens were immersed in a bath of Hank's solution at $37 \pm 0.5C$ for up to 1700 h</p>	<p>Flexural and shear strength testing</p>	<p>The 3D braided carbon/Kevlar/epoxy hybrid composite exhibited Fickian diffusion behavior. No hybrid effects for characteristic parameters were found for the 3D braided carbon/Kevlar/ epoxy hybrid system. After aging in Hank's solution at $37 \pm 0.5C$ for 1700 h, the hybrid composite showed lower reductions in the flexural and shear strengths than the Kevlar-only composite but higher than the carbon-only composite. By hybridizing with hygroscopic Kevlar fibers, both moisture absorption and mechanical degradation were enhanced with respect to the carbon-only composite. Despite the mechanical degradation, the moisture-saturated hybrid composites still kept high flexural strength.</p>		<p>107</p>
<p>Three-dimensional (3D) braided carbon fiber-epoxy composites</p>	<p>Specimens were immersed in a bath of distilled water. The medium temperature was kept at $37 \pm 0.5C$, unless otherwise indicated.</p>	<p>Interlaminar shear test was performed on a CL/EP composite to measure the interlaminar shear strength according to national test standard GB 1450.1-83 Three-point bending fixture was chosen to test the flexural strength and modulus of the composites.</p>	<p>The 3D composites displayed a Fickian diffusion behavior during absorption and desorption processes. The difference in diffusion rate was observed between the 3D and unidirectional composites during adsorption, the 3D fabric showing a higher hindrance effect on moisture diffusion. During desorption, fiber structure did not show obvious effect on the diffusion behavior. Mechanical tests revealed that the 3D composites presented lower losses in mechanical properties suggesting the 3D composites possessed higher moisture resistance than the unidirectional ones.</p>		<p>108</p>

<p>Glass fiber reinforced epoxy resin composite (GF/CYD-128) laminates</p>	<p>The deep-sea environment was simulated through pressure vessels with nitrogen pressing system.</p>	<p>Seawater absorption data was obtained by weighing method.</p>	<p>The saturated seawater absorption of GF/CYD-128 laminates firstly decreases with the seawater pressure then increases with the increasing pressure. The saturated seawater absorption of GF/CYD-128 laminates decreases to the minimum value at the pressure of 2.5 MPa. The relationship between the saturated seawater absorption and the seawater pressure can be depicted by the quadratic polynomials. The seawater absorption behavior of GF/CYD-128 laminates at the deep-sea environment is non-Fickian, however, it can be simulated by the Langmuir-type model. The seawater absorption behavior of GF/CYD-128 laminates under the deep-sea pressure is successfully predicted by the Langmuir-type model.</p>		<p>109</p>
<p>Cyanate ester resin (Fiberite 954-2) and its IM8/954-2 composites, and a semi-crystalline thermoplastic (Fiberite ITX) and its IM8/ITX composites</p>	<p>Aging times of 0.67, 2.0, 6.0, 18.0, and 54.0 h were used for all creep tests. Tests were conducted at 140, 150, 160, 180, 190 and 200°C for the 954-2 based specimens and the IM8/ITX specimens.</p>	<p>Dynamic mechanical analysis (DMA) and tensile creep tests. Creep tests were conducted up to an aging time of 54 h with the logarithmic aging shift rate.</p>	<p>Creep test results indicated that the physical aging had a significant effect on the creep behavior of the 954-2 and ITX resin-based composite systems. As aging time increased, the creep compliance decreased consistently. Analysis indicated that an increase in a decade of aging time was approximately equivalent to a reduction of 4-5°C in test temperature for the cyanate ester polymer. In the case of the ITX polymer, an increase in one decade of aging corresponds to a 7-8°C decrease in the testing temperature. Experimental results indicated that at longer creep times the creep curve appeared linear on a log-log plot, indicating a power law relationship.</p>		<p>110</p>

<p>E-glass/vinyl ester quadriaxial composites</p>	<p>All samples were preconditioned by storage at 23°C and 55% RH for 3 months prior to the initiation of the exposure. 0-, 1-, 3-, 6-, 9-, and 12-month exposure in (1) 23°C and 55% RH conditions (2) Synthetic sea water prepared following ASTM D1141 and stored at 23°C (having a pH of 8.24) (3) Seawater collected from La Jolla shores at some distance away from the shore and stored at 23°C (and having a pH of 8.24) (4) Deionized water at 23°C (having a pH of 6.95)</p>	<p>Tensile tests (ASTM D3039) and interlaminar shear tests (ASTM D790) in the weft, or 0° direction. Thermal analysis of the sample to determine the glass transition temperature and viscoelastic response was conducted using dynamic mechanical thermal analysis (DMTA) between 23 and 250°C at a rate of 10°C/min and at a frequency of 1 Hz.</p>	<p>There are substantial differences based on the solution type, with deionized water immersion causing the maximum drop in interlaminar shear performance and seawater causing the maximum reduction in tensile performance. The maximum reduction in tensile strength after 12 months of exposure was in sea water at a level of 13.5%, whereas the minimum, 8.26%, was recorded for the case of cycling in seawater. The effect of cycling, simulating the tidal zone or the splash zone, is seen to be more pronounced in a resin-dominated response. Drying of specimens, even over prolonged periods of time, does not result in complete regain of performance degradation due to absorption processes.</p>	<p>Table 1 - Levels of Tensile Strength (MPa) as a Function of Exposure Type and Time Fig. 2 - (a) Comparison of change in tensile modulus due to immersion in different aqueous solutions. (b) Comparison of change in tensile modulus due to seawater immersion conditions. Fig. 3 - Effect of immersion on short-beam shear strength.</p>	<p>111</p>
<p>Pultruded unidirectional carbon fiber/vinyl ester resin (CF/VE) composite</p>	<p>Specimens were immersed in a 5% H₂SO₄ aqueous solution at 65°C and 95°C.</p>	<p>Moisture absorption and changes in the static and dynamic mechanical properties were measured.</p>	<p>At the early immersion stage in the solution, the moisture absorption behavior of the composite was similar to the Fick's second law. The storage modulus of the pultruded CF/VE composite decreased with the immersion time, while the loss factor (tan δ) increased. Increasing temperature worsened the effects. The decrease in the glass transition temperature, flexural strength and the interlaminar shear strength of the composite were related to the increase in the moisture content.</p>		<p>112</p>

Pultruded unidirectional carbon fiber/vinyl ester resin (CF/VE) composites	Composite specimens were immersed in distilled water and salt solution (3% NaCl) at 95 and 65°C for more than 1000 h	Three-point flexural and interlaminar shear tests. Dynamic mechanical thermal analysis (DMTA).	The fiber-matrix interface was weakened due to the invasion of moisture leading to debonding. Both flexural strength and interlaminar shear strength (ILSS) of the composite specimens deteriorated to some extent after hygrothermal aging, while stiffness was less affected. The glass transition temperature of the matrix underwent complicated changes, which was attributed to the combinational effects of plasticization and the formation of hydrogen bonds in the systems.		113
Pultruded carbon fiber/vinyl ester (CF/VE) resin composites	Exposure to distilled water, 3% NaCl aqueous solution, 5% H2SO4 aqueous solution, and 10% NaOH aqueous solution at 65C.	Dynamical mechanical thermal analysis (DMTA)	The loss factor ($\tan\delta$) of the composites in the four media increased to various degrees with immersion time, there being the largest degree of increase and a split in $\tan\delta$ in 10% NaOH aqueous solution. Glass transition temperature (T_g) of the composites decreases at various degrees in the four media at the early immersion stage, that tends to a constant except for decreasing with the farther prolongation of immersion time in 10% NaOH aqueous solution. When re-dried, T_g of the composites in distilled water, 3% NaCl and 5% H2SO4 aqueous solutions nearly recovers to the same as that before immersion, but is higher in 10% NaOH aqueous solution due to hydrolysis.	Fig. 3 - $\tan\delta$ curves of pultruded CF/VE composites before and after immersion in various media at 65C.	114
Unidirectional T300/934 graphite/epoxy composite	After conditioning at 80°C for 6 h, specimens were placed into distilled water chambers heated to constant temperatures of 45,	Specimens were weighed by using an analytical balance with 0.01 mg resolution, and the percentage weight change was determined. Moisture-induced	Water absorption in graphite/epoxy (T300/934) material exhibited both Fickian and non-Fickian diffusion behavior. Diffusion data showed that time for the onset of non-Fickian behavior was inversely related to the exposure temperature. Non-Fickian		115

	60, 75, and 90°C.	expansion of T300/934 composite was measured in length (fiber direction), width, and thickness directions. Optical and scanning electron microscopy were used to investigate surface modification associated with cracking, mass loss, and swelling.	behavior in the composite resulted from chemical modification and physical damage to the epoxy resin. No expansion due to water absorption was detected in the fiber direction dimension. Considerable dimensional changes resulting from moisture-induced expansion were observed in the width and thickness directions of the laminate. The thickness decrease of the specimen at high temperature was associated with surface resin dissolution and peeling. A crack/mass-loss model favorably describes the phenomenological behavior of graphite/epoxy composite resulting from water absorption processes. At a low exposure temperature compared to T _g , there is no surface dissolution or physical damage of the material and the weight gain behavior is Fickian. With increasing exposure temperature, cracks, voids, surface peeling, and dissolution occur. Cracks can retain water which contribute to absorption behavior higher than the theoretical Fickian diffusion curve. Surface peeling and dissolution contribute to reduction in the specimen weight and, consequently, the weight change profile data falls below the theoretical Fickian diffusion curve.		
--	-------------------	--	---	--	--

Glass-vinyl ester composite	Hygrothermal freeze-thaw cycling exposures. Cycling conditions used were 80°C/saturated steam/48 h and -17.8°C/dry/24 h.	Compression tests and thermal analysis	The degradation in compression strength for hygrothermally cycled composites was less significant than that of samples simply experienced isothermal holding at the same temperature and with the same exposure duration. Glass transition temperature of the composite increased with an increase in hygrothermal cycling duration and leveled off after about 1000 h of the exposure, while thermal decomposition temperature of the composite was only slightly influenced by the hygrothermal exposures.		116
Vinyl ester resin (VE) and carbon fiber composite (CF/VE)	Samples immersed in distilled water at 65°C and 95°C	Flexural strength tests	CF/VE absorption can be divided into 2 stages which are mainly affected by the resin and interfaces separately according to the absorption behavior of VE resin. During immersion the decrease of the flexural strengths of VE and CF/VE are consistent with each other. Flexural strengths are very relative to the increase of their moisture contents. The decrease of the flexural modulus of VE is more marked than that of CF/VE. Glass transition temperature of VE and its composite decrease with immersion time and become steady when their absorption reaches saturation, while the change of peak of their loss factor ($\tan\delta$) is just the opposite.	Fig. 1 - Moisture absorption curves of VE and CF/VE composite Fig. 2 - Mechanical property retentions of VE and CF/VE composite vs. immersion time Fig. 3 - DMTA $\tan\delta$ thermal graphs of the unimmersed and immersed VE and CF/VE composite in distilled water at 65C Fig. 4 - DMTA $\tan\delta$ thermal graphs of the unimmersed and immersed VE and CF/VE composite in distilled water at 95C Table 2 - Moisture parameters of VE and CF/VE composite	117

6. Recommendations

Indisputably, composites are an important and growing part of a great number of applications. In terms of their long-term performance, though, there is a remarkably low insight into the aging behavior of composites. This inadequate level of understanding has created an undeniable need for the development of overarching principles to better forecast composite behavior. Consider the case of strain rate sensitivity of nonmetallic composite materials under dynamic deformation. This process has not been well developed due to inadequate materials data and lack of constitutive equations.

One lofty obstacle to the advancement of composite aging knowledge is the relative scarcity of aging literature. Despite the number of articles referenced in this investigation, there has not been enough research conducted on this topic. Kootsookos claims to have been “one of the first reported studies to examine the effect of seawater immersion on the durability of these types of carbon fiber composite.” This is a relatively recent study⁶³ conducted in 2004, and the total count of similar studies emerging since then is disappointing.

Another hindrance standing in the way of progress is the daunting difficulty of sorting through the disorganized array of available results. As stressed throughout this paper, there is far too much variance in investigations, and an insufficient number of people have undertaken summarizing all this information. The research lacks cohesiveness. There was a lack of clarity in many graphs, and many studies did not make good use of numbers in explaining their results.

Clearly, the magnitude of the task of condensing all aging information is exceedingly great and complex. For that reason, the benefits of organizing information in an optimal manner are considerable. Minimal changes in organization can have large bottom-line impacts. It is

recommended that more future studies use test matrices, like the one found in McBagonluri, to tabulate their test procedures.⁷² This would reduce much of the ambiguity found in research on this topic. Similarly, it is recommended that future studies stick to standard procedures as much as possible. Future studies are also encouraged to summarize any results, such as changes in the static mechanical properties, using tables, as Tang et al. neatly does.¹⁰²

These suggestions seek to facilitate an understanding of the response of fiber-reinforced composite systems to the applied environment and thus serve as a precursor to the development of reliable analytical and prediction tools. These modifications would allow consolidation efforts of all these relevant data a much quicker and efficient. These modifications would allow a smoother union of all these relevant data. The given suggestions would allow consolidation of relevant data to be quicker and more efficient. Once synthesizing aging data was facilitated, testing and prediction software could be better developed to make future design more reliable.

7. Conclusions

Today, polymeric composites have experienced increased use in critical applications, particularly in the marine and infrastructure sector, where reliable performance is of utmost importance. This, in turn, necessitates a proper understanding of the effects of aging on these materials. This report, via resources provided by MIT, set out to survey the information that has until now been presented in many relevant studies.

Over the course of this survey, many materials were looked at; numerous different matrix-fiber combinations were considered. The matrices and fibers looked at included, but were not limited to, FRP-wood composites, isophthalic polyesters, epoxy resins, and aramid fibers. However, special emphasis was placed on thermosetting plastics and polymeric fiber-

reinforced composites. Of particular interest were composites with vinyl ester as the matrix reinforced with glass or carbon fibers. Different specimen preparations were encountered. Narasimha Murthy and McBagonluri used panels in their experimentation^{78,72}, whereas other studies, such as Banna and Gasem, used glass fiber reinforced pipe specimens^{9,34}.

The aging mechanism that samples were put through before testing was another point of variance. Of the articles that analyzed seawater exposure, salinity content ranged from 2.9 to 3.5%. In some cases, such as Gasem, the salinity of the simulated seawater was not mentioned³⁴. Immersion times ranged from 300 hours³⁴ with Gasem to over 2 years⁶³ with Kootsookos. Water uptake was generally measured by weighing the specimens upon retrieval from tanks,¹¹² as in the case of Yu et al.

Diverse testing procedures and parameters were explored. Some specimens were tested underwater; others were tested in air. Tests in air were at times conducted at different temperatures. Fatigue tests were common, often being conducted at a minimum-to-maximum load ratio of $R=0.1$ at frequencies of 2 Hz and 10 Hz. Flexural strength was often determined using the three-point bend test. Narasimha Murthy, Yu et al., and Gellert were a few of the many studies that conducted three-point bend tests according to the standard set by ASTM-D790.^{78,112,36} Tensile tests were oftentimes performed at strain rates in the neighborhood of 10^{-5} s⁻¹. The tensile fracture surfaces were examined for seawater degradation effect using scanning electron microscopy.

The grand variety of aging and testing methods naturally gave way to the development of an impressive pool of results. Data on the effects of the environments on the mechanical properties of composites strongly depended on the specific formulation of the resin and the processing techniques employed. Regardless, several correlations proved worthy of discussion.

There's no question that water immersion has significant aging effects on a polymeric composite. Overwhelmingly, evidence suggested that the material properties of composites decline over time. One of the earliest articles in the collection reported that the fatigue life of a chopped glass mat/polyester composite decreased with exposure to water. In this case, the resin debonded from the fiber after a short 40-day exposure to water at 51°C. Overall, flexural strength of composite specimens was observed to decrease with increasing time of immersion. Decreases in flexural strength were reported as great as 48%.⁷⁸ Haque reported the maximum degradation of failure stress and failure strains due to moisture absorption were approximately 8 and 12%, respectively for samples loaded in the fiber direction and thickness direction.⁴⁵ Roy Xu et al. reported the maximum compression after impact (CAI) strength reduction is around 10% after a 29-month seawater exposure.⁹³ This is much smaller than the 42% CAI strength reduction that was reported by Imielińska.⁵⁰ There are similar observations made by McBagonluri and Schultheisz.⁷² Typically, water uptake weakens the fiber-matrix interface, exposing the fibers. Subsequently, there are chemical interactions that occur due to hydrolysis and leaching. Some authors theorize that water breaks down the ester chain and diffuses into the matrix materials, leading to further degradation. SEM observations in Yu et al. revealed that water absorption caused heavy debonding of the matrix from fiber, resulting in degradation in flexural and interlaminar shear strengths.¹¹² It was also found that, in cyclic exposure to moisture, most of the reduction in strength is observed after the first cycle. Sample properties do not change much after that.

A common theme was also that composite materials experienced no further loss of strength beyond the point of saturation. This was supported in Gellert when the unloaded phenolic lost 25% of initial strength at saturation, with no further loss as immersion continued

from 200 to 800 days.³⁶ In Yu et al., the transverse flexural strength and interlaminar shear strength (ILSS) of the pultruded carbon fiber/vinyl ester composite decreased rapidly during initial immersion and then leveled off to constant values up to saturation.¹¹²

The permanent detrimental effects of aging remain inevitable. Yet, some composite materials, after aging, recover part of their strength. Findings in Yu et. al confirm that the ultimate retentions of the flexural strength and ILSS were of the order of 49 and 54% in distilled water, and 63 and 66% in salt solution, respectively. Haque, after temperature aging, reported that load bearing structures exposed to temperatures up to 400° F still retain up to 70% of their original flexural properties.

Moisture absorption is also seen to change the glass transition temperature of composites. When re-dried, the glass transition temperature of the composites in distilled water, 3% NaCl, and 5% H₂SO₄ aqueous solutions nearly recovers to the same as that before immersion, but is higher in 10% NaOH aqueous solution due to hydrolysis.¹¹⁴ Haque reported that physical interaction of moisture with the vinyl ester resin reduces the glass transition temperature from 121 to 118°C via plasticization and swelling.⁴⁵

It was also found that distilled and salt water affect composites similarly. No clear difference between their aging effects was observed. Salt water was reported by some to be more slowly absorbed, and Narasimha correlated higher levels of saturation with decreased strength.⁷⁸

All papers agreed that the physical mechanism for moisture absorption is generally observed to be a mass diffusion process followed by Fick's law of diffusion. The Fickian model was used to describe moisture absorption for pultruded CF/VE in Yu et al. In this same study, it was noted that temperature did not change the Fickian behavior of the composite.¹¹² However,

according to Gellert, the weight uptake plots indicate deviations from classical Fickian diffusion uptake for the polyester and vinyl ester GRPs with continuing uptake rather than a plateau at long immersion times.³⁶

All in all, it was observed that increasing temperature lowered the strength of composites, regardless of whether the sample was subjected to a sustained load during conditioning. Results from Haque show that the average strength degradation at temperatures close to the glass transition temperature is in the range of 9-13% for specimens loaded in the thickness direction and 20-25% for specimens loaded in the fiber direction, respectively.⁴⁵ According to Sorathia, between the temperatures of 150°F and 400°F, glass/ vinyl ester samples begin to exhibit thermal damage.⁹⁸

To fully address the urgent, pending, and hence risky issue of the long-term performance of composites, there is a clear need for the development of overarching principles that can better predict their aging behavior. But to do so, condensing all the observations from the myriad sources must become a simpler and easier process. It is recommended that more future studies use test matrices, like the one found in McBagonluri, to tabulate their test procedures.⁷² Future studies are also encouraged to summarize any results, such as changes in the static mechanical properties, using tables, as Tang et al. neatly demonstrates¹⁰².

The given suggestions would allow consolidation of relevant data to be quicker and more efficient. Once synthesizing aging data was facilitated, testing and prediction software could be better developed to make future design more reliable.

References

1. (2001). Polymer Glasses, Mechanical Properties of: Physical Aging of Polymer Glasses. In *Encyclopedia of Materials: Science and Technology*. Elsevier Science.
2. Abdel-Magid, B., Ziaee, S., Gass, K., & Schneider, M. (2005). The combined effects of load, moisture and temperature on the properties of E-glass/epoxy composites. *Composite Structures*, 320–326.
3. Alamri, H., & Low, I. (2012, December). Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites. *Materials and Design*, 214–222.
4. Alamri, H., & Low, I. (2013). Effect of water absorption on the mechanical properties of nanoclay filled recycled cellulose fibre reinforced epoxy hybrid nanocomposites. *Composites Part A: Applied Science and Manufacturing*, 23–31.
5. Alp, T., Alzaydi, A., & Shihata, S. (1990). The influence of environment on the strength of a ureaformaldehyde-based composite. *Plastics and Rubber Processing and Applications*, 187–96.
6. Apicella, A., Migliaresi, C., Nicolais, L., Iaccarino, L., & Roccotelli, S. (1983). The water ageing of unsaturated polyester-based composites: influence of resin chemical structure. *Composites*, 387–92.
7. Arun, K., Basavarajappa, S., & Sherigara, B. (2010). Damage characterisation of glass/textile fabric polymer hybrid composites in sea water environment. *Materials and Design*, 930–939.
8. Bank, L. C., & Puterman, M. (1997). Microscopic study of surface degradation of glass fiber-reinforced polymer rods embedded in concrete castings subjected to environmental conditioning. *ASTM Special Technical Publication*, 191–205.
9. Banna, M. H., Shirokoff, J., & Molgaard, J. (2012). Effects of two aqueous acidic solutions on glass reinforced vinyl ester resins tubes. *Canadian Metallurgical Quarterly*, 51(1), 91–100.
10. Baschek, G., Hartwig, G., & Zahradnik, F. (1999). Effect of water absorption in polymers at low and high temperatures. *Polymer*, 3433–3441.
11. Bishop, S. (1983). Effect of moisture on the notch sensitivity of carbon fibre composites. *Composites*, 201–5.
12. Boyd, S., Case, S., & Lesko, J. (2007). Compression creep rupture behavior of a glass/vinyl ester composite subject to isothermal and one-sided heat flux conditions. *Composites Part A (Applied Science and Manufacturing)*, 1462–72.
13. Brinson, L., & Gates, T. S. (1995). Effects of physical aging on long term creep of polymers and polymer matrix composites. *International Journal of Solids and Structures*, 827–846.
14. Buck, S. E., Lischer, D. W., & Nemat-Nasser, S. (1997). Combined effects of load, temperature, and moisture on the durability of E-glass vinyl ester composite. *42nd International SAMPE Symposium*.
15. Burks, B., & Kumosa, M. (2012). The effects of atmospheric aging on a hybrid polymer matrix composite. *Composites Science and Technology*, 1803–1811.
16. Cervenka, A., Bannister, D., & Young, R. (1998). Moisture absorption and interfacial failure in aramid/epoxy composites. *Composites Part A (Applied Science and Manufacturing)*, 1137–44.

17. Chiou, P., & Bradley, W. (1995). Effects of seawater absorption on fatigue crack development in carbon/epoxy EDT specimens. *Composites*, 869-76.
18. Chow, C., Xing, X. S., & Li, R. (2007). Moisture absorption studies of sisal fibre reinforced polypropylene composites. *Composites Science and Technology*, 306–313.
19. Cogswell, F., & Hopprich, M. (1983). Environmental resistance of carbon fibre-reinforced polyether etherketone. *Composites*, 251-3.
20. Collings, T., & Stone, D. (1985). Hygrothermal effects in CFRP laminates: strains induced by temperature and moisture. *Composites*, 307-16.
21. Cowie, J., Ferguson, R., Harris, S., & McEwen, J. (1998). Physical ageing in poly(vinyl acetate). 3. Structural relaxation and its effect on the stress relaxation modulus. *Polymer*, 4393-7.
22. Curtis, P., & Moore, B. (1983). The effects of environmental exposure on the fatigue behaviour of CRFP laminates. *Composites*, 294-300.
23. d'Almeida, J., de Almeida, R. C., & de Lima, W. R. (2008). Effect of water absorption of the mechanical behavior of fiberglass pipes used for offshore service waters. *Composite Structures*, 221–225.
24. d'Almeida, J. (1991). Effects of distilled water and saline solution on the interlaminar shear strength of an aramid/epoxy composite. *Composites*, 448–450.
25. Davies, P., Mazéas, F., & Casari, P. (2001). Sea water aging of glass reinforced composites: Shear behaviour and damage modelling. *Journal of Composite Materials*, 1343-1372.
26. Davies, P., Pomiès, F., & Carlsson, L. A. (1996). Influence of Water and Accelerated Ageing on the Shear Fracture Properties of Glass/Epoxy Composite. *Applied Composite Materials*, 71–87.
27. De La Osa, O., Alvarez, V. A., Fraga, A. N., & Martí, E. (2006). Loss of Mechanical Properties by Water Absorption of Vinyl-ester Reinforced with Glass Fiber. *Journal of Reinforced Plastics and Composites*.
28. Deniz, M. E., & Karakuzu, R. (2012). Seawater effect on impact behavior of glass-epoxy composite pipes. *Composites Part B: Engineering*, 1130-1138.
29. Deniz, M. E., Ozen, M., Ozdemir, O., Karakuzu, R., & Icten, B. M. (2013). Environmental effect on fatigue life of glass-epoxy composite pipes subjected to impact loading. *Composites Part B: Engineering*, 304-312.
30. Ellis, B., & Found, M. (1983). The effects of water absorption on a polyester/chopped strand mat laminate. *Composites*, 237-43.
31. El-Tayeb, N., & Gadelrab, R. (1996). Friction and wear properties of E-glass fiber reinforced epoxy composites under different sliding contact conditions. *Wear*, 112-17.
32. Faza, S. S., GangaRao, H. V., & Ajjarapu, S. (1993). Strength and stiffness degradation of fiber reinforced polymers under accelerated environmental conditioning. *International SAMPE Symposium and Exhibition (Proceedings)*, 1967-1977.
33. Fifield, L. S., Simmons, K. L., Laddha, S. G., & Kafentzis, T. A. (2010). Performance enhancement of compression molded kenaf fiber reinforced vinyl ester composites through resin additive. *International SAMPE Symposium and Exhibition (Proceedings)*.
34. Gasem, Z. M. (2007). Environmental Degradation of Flexural and Fracture Properties of Glass/Vinyl Ester Filament Wound Pipes. *Key Engineering Materials*, 501-504.

35. Gates, T., Veazie, D., & Brinson, L. (1997). Creep and physical aging in a polymeric composite: comparison of tension and compression. *Journal of Composite Materials*, 2478-505.
36. Gellert, E. P., & Turley, D. M. (1999). Seawater immersion ageing of glass-fibre reinforced polymer laminates for marine applications. *Composites Part A: Applied Science and Manufacturing*, 1259-1265.
37. Gentry, T., Bank, L., Barkatt, A., & Prian, L. (1998). Accelerated test methods to determine the long-term behavior of composite highway structures subject to environmental loading. *Journal of Composites Technology and Research*, 38-50.
38. Ghasemzadeh, S., Haddadi-Asl, V., Kajorncheappunngam, S., GangaRao, H., & Gupta, R. (2009). Dynamic Mechanical Study of Epoxy, Epoxy/Glass, and Glass/Epoxy/Wood Hybrid Composites Aged in Various Media. *Polymer Composites*, 1761-70.
39. Ghorbel, I., & Spiteri, P. (1996). Durability of closed-end pressurized GRP pipes under hygrothermal conditions. Part I: monotonic tests. *Journal of Composite Materials*, 1562-1580.
40. Ghorbel, I., & Valentin, D. (1993). Hydrothermal effects on the physico-chemical properties of pure and glass fiber reinforced polyester and vinylester resins. *Polymer Composites*, 324-334.
41. Gong, M., Wang, X., & Zhao, J. (2007). Experimental study on mechanical behavior of laminates at low temperature. *Cryogenics*, 1-7.
42. G'Sell, C., & McKenna, G. B. (1992). Influence of physical ageing on the yield response of model DGEBA/poly(propylene oxide) epoxy glasses. *Polymer*, 2103-13.
43. Guerdoux, L., Duckett, R., & Froelich, D. (1984). Physical ageing of polycarbonate and PMMA by dynamic mechanical measurements. *Polymer*, 1392-6.
44. Gustafson, C.-G., & Echtermeyer, A. (2006). Long-term properties of carbon fibre composite tethers. *International Journal of Fatigue*, 1353-62.
45. Haque, A., & Hossain, M. K. (2003). Effects of moisture and temperature on high strain rate behavior of S2-glass-vinyl ester woven composites. *Journal of Composite Materials*, 627-647.
46. Herzog, B., Goodell, B., Lopez-Anido, R., Muszyński, L., Gardner, D. J., Halteman, W., et al. (2004). The effect of creosote and copper naphthenate preservative systems on the adhesive bondlines of FRP/glulam composite beams. *Forest Products Journal*, 82-90.
47. Hu, H. W. (2007). Physical aging in long term creep of polymeric composite laminates.
48. Hu, H., & Sun, C. T. (2000). The characterization of physical aging in polymeric composites. *Composites Science and Technology*, 2693-8.
49. Hutchinson, J. M. (1995). Physical aging of polymers. *Progress in Polymer Science (Oxford)*, 703-760.
50. Imielińska, K., & Guillaumat, L. (2004). The effect of water immersion ageing on low-velocity impact behaviour of woven aramid-glass fibre/epoxy composites. *Composites Science and Technology*, 2271-2278.
51. Ishai, O., Garg, A., & Nelson, H. G. (1986). Hygrothermal effects on the mechanical behaviour of graphite fibre-reinforced epoxy laminates beyond initial failure. *Composites*, 23-32.
52. Janas, V., & McCullough, R. (1987). Effects of physical aging on the viscoelastic behavior of a thermoset polyester. *Composites Science and Technology*, 99-118.

53. Jones, C., Dickson, R., Adam, T., Reiter, H., & Harris, B. (1983). Environmental fatigue of reinforced plastics. *Composites*, 288-93.
54. Jones, F., & Mulheron, M. (1983). The effect of moisture on the expansion behaviour and thermal strains in GRP. *Composites*, 281-7.
55. Joshi, O. (1983). The effect of moisture on the shear properties of carbon fibre composites. *Composites*, 196-200.
56. Karalekas, D., Cugnoni, J., & Botsis, J. (2009). Monitoring of hygrothermal ageing effects in an epoxy resin using FBG sensor: A methodological study. *Composites Science and Technology*, 507-514.
57. Kasturiarachchi, K., & Pritchard, G. (1983). Water absorption of glass/epoxy laminates under bending stresses. *Composites*, 244-50.
58. Kenig, S., Moshonov, A., Shucrun, A., & Marom, G. (1989). Environmental effects on shear delamination of fabric-reinforced epoxy composites. *International Journal of Adhesion and Adhesives*, 38-45.
59. Khan, Z. (2011). Degradation of fatigue resistance of filament wound glass fibre reinforced/vinyl ester pipes exposed to aqueous environments. *Plastics, Rubber and Composites*, 397-401.
60. Kim, H. J., & Seo, D. W. (2006). Effect of water absorption fatigue on mechanical properties of sisal textile-reinforced composites. *International Journal of Fatigue*, 1307-1314.
61. Kim, H., & Zhang, J. (2001). Fatigue Damage and Life Prediction of Glass/Vinyl Ester Composites. *Journal of Reinforced Plastics and Composites*, 834.
62. Kootsookos, A., & Burchill, P. (2004). The effect of the degree of cure on the corrosion resistance of vinyl ester/glass fibre composites. *Composites Part A (Applied Science and Manufacturing)*, 501-8.
63. Kootsookos, A., & Mouritz, A. (2004). Seawater durability of glass- and carbon-polymer composites. *Composites Science and Technology*, 1503-11.
64. Lai, J.-Y., & Young, K.-F. (1995). Dynamics of graphite/epoxy composite under delamination fracture and environmental effects. *Composite Structures*, 25-32.
65. LeBlanc, J., & Shukla, A. (2011). Resp onse of E-glass/v inyl ester compo site panels to underwater explosive loading: Effects of laminate modi fications. *Internation al Journal of Impact Engineering*.
66. Lee, S.-B., & Rockett, T. (1992). Interactions of water with unsaturated polyester, vinyl ester and acrylic resins. *Polymer*, 3691-3697.
67. Levita, G., & Struik, L. (1983). Physical ageing in rigid chain polymers. *Polymer*, 1071-4.
68. Mahale, S., Rajamani, D., Revathi, A., Prakash, M., Srihari, S., & Rao, R. (2004). Hot-wet property characterisation of a high-temperature cured glass-epoxy composite in immersion environment. *Journal of Reinforced Plastics and Composites*, 1883-92.
69. Mahfuz, H., Zaman, K., Haque, A., Foy, C., Mohamed, H., & Jeelani, S. (2000). Fatigue life prediction of thick-section S2-Glass/Vinyl-ester composites under flexural loading. *Journal of Engineering Materials and Technology*, 402-408.
70. Marceau, C., & Hilaire, B. (1993). Thermal ageing of PMR15 polyimide matrix. *Polymer*, 2458-9.

71. Maurin, R., Perrot, Y., Bourmaud, A., Davies, P., & Baley, C. (2009). Seawater ageing of low styrene emission resins for marine composites: Mechanical behaviour and nano-indentation studies. *Composites Part A: Applied Science and Manufacturing*, 1024-1032.
72. McBagonluri, F., Garcia, K., Hayes, M., Verghese, K., & Lesko, J. (2000). Characterization of fatigue and combined environment on durability performance of glass/vinyl ester composite for infrastructure applications. *International Journal of Fatigue*, 53-64.
73. Miri, V., Persyn, O., Lefebvre, J.-M., & Seguela, R. (2009). Effect of water absorption on the plastic deformation behavior of nylon 6. *European Polymer Journal*, 757-762.
74. Miyano, Y., Nakada, M., & Sekine, N. (2004). Accelerated testing for long-term durability of GFRP laminates for marine use. *Composites Part B (Engineering)*, 497-502.
75. Monaghan, M., Brinson, L., & Bradshaw, R. (1994). Analysis of variable stress history on polymeric composite materials with physical aging. *Composites Engineering*, 1023-32.
76. Morii, T., Tomioka, S., & Hamada, H. (2011). Effect of water environment on jute/polypropylene composites. *Science and Engineering of Composite Materials*, 87-92.
77. Mouritz, A. P. (2012). Environmental durability of z-pinned carbon fibre-epoxy laminate exposed to water. *Composites Science and Technology*, 1568-1574.
78. Narasimha Murthy, H. N., Sreejith, M., Krishna, M., Sharma, S. C., & Sheshadri, T. S. (2010). Seawater Durability of Epoxy/Vinyl Ester Reinforced with Glass/Carbon Composites. *Journal of Reinforced Plastics and Composites*, 1491 .
79. Olmos, D., López-Morón, R., & González-Benito, J. (2006). The nature of the glass fibre surface and its effect in the water absorption of glass fibre/epoxy composites. The use of fluorescence to obtain information at the interface. *Composites Science and Technology*, 2758-2768.
80. Ozes, C., Kolat, K., & Naser, G. (2007). The effect of sea water exposure on the interfacial fracture of some sandwich systems in marine use. *Composite Structures*, 11-17.
81. Parvatareddy, H., Wang, J., Dillard, D., Ward, T., & Rogalski, M. (1995). Environmental aging of high-performance polymeric composites: effects on durability. *Composites Science and Technology*, 399-409.
82. Parvatareddy, H., Wilson Tsang, P., & Dillard, D. (1996). Impact damage resistance and tolerance of high-performance polymeric composites subjected to environmental aging. *Composites Science and Technology*, 1129-40.
83. Perreux, D., & Suri, C. (1997). A study of the coupling between the phenomena of water absorption and damage in glass/epoxy composite pipes. *Composites Science and Technology*, 1403-1413.
84. Phillips, M. (1983). Prediction of long-term stress-rupture life for glass fibre-reinforced polyester composites in air and in aqueous environments. *Composites*, 270-5.
85. Pillay, S., Vaidya, U. K., & Janowski, G. M. (2007). The durability of liquid molded carbon nylon 6 composite laminates, exposed to an aggressive moisture environment. *ICCM International Conferences on Composite Materials*.
86. Potter, R., & Purslow, D. (1983). The environmental degradation of notched CFRP in compression. *Composites*, 206-25.
87. Prian, L., Pollard, R., Shan, R., Mastropietro, C. W., Gentry, T., Bank, L. C., et al. (1997). Use of thermogravimetric analysis to develop accelerated test methods to

- investigate long-term environmental effects on fiber-reinforced plastics. *ASTM Special Technical Publication*, 206-222.
88. Ray, B. C. (2004). Effects of crosshead velocity and sub-zero temperature on mechanical behaviour of hygrothermally conditioned glass fibre reinforced epoxy composites. *Materials Science and Engineering: A*, 39-44.
 89. Ray, B. C. (2006). Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites. *Journal of Colloid and Interface Science*, 111-117.
 90. Rege, S., & Lakkad, S. (1983). Effect of salt water on mechanical properties of fibre reinforced plastics. *Fibre Science and Technology*, 317-324.
 91. Rezgani, L., Bachir Bouiadjra, B., Belhouari, M., Madani, K., Serier, B., & Feugas, X. (2010). Effect of composite hygrothermal aging on the SIF variation in bonded composite repair of aircraft structures. *Journal of Reinforced Plastics and Composites*, 3631-6.
 92. Rhee, K., Lee, S., & Park, S. (2004). Effect of hydrostatic pressure on the mechanical behavior of seawater-absorbed carbon/epoxy composite. *Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing)*, 308-13.
 93. Roy Xu, L., Krishnan, A., Ning, H., & Vaidya, U. (2012). A seawater tank approach to evaluate the dynamic failure and durability. *Composites: Part B*, 2480-2486.
 94. Salleh, Z., Taib, Y. M., Hyie, K. M., Mihat, M., Berhan, M. N., & Ghani, M. (2012). Fracture Toughness Investigation on Long Kenaf/Woven Glass Hybrid Composite Due To Water Absorption Effect. *Procedia Engineering*, 1667-1673.
 95. Sekine, H., Shimomura, K., & Hamana, N. (1987). Strength deterioration and degradation mechanism of glass chopped strand reinforced plastics in water environment. *Nippon Kikai Gakkai Ronbunshu, A Hen/Transactions of the Japan Society of Mechanical Engineers, Part A*, 684-692.
 96. Shan, Y., & Liao, K. (2002). Environmental fatigue behavior and life prediction of unidirectional glass-carbon/epoxy hybrid composites. *International Journal of Fatigue*, 847-859.
 97. Siriruk, A., & Penumadu, D. (2012). Effect of sea environment on carbon fiber vinyl/ester facing composites and anisotropy of sea water induced expansion. *International SAMPE Technical Conference*.
 98. Sorathia, U., & Dapp, T. (1997). Structural Performance of Glass/Vinyl Ester Composites at Elevated Temperatures. *International SAMPE Symposium and Exhibition Proceedings*, 1020-31.
 99. South, J. T., Reifsnider, K. L., & Case, S. W. (2001). Strain Rate and Temperature Effects on the Mechanical Properties of an E-Glass/Vinyl Ester Composite System. *Journal of Composites Technology & Research*, 189-96.
 100. Sullivan, J. (1990). Creep and physical aging of composites. *Composites Science and Technology*, 207-32.
 101. Tanaka, K., Minoshima, K., Witold, G., & Komai, K. (2002). Characterization of the aramid/epoxy interfacial properties by means of pull-out test and influence of water absorption. *Composites Science and Technology*, 2169-2177.
 102. Tang, H., Nguyen, T., Chuang, T.-J., Chin, J., Lesko, J., & Felix Wu, H. (2000). Fatigue model for fiber-reinforced polymeric composites. *Journal of Materials in Civil Engineering*, 97-104.

103. Thomason, J. (1995). Interface region in glass fibre-reinforced epoxy resin composites: 2. Water absorption, voids and the interface. *Composites*, 477-485.
104. Tsotsis, T., & Lee, S. (1998). Long-term thermo-oxidative aging in composite materials: failure mechanisms. *Composites Science and Technology*, 355-68.
105. van den Oever, M., & Snijder, M. (2008). Jute Fiber Reinforced Polypropylene Produced by Continuous Extrusion Compounding, Part 1: Processing and Ageing Properties. *Journal of Applied Polymer Science*, 1009–1018.
106. Wan, Y. Z., Wang, Y. L., Huang, Y., Luo, H. L., He, F., & Chen, G. C. (2006). Moisture absorption in a three-dimensional braided carbon/Kevlar/epoxy hybrid composite for orthopaedic usage and its influence on mechanical performance. *Composites Part A: Applied Science and Manufacturing*, 1480–1484.
107. Wan, Y., Wang, Y., Huang, Y., He, B., & Han, K. (2005, August). Hygrothermal aging behaviour of VARTMed three-dimensional braided carbon-epoxy composites under external stresses. *Composites Part A (Applied Science and Manufacturing)*, 1102-9.
108. Wan, Y., Wang, Y., Huang, Y., Zhou, F., He, B., Chen, G., et al. (2005). Moisture sorption and mechanical degradation of VARTMed three-dimensional braided carbon-epoxy composites. *Composites Science and Technology*, 1237-43.
109. Wang, C., Jiang, D., Zeng, J., & Xiao, J. (2012). Deep-sea water absorption behavior of glass fiber reinforced epoxy composite materials. *Fuhe Cailiao Xuebao/Acta Materiae Compositae Sinica*, 230-235.
110. Wang, J., Parvatareddy, H., Chang, T., Iyengar, N., Dillard, D., & Reifsnider, K. (1995). Physical aging behavior of high-performance composites. *Composites Science and Technology*, 405-15.
111. Wu, L., Murphy, K., Karbhari, V. M., & Zhang, J. S. (2002). Short-Term Effects of Sea Water on E-Glass/Vinylester Composites. *Journal of Applied Polymer Science*, 2760-2767.
112. Yu, Y., Yang, X., Wang, L., & Liu, H. (2006). Hygrothermal aging on pultruded carbon fiber/vinyl ester resin composite for sucker rod application. *Journal of Reinforced Plastics and Composites*, 149-60.
113. Yu, Y.-H., Wang, L.-L., Yang, X.-P., & Liu, H.-L. (2005). Aging behavior of pultruded carbon fiber/vinyl ester resin composite used for sucker rods in acid solution. *Beijing Huagong Daxue Xuebao (Ziran Kexueban)/Journal of Beijing University of Chemical Technology (Natural Science Edition)*, 53-56.
114. Yu, Y.-h., Zhou, T.-y., Wang, L.-l., Yang, X.-p., & Liu, H.-l. (2007). Effect of Environmental Ageing on Dynamic Mechanical Properties of Pultruded Carbon Fiber/Vinyl Ester Resin Composites. *Polymer Materials Science and Engineering*, 140-143.
115. Zhou, J., & Lucas, J. (1995). The effects of a water environment on anomalous absorption behavior in graphite/epoxy composites. *Composites Science and Technology*, 57-64.
116. Zhou, J., & Zhong, Y. (2004). Effects of hygrothermal cycling on properties of glass-vinyl ester composite. *Journal of Reinforced Plastics and Composites*, 483-490.
117. Zhou, T.-Y., Yu, Y.-H., Chen, W.-M., Wang, L.-L., & Yang, X.-P. (2006). Hydrothermal aging behavior of vinyl ester resin and its CF composite. *Gaofenzi Cailiao Kexue Yu Gongcheng/Polymeric Materials Science and Engineering*, 166-9, 174.