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FRP for Marine Application

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Abstract

Fiber Reinforced Plastics (FRPs) are widely used in marine sector owing to their high specific strength and resistance to marine corrosion. For naval application, additional advantages are transparency to radar wave and better vibration damping than metals. The use of various FRPs in off-shore structures and marine vessels needs analysis of desired properties considering the types of matrices and fiber. The common consideration is effect of sea water on the properties of the FRP. This chapter gives a brief on use of different FRPs in various areas such as off-shore pillars, Reinforced Cement Concrete (RCC) enclosures, primary and secondary marine components. A brief discussion is included here on diffusion models and estimation of durability by a time-temperature superposition principle applied to water ingress and corresponding change in mechanical strength of FRPs with examples. The effect of microbial activity on the damage of FRP is not very much reported in literature. It is known that sulfate-reducing bacteria (SRB) are the most damaging microbes for FRP. In conclusion, it is highlighted that vinyl-ester-based FRPs using glass and carbon fibers are best for marine application. To determine the realistic service life in marine environment, Vinyl Ester- FRP (VE-FRP) are to be simultaneously studied for damage due to sea water and the microbes such SRB.

Keywords: GFRP, CFRP, epoxy, unsaturated polyester, vinyl ester, marine environment, sea water diffusion, time-temperature superposition, life time, microbial activity, sulfate-reducing bacteria

1. Introduction

Use of Fiber Reinforced Plastics (FRPs) is rapidly expanding in all fields such as medical equipment, engineering plants, packaging, transportation, aviation, space technology, building construction, heavy vehicles, and defense forces. Application of FRPs in marine construction industry is also not new and ever increasing with rapid advancements in exotic fibers, nanoparticles, and special polymers. For engineering application, principal requirements are inherent strength and a defined temperature limit up to which the strength is sustained to the desired level. The secondary requirements are high toughness, resistance to cyclic fatigue, low creep, low relaxation, environmental stability, and ease of joining and maintainability. The third most important factor is investment cost and processing cost. So far as mechanical strength is concerned, the Elastic Modulus in all modes and ultimate strengths are important. However, too stiff composites lack toughness, which often cause premature brittle failure. It has to be a tread-off between ultimate property and elastic modulus for restricting strain on the one hand and sustain low/high cycle fatigue on the other hand. The toughness imparted by flexible long-chain resin matrix results in high creep and relaxation, which are undesirable for engineering

structures but improve the fatigue life. Inclusion of rubbery moieties in a stiff matrix may result in phase separation and stress concentration at the interface and may cause premature failure. Toughening by nanoparticles, such as functionalized carbon nanotubes and reduced graphene oxide and derivatives, are being actively researched at present with apparently encouraging results. Detailed study of creep and stress relaxation of CNT-polymer or graphene-polymer composites is not done yet in a comprehensive manner, but with a general understanding, it is expected to be even better than the pristine polymer.

Thermal properties are more extensive, since the thermal agitation of polymers undergoes very drastic rise beyond a characteristic temperature called glass transition, where the stiff polymer transforms into a rubbery soft material. For polymers with partial crystallinity, flow takes place at further enhancement of temperature, and finally, a polymer starts to decompose at even higher temperature. A design of structural element then has to depend on the limit of temperature at which the modulus starts decreasing. Ideally it should be glass transition temperature. However, in practice, dynamic mechanical analysis shows that the modulus decreases even about 10–15°C below the glass transition. The extreme hazards of heat for an organic polymer (and FRP) are the fire propagation and evolution of toxic gases. The fire-retardant additives both as physical addition and chemical modification of resins are widely used and are also currently being researched in the light of possible benefits of nanoparticle reinforcements.

Marine application both for static off-shore structures and sea-going vessels needs robust and durable FRP composites, which can compete well with metals in terms of specific strength, durability, and cost-effectiveness. The replacement of a metal requires some special properties in FRPs apart from strength and degradation. One of the most difficult solutions is joining the Thermoset FRP elements since the joint should be almost similar in mechanical strength and toughness. Identical thermoset as the FRP element is best preferred, with a short fiber dough molding system that must be cured at ambient, yet provide acceptable joint strength. There can be special drilling technique for joining through riveting using the dough as rivets. Thermoplastics can be “welded” by melt joining as metals, most suitable for particulate reinforced composites and short fiber composites. The second and very important property of an FRP to qualify marine standard is effect of sea water aging considering all the chemical and biological adversaries of the sea. This single factor mostly decides the design and service life of a marine-grade FRP structure.

Although marine corrosion of FRP is not so severe as for steel, the FRP structures and underwater hulls need to be protected from bio-fouling. With the advancement of anti-fouling coatings, it is possible to protect a hull for minimum 3 years without any maintenance painting. Modern low surface energy foul release coatings based on silicones and fluoro-silicones are environment-friendly as they do not release toxins in the sea. These are non-depleting coatings and hence can have higher service life. However, These types of coatings are more effective for high-speed boats.

2. FRP components in marine vessels

The different elements of a ship can be defined as primary, such as superstructure, hull, SONAR Dome, bulkhead, decks, propeller shafts, masts, doors, hatches, machinery foundations, support frames, etc. Secondary items are rudder, pipes, valves, ladder, stanchions, guard rails, etc.

In naval vessels, three important advantages of using FRP composite are (1) ability to damp vibration, thereby reducing the radiated noise in the sea. In addition, FRPs are acoustically transparent, hence reduce the acoustic reflection (2)

FRPs without carbon or conducting material inclusions are radar transparent. These two features enhance the stealthy character of a battle ship and submarine and importantly (3) most common reason is no corrosion of FRP in sea water and saline atmosphere.

The most used application areas for FRP in ships are superstructure and bulk-head, where thick FRP panels are used with flap joint overlapping at the corner to flush the sides. Riveting with composite rivets can be done along with interface adhesion using a hand layup of fabric with resin so that the joint is sufficiently strong.

Vibration and fatigue are other important aspects. Machinery and propeller movement cause vibration of the hull and hull-mounted SONAR dome, which adversely affect SONAR performance and also results in fatigue. Normally, the fundamental frequency of machinery and propeller is up to 34 Hz, and prominent modes are up to about 200 Hz. Also, slow cycle fatigue results from sea waves, which is approximately 0.8 Hz. It is well known that slow cycle fatigue is quite important to decide the service life for steel hulls and is expected to have similar effect on FRP hull. Till now, there is no such detailed study on fatigue at various frequency envelopes for marine FRPs, which are actually exposed in sea water with vibrations.

2.1 FRP hull

Hull construction using FRP is very common for speed boats, small to medium size (8–80 m) patrolling boats, research ships for acoustic and underwater mapping studies, coastal ships, corvettes, etc. [1–4]. A very comprehensive list of literature is given by Galanis [3] in his M.S. thesis. One very interesting naval ship is mine countermeasure vessel (MCMV) which is about 60 m long [1]. MCMV uses passive magnetic sensors to detect underwater mines, which use a magnetic sensor to trigger the mine. Therefore, the ship as such should not have any magnetic signature. Conventional hull material of MCMV is nonmagnetic steel. However, FRP is preferred because of lightweight and corrosion-free nature in addition to nonmagnetic character. Miller [4] reported one such MCMV of Royal Navy (U.K.) made of GFRP way back in 1973 and a bigger one (60 m long) in 1980s. FRP is being used since World War II by the United States in noncritical areas and small boats [2]. Till now, large commercial or Naval ships such as Frigates, etc., are not made with FRP. The FRP hull of ships of 60–80-m size is a sandwich construction with thick FRP skin and a foam core. Thickness of the FRP skin on both sides of the foam core can be 8–10 mm each, and the foam core can be 50–80 mm thick. Previously PVC foam core was very common. However, with the large variety of polyurethane foam available today, even fire-retardant type including polyisocyanurate-modified polyurethane [5], the scope and ease of foam filling in between two hull panels have facilitated production system, and also large seamless foam core is easily made by foam spray machine.

Generally, unsaturated polyester made with isophthalic acid and neopentyl glycol and epoxy-based vinyl ester resins is widely used for marine boats and ship hull. Both of these resins are cross-linked by styrene monomer to form a thermosetting polymer.

FRP hull of boats of maximum 8 meters contains six types of fiber and fabric layers arranged in a sequence and requires minimum 25 layers of reinforcing mats and fabrics. The different fiber-based layers are random chopped strand mat, 300–450 GSM, woven roving mat 400–600 GSM, fabric of different thicknesses (approximately 0.25 mm), core mat of 1 mm and 3 mm thickness, and a 1 mm skin layer of the resin with particulate fillers (titanium dioxide, aerosil, barytes, etc.). Aerosil (fumed silica) is used with the resin to make it more impermeable to water. However, aerosil makes the resin somewhat thixotropic. Due to large size, and to

make seamless hull, wooden mold is first made, and hand lay-up technique is used for fabrication. In an elaborate arrangement, vacuum bagging or vacuum-assisted resin infusion can be used for at least small boats. Vacuum-assisted molding can make composite with about 70% fiber and 30% resin, which is obviously advantageous for strength.

2.2 SONAR dome

A special application of naval ships, submarines and fishing vessels is SONAR dome, which houses the arrays of acoustic transmitting and receiving transducers for detection of underwater objects. Conventionally titanium is used to make sonar domes due to its fair acoustic transparency, high strength-to-weight ratio, and good resistance to sea water corrosion and bio-fouling. However, acoustic impedance of titanium is not as close to that of sea water compared with glass-fiber based FRPs. Therefore, titanium domes are less efficient in underwater acoustic transmission and have underwater acoustic reflectivity more than FRP. For naval vessels such as submarines and battleships, FRP SONAR domes are being used in some countries, for example, the United Kingdom France, Sweden, Australia, Holland [1–3]. Such SONAR domes are very critical with respect to high drag force, compressive stresses at high depth in sea for submarines, and requirement of high acoustic transmission characteristics. The thickness of the dome is decided by the strength and modulus of the FRP, but higher thickness results in loss in acoustic transmission power. Therefore, the design and fabrication of an FRP dome are very critical and are done using Finite Element Method (FEM) so that the dimensional features, strain levels at different sections, and maximum stress can be somewhat accurately determined for both static and dynamic conditions. A prediction of acoustic transmission can also be done using general acoustic attenuation theories. Fabrication method can be very important, so that the dome would have nearly same theoretical strength and dimensional accuracy with acceptable tolerances. Among many possibilities, resin film infusion technique or vacuum-assisted resin infusion can be adopted to make the domes with precise dimensions, strength, and flawless integrity. The thickness of such domes can vary from 20 mm to 80 mm depending on the size. The vacuum process has two advantages, (1) the high fiber content resulting in high strength and (2) nearly zero air gap/ flaw in the composite. The air gap is undesirable in sonar dome since any such air bubble would increase acoustic reflection, thus reducing the acoustic transmission across the dome thickness. The aspect of sea water diffusion and corresponding loss of strength, lowering of glass transition, and deterioration of acoustic transparency are main consideration of its long usability and depend on both material and fabrication process. Commonly used fabric is E-glass and S-glass while the resin can be a hybrid of vinyl ester and epoxy resin. For the purpose of enhancement of strength, carbon fibers are preferred over glass fiber, since a carbon fabric-epoxy FRP would have Young's modulus of nearly 70 GPa compared with GFRP of about 30 GPa.

Recently aligned carbon nanotube containing GFRP domes are being considered for mid-frequency acoustic application to reduce the thickness of the dome and to impart better structural vibration damping.

2.3 Secondary marine components

Of the superstructural components, carbon fiber-epoxy combination is best, provided there is no necessity of radar stealth features. However, carbon fiber-epoxy composites are used in cabinets and covers of power electronics in ships and submarines for EMI shielding purpose.

Composite pipe can be made using a combination of prepreg lay-up on a mandrel followed by filament winding technique. This fabrication method can give sufficient Hoop Stress. A best possible fiber alignment in subsequent layers on the mandrel is determined by a stress-strain analysis by FEM method. Resin pick-up by the fiber strands in automatic winding method is minimized by two doctor's blades fixed on the fiber running line as one of the guide systems for the strands before winding onto the mandrel. Autoclave curing at high pressure and temperature can be adopted for such pipes.

Composite valves are made by dough molding compounds because of intricate dimensional requirement to make them leak-proof. Pipes and valves are special among all items because the fluid pressure (Pascal's pressure) in most commercial ships is designed for 12 bar, and for Naval standard, it should be 20 bar with continuous use and should withstand maximum 30 bar pressure for 24 h. This stringent requirement makes the fabrication method very critical, for example, the surface of the pipe must not "sweat" at high hydrostatic pressure and circularity and movement of the ball in a Ball valve must be very precise to avoid leakage of liquid, besides resistance to the "sweating." The processing and fabrication with dough molding compounds are best done by application of high pressure of 1–3 MPa to eliminate excess resin and to ensure compactness with precise dimensional tolerance and without layer gaps or air entrapment. Vacuum application is not beneficial since the dough, containing 20% short fiber, would have very poor flow property. Instead, kneader mixing can produce dough without air entrapped in the green dough. The molds are made with die steel for high-pressure molding.

The elements that are used on board such as ladder, stanchion, and guard rails are critical due to shape and require high-impact energy to resist crack or breakage on impact. Hence, a method of flexibilizing or nanoparticle reinforcement must be attempted to improve impact energy of common reins. As an example, a common epoxy thermoset Glass FRP has an impact energy of 750–850 J/m (Charpy impact), while a modified epoxy-Glass FRP would have 1300–1500 J/m, which may qualify the impact requirement. The strength must not be compromised too much. A maximum 10% reduction for the FRP could be accepted by a designer to prefer a flexibilized resin matrix. For such small and shaped components, hand lay-up of fabric and resin or prepreg lay-up in metallic mold can be adopted. High compression would be beneficial to eliminate any flaw, air gap, and better compactness. In these on-board components, carbon fabric prepregs cannot be used in naval vessels since carbon-based composites increase radar signature.

3. Off-shore structures

Off-shore marine structures such as oil rigs and columns of bridges, underwater pipe line supports, etc., are conventionally made using reinforced cement concrete having steel rods as reinforcements inside the concrete. In some other cases, steel pipes, pillars, and column supports are used.

The underwater static steel structures are protected from corrosion and fouling by electrochemical protection system and paints. A new method of protecting the steel structure is to provide a wrap of composite as an outer lining, which is far more durable than painting and more maintenance-free. Steel pipes are used as a mandrel for a filament winding technique to provide a composite lining. Steel structures require underwater welding, etc., for repair and maintenance, which is very complicated and costly. The FRP lining provides a very convenient solution to reduce such maintenance cost and frequency of repair.

The concrete with diffused sea water generates more alkali, and the pH of this alkaline seawater increases from normal range of 8–8.3 to about 12–13 and

accelerates the corrosion of the steel reinforcement in the RCC structure. Therefore, FRP reinforcements are modern way of construction for higher durability and lesser maintenance. However, in a higher alkaline sea water environment, the FRP degradation is expected to be faster than in normal sea water.

For off-shore and maritime civil engineering structures, carbon fiber composites (CFRP) are preferred over glass fiber (GFRP) because of higher mechanical strength of CFRP. In addition, sea water uptake and degradation of GFRP in sea water are higher than those in CFRP. There are very few applications of GFRP in marine structures despite the fact that GFRP is cheaper compared with CFRP.

The durability is also dependent on the resin type and its interface bonding with the fiber. Generally, thermosetting polymers such as epoxy, polyurethane, phenolic resin, vinyl ester, and unsaturated polyester resins are used for composites. These resins and corresponding composites are to be evaluated for long period of sea water exposure in an RCC construction for durability. As accelerated studies might give some extrapolated figures of service life, but such studies cannot determine the effect of microorganisms on degradation of a composite. A very common example is sulfate-reducing bacteria (SRB) in the sea water. These organisms use sulfates dissolved in the sea (for example, MgSO_4) for metabolism and produce hydrogen sulfide, which is highly corrosive to metals and may also increase the degradation of composites after settling onto the surface. The effect of such organisms is much more important for static structures rather than moving objects. Fouling by other micro and macro-organisms and subsequently the effect on the composite is another aspect of static structures. The protection from bio-fouling by application of anti-fouling coating is another subject of study. However, this type of coatings work either on toxin release mechanism or by providing a low surface energy coating. In case of toxin release coating, the toxin release depends on the hydrolysis and dissolution of the toxin in water, which is more effective in moving condition than stagnant water. Because of toxin depletion, the coating requires renewal after a certain time, mostly 3 years. In case of low surface energy coating, the effectiveness is far less for static structures, as this type of coating is quite good for moving objects, that too at certain minimum speed. However, the advantage is that the settlement of bio-fouling species on these low surface energy coating is very weak and can be removed by a soft cleaning mop. The second most important aspect of static structures is stress. Most supports and beams are under stress, small or large. The pre-stressed composite structure may have lesser service life compared with no-stress elements. The third consideration is fatigue. A bridge column, pipeline carrying liquids under the sea are subjected to vibrations. Hence, the composite elements are to be evaluated by fatigue for a predetermined frequency and number of cycles. This should be done in a repeated experiment and at a regular immersion period. The effect of pre-stress and vibration parameters may reveal some results, which could be different from normal static experiments.

4. Quality of a marine-grade resin and FRP

A general understanding of large-scale application of FRP is that there can be three main alternatives for a techno-commercially viable thermoset selection, e.g., (1) unsaturated polyester resin (USP) cross-linked with styrene, (2) vinyl ester resin (VE) cross-linked with styrene, and (3) epoxy resin cross-linked with amine. Whereas, there can be two common fibers such as glass and carbon.

Service life of a structural element for marine vessels has to be minimum 25 years for reducing the investment for replacement and should be maintenance-free for at least 8 years to reduce the cost of refits in drydocks. For off-shore

structures, where FRPs are used to make barrier for underwater cement concrete structures, the maintainability is even more difficult, requiring high service life without maintenance activity. Apart from the general physical and mechanical properties, an FRP for marine application must have additional characteristics of low moisture/sea water ingress, minimum hydrolysis, good bond strength between fiber and polymer, minimum physical damage of fiber and polymer due to water ingress and retention of mechanical properties even after prolonged sea water immersion. However, all the properties are primarily dependent on the matrix polymer and fiber and their interaction, secondary parameter being processing technique and fabrication methods to make flawless FRP components with fairly accurate dimensions, such as for a marine ball valve or pipe joint. Processing assumes larger importance since partially cured samples are prone to poorer physico-mechanical properties and higher degradation in water.

A significant improvement in properties of marine composites can be achieved by prepreg method and resin transfer molding (RTM) assisted by vacuum. Good compaction and high fiber volume fraction can be achieved by these processes. The process of prepreg molding is feasible where the resin-hardener reaction does not take place at ambient or storage temperature, and the curing is done at a fixed higher temperature. There are high-temperature reacting systems such as epoxy resin 4,4'-methylenedianiline tetraglycidyl ether (TGDDM), to be cured with hardener such as 4,4'-diaminodiphenyl sulfone (DDS), modified polyamines, etc., which are used for making prepreps. The shelf life of such prepreps at storage temperature of -20°C is about 10–12 months, but few weeks at 20°C . The prepreps are cured in compression at above 100°C . However, prepreg system may not be possible for vinyl ester or polyester resins. RTM process requires low viscosity resin and hardener to facilitate good flow in the fabric stacked in the mold for proper wetting at all corners and contours. Trujillo et al. [6] reported the properties of RTM processed composites based on three common resins, i.e., epoxy, vinyl ester, and unsaturated polyester with glass and carbon fabrics. The flexural modulus of the glass composites was about 40 GPa and about 110–120 GPa for carbon fabric composites, while the flexural strengths were seen to be in the range of 600–800 for glass composites and 1300–1400 MPa for carbon fabric composites.

Sea water absorption causes changes in the matrix by both plasticization and hydrolysis. Initial effect of water ingress is a plasticizing effect and swelling of the polymer matrix. The results are lowering of glass transition temperature due to plasticization and a possibility of debonding of the polymer-fiber interface due to swelling of the polymer. The initial effect of water ingress also causes hydrolysis of the fiber sizing and generates alkali (Na^+ and K^+) and the Fiber-polymer interface weakens. All these events result in reduction of ultimate strength and elastic modulus of an FRP.

On prolonged exposure, several chemical reactions may take place, such as hydrolysis of the polymer resulting in small molecules such as glycol, chain breaking, and release of low-molecular-weight polymer (especially polyester), release of the constituents of the resin (typically maleic/fumaric acid), release of styrene (cross-linker for polyester and vinyl ester), and extraction of these species from the FRP to the sea water. Prolonged water immersion of FRP may also cause mechanical damage to the fiber and polymer both, which may not be observed in short period, even in few months of exposure. SEM analysis of all FRPs irrespective of the fiber showed detachment of matrix from the fiber, which is the main reason for such drastic decrease in strength of the composite laminates as reported in literature.

The polymer plays the most important role in the hydrolytic durability of an FRP. As a special case of glass fiber reinforcement, the coated material used as coupling agent chemically degrades and causes weak interface of fiber-polymer.

Therefore, a polymer-fiber combination is ultimately the consideration for optimization of hydrolytic properties.

The main reason why GFRP is not used in maritime civil construction applications is because sea water environment degrades the long-term mechanical properties of GFRP composites and interlaminar shear strength (ILSS). The glass fiber-polymer interface is strengthened by a coupling agent coated on the glass fibers and the process is called "Sizing." The sizing formulations are very complicated, may contain many different chemicals, and are proprietary to the manufacturers [7]. Most common are γ -amino propyl tri ethoxy silane (APTES), γ -glycidoxy propyl trimethoxy silane (GPTMS), γ -methacryloxy propyl trimethoxy silane (MPTMS), and vinyl tri ethoxy silane (VTES) having Si-OH groups on the fiber surface for improving the interface adhesion with the resin. The sea water diffused to the interface of fiber and polymer very quickly degrades the glass to produce alkaline oxides unless protected by sizing. Even then, prolonged immersion of the GRP with fiber with appropriate sizing may cause leaching of alkali oxides (sodium and potassium) from the surface of the fiber and degrade the composite mechanical property [8].

4.1 Epoxy thermoset-based FRP for marine application

Epoxy resin is a versatile thermoset, widely used in many marine structures for many years. It has good mechanical properties, is highly polar and compatible to most fibers including metals, glass, carbon, Kevlar, and polybenzimidazole. Epoxy nanocomposites are gaining importance due to lightweight and high performance in some functional properties when used with carbon nanotubes, nanofibers, graphene, and also natural nanofibers. The conventional epoxy resin thermosets are somewhat brittle and, in many occasions, modifications are done either by physical mixing or chemical reaction onto the epoxy oligomer or use of high-molecular-weight epoxy and/or the amine curing agent to make optimum tough thermoset. However, flexibilization means increase in free volume in the polymer and subsequent increase in moisture absorption. As such the degradation of conventional epoxy thermoset and composites is very widely studied by many researchers since last 45 years, for example, by Augl and Berger [9] in 1976 on carbon fiber-epoxy composites, McKague et al. [10], Delasi and Whiteside [11], and Whitney and Browning [12] studied moisture diffusion in epoxy matrix and composite, during 1976–1978, to name a few. Similarly, Loos and Springer [13], Bohlmann and Derby [14], Shirrell [15] studied moisture diffusion and its effect on graphite epoxy composites way back during 1976–1979. Glass fiber-epoxy composites are most widely evaluated for effect of moisture or water or sea water absorption from those periods and are still being the subject of study. A few are listed here as references [16–30].

The glass transition temperature of cured epoxy matrix and composites is reduced from 120°C to as low as 66°C on a 2-month sea water exposure, but was observed to be almost constant around 85–88°C from 4 months onward till the end of the study period (12 months), as reported by Chakraverty et al. [31]. The authors explained this anomaly by probable osmotic effect of the bulky molecules of dissolved salts in sea water, which might have initially facilitated the creation of more free volume in the cross-linked epoxy matrix, but on prolonged exposure, deposition of these salts could have reduced the water ingress. Murthy et al. [32] have shown that the water uptake by epoxy-glass composite is more (about 0.9%) compared with 0.7% by epoxy-carbon composites after 12 months and remained unchanged. However, their study was limited to 16 months. The ILSS was reduced by 38% for epoxy-carbon and by 31% for 450 days at ambient temperature. SEM analysis revealed that the moisture penetration along the fiber/matrix interfaces

caused interfacial debonding and consequently degradation of the interface. Espinel et al. [28] also showed that for an epoxy-glass composite, the saturation level of sea water was 0.4% at 25°C attained after 30 days. The tensile and flexural strength reduced by about 24% and 35% respectively after 90 days sea water immersion at 25°C, but observed that the strength did not decrease much after saturation of sea water. Contrary to these results, Murad et al. [25] showed that the sea water intake in epoxy-glass unidirectional composite was 2.5% after 12 months, but the strength and elastic modulus had no noticeable change compared with fresh sample. However, the fiber volume % was only 52. Wood and Bradley [20] also reported about 2.2% sea water uptake for 5 months at ambient temperature for an epoxy-glass-graphite hybrid composite, each layer fabricated by a similar process as filament winding, and hence the layers were unidirectional. The glass and carbon were in transverse direction to each other. However, the resin used had a 5% flexibilizer (rubber) and fiber volume % was 60. Komorek et al. [29] used fabrics of glass and carbon in epoxy resin. The bending strength was found to be 8% less for the samples immersed for 36 days at 15°C in sea water.

A unique study on fatigue and sea water aging of epoxy-glass and epoxy-Kevlar composite was done by Menali et al. [33]. The authors studied the effect of sea water (artificial) immersion (40 days) after fatigue for 100–50,000 cycles for these composites. There was about 19% reduction in tensile strength for the Glass-epoxy composite samples and about 15% for Kevlar-epoxy samples which had undergone 50,000 cycles of straining and aged in sea water for 40 days. The stiffness of the composite laminates was also degraded by almost similar extent. This result, when compared with that of Komorek [29], clearly shows the additional degradation under cyclic loading.

There is another interesting review report by Li et al. [34] on effect of alkaline sea water (pH at 12–13) for pre-stressed FRP laminate and FRP tendons. The alkaline sea water simulates the property of the sea water sea sand concrete (SWSSC), which is now very much used in civil construction of marine static structures such as off-shore platforms. The authors compiled several results by some researchers. It is seen from the review article that the alkaline SWSSC at pH of 12–13 has a higher degrading effect under such condition.

A comprehensive study was done on the effect of sea water immersion at various temperatures for an epoxy thermoset plaque and its E-glass fabric composite having 55% fiber by volume. The report is not for publication. The composite samples were made by vacuum bagging process followed by compression molding at 120°C. The curing of plaque and composite was done after thorough degassing of the resin-hardener mix. It was observed that after 360 days of immersion, the flexural strength reduced from about 90 MPa to about 65 MPa, and the dynamic flexural modulus was reduced from about 3.20 GPa to about 2.5 GPa at 30°C in natural sea water. The E-glass composites of the same resin were seen to deteriorate in flexural strength and modulus. The strength reduced from 250 MPa to about 180 MPa, and the dynamic modulus reduced from 8 GPa to about 5.5 GPa. The results clearly show the effect of debonding of the fiber from the epoxy matrix interface thereby drastically reducing the loadbearing capability. The water had a plasticizer effect too, as the glass transition temperature changed from 60 to 62°C to about 52–54°C in 12 months, and the SEM micrograph showed separation of the fiber from the matrix at the interface very clearly. However, the effect of the microbes on degradation could not be quantified separately.

The studies done so far indicate a common observation and conclusion that the degradation of epoxy-based composites is significantly high in terms of delamination, loss of mechanical properties and glass transition on exposure in sea water even for a year. The initial moisture ingress has a plasticizing and swelling effect,

due to which the glass transition temperature reduces with a drop in mechanical properties. In prolonged exposure, the water molecules chemically react with the resin (hydrolysis) producing small chemical substances, which tend to diffuse out of the resin, causing blisters. Also, various salt components of the sea water may affect the moisture absorption rate compromising some properties of FRP in sea water. It is also known that the effect of sea water on glass fiber reinforced composites differs according to the type of matrix and fiber. The mode of failure of glass/epoxy composite is altered from a brittle matrix and ductile fiber to ductile matrix and brittle fiber. However, in some opinion, the strength stabilizes after the absorbed moisture attains saturation.

In construction of FRP elements of ships, the items that are not in continuous immersed condition such as superstructures, ladders, stanchions, guard rails, etc., are better designed with toughened epoxy resin and carbon/glass fabric composites since the degradation is limited in the atmosphere and the composites can have sufficient strength, reasonable glass transition temperature even after the toughening process of the resin. For naval ships of stealth features, carbon fiber and nanocarbons cannot be used as the radar reflection will be increased. For elements to be used underwater, epoxy resin is not that superior to the vinyl ester class of resins.

4.2 Vinyl-ester-based FRP composites

Vinyl ester resins are most commonly used for marine composites for two main reasons, the mechanical strength retention on prolonged exposure in sea water and the strength is comparable to epoxy composites and higher than polyester-based composites. The resin has inherent resistance to water diffusion and consequently lesser effect on its glass transition and strength. For large ship structures, vinyl ester resin is a better thermoset due to suitability for processing large items such as hulls, using vacuum infusion due to its low viscosity, apart from its durability in marine environment.

Conventional vinyl esters are having aromatic backbone of epoxy base and the double bond of the unsaturated ester is cured by styrene, exactly the same process as a polyester resin. The presence of the higher content of stiff aromatic epoxy backbone provides the higher mechanical strength compared with phthalic-acid-based polyesters. The higher aromatic content also restricts the diffusion of fluids. Unlike epoxy matrix cured by amines, the vinyl ester matrix is cured by hydrophobic monomer styrene, and hence, the water ingress is lesser than epoxy resin.

VE-CFRP and VE-GFRP have different strength ratios depending on the mode of force application. Wonderly et al. [35] compared these two types of composites in terms of tensile strength and found that CFRP was about 850–950 MPa and was 1.6–1.75 times higher than GFRP, but the open hole tensile strength was comparable at about 250–265 MPa, and compression strength of GFRP was about 330–360 MPa for CFRP and was about 17% lower than GFRP. Transverse tensile strength of CFRP was also about 75% of GFRP. One interesting study was done by the authors on ballistic impact test, which is important for military application. At a comparable areal density, the specific energy (J/kg/m^2) required to penetrate the panels for CFRP was higher by about 25% compared with GFRP for identical muzzle velocity.

In general, the glass transition temperature of a vinyl ester matrix is about 115–120°C. The flexural modulus and strength of a vinyl ester plaque are about 3.0–3.5 GPa and 80–120 MPa respectively, almost same as epoxy plaque. GFRP of vinyl ester has flexural modulus of about 10–12 GPa and flexural strength of about 270–300 MPa, ILSS of about 30–35 MPa, depending on the fiber type and fiber volume fraction in the composite. The CFRP of vinyl ester has much higher strength

and modulus, about 3–3.5 times higher than GFRP at the identical volume fraction of fiber.

Water diffusion studies show on an average 0.6% water intake at equilibrium for GFRP and about 0.4% for CFRP, which are almost half of corresponding figures for epoxy CFRP. Murthy et al. [32] showed that the sea water saturation levels in both GFRP and CFRP of vinyl ester are about 0.7% and approximately 0.4% respectively, and there was no reduction in the total weight of the samples even after 450 days of immersion. The interlaminar shear strength was reduced by about 35% after 365 days for both CFRP and GFRP of vinyl ester. Similar extent of degradation was observed for flexural strength. The reduction of tensile strength was about 30% for the same period of immersion. However, it is observed that the mechanical properties and the water uptake almost became steady after 365 days. The authors showed that after immersion in artificial sea water for 450 days, the strength reduced by about 35% for both the composites. Similarly, the ILSS also reduced by about same extent. CFRP is marginally better in ILSS on aging in sea water. The maximum water intake for CFRP was about 0.4% compared with about 0.48% for GFRP.

A study by Mungamurugu et al. [36] showed about 1% water absorption at 20°C for vinyl ester GFRP composite for glass fiber volume of 58% compared with about 0.75% for the plaque after 450 day and the reduction in flexural strength (original 250 MPa) by about 25% for the composite after 300 days.

However, most experiments reported in literature are done with artificial sea water, and the effect of the microorganisms and of the evolved materials due to the metabolism of the microbes present in sea water was not possible to observe. Therefore, the drastic decrease in mechanical strength for thermosets resin plaques is due to reaction with water and hence loss of molecular integrity of the cross-linked matrix.

4.3 Unsaturated-polyester-based FRP composites

Unsaturated polyesters (USPs) are also widely used in marine construction since it is very cost-effective, easy to process by vacuum-assisted resin transfer process due to low viscosity. Easy to cure, and intricate shapes can be made with a large variety of USP. The oligomer resin is cured conventionally by styrene in presence of catalysts such as methyl ethyl ketone peroxide (MEKP) and in some cases added accelerators such as a cobalt salt or those based on a tertiary amine. The cross-link density and corresponding mechanical properties are controlled by styrene content and the unsaturation in the oligomer. There are new USPs developed where styrene is replaced by acrylic monomers such as tri- or tetraethylene glycol dimethacrylate (TEGDM) [37], which are comparatively less toxic than styrene. The general-purpose and marine-grade USPs are synthesized with different glycols such as isomers of pentyl glycol and isomers of phthalic acid with small amount of an unsaturated acid such as fumaric acid or malic acid. The average flexural strength of USP-based GFRP is about 250 MPa with 58–60% glass fiber by volume.

A study on long-term natural sea water immersion of USP was done by Norwood [38]. The USPs of orthophthalic-acid-based marine resin and isophthalic acid-neopentyl glycol (IST-NGP)-based marine-grade resin were used with about 2.25:1 ratio of CSM: resin by weight in the form of chopped strand mat (CSM) and 1:1 ratio by weight for woven roving (WR): resin. The surface tissue coating of the same resin with 5% filler content and a gel coat was used to reduce water permeation. The study revealed that the IST-NGP-glass composite showed best water resistance in terms of appearance of blisters. The best performance was of high HDT (heat deflection temperature) IST-NGP where the blister formation was seen only after 200 weeks, while orthophthalic-acid-based conventional marine resin (medium HDT) showed blisters in about 52 weeks as the best performance. The conclusion in

that study was significant for subsequent research on marine-grade FRPs. It was suggested to use a tissue layer of about 5% (by weight) CSM in the IST-NGP resin (high HDT grade marine resin) over the outer layer of the composite and a top layer of the gel coat (white) to ensure longer life in continuous sea water immersion for at least 4 years. However, the study was restricted to only blister formation, but did not indicate change in mechanical properties on sea water aging.

Mechanical properties for short period were investigated by Espinel et al. [28], which revealed that the tensile strength for USP-glass FRP reduced by 20% after 125 days immersion, and interestingly, while the tensile strength attained a constant value after 30 days of saturation, the transverse strength in flexure continued to decrease till 125 days, indicating that the fiber-polymer delamination is more observed if flexural properties are considered. The reason for difference in behavior in these two modes is that the interface delamination affects the bending load-bearing capacity, while in tension, the maximum load is taken by the fiber as such. Unless the fibers are damaged to very high extent as to break down below a critical length, the longitudinal strength will not decrease significantly. This is perhaps the reason for most researchers to measure flexural properties of composites rather than tensile for sea water aging study.

Kootsookos et al. [39] studied the sea water durability of GFRP and CFRP based on USP containing about 32–35% fiber by volume. The flexural modulus of GFRP was about 50% of that for CFRP. The water uptake trend was similar to many other observations, a peak water uptake of about 0.75% for GFRP and 0.5% for CFRP after 16–20 days. However, the water ingress curve had a negative slope after 20 days for both composites. The corresponding flexural modulus of GFRP showed an initial increase, and then finally after 145 days, there was no significant change. Whereas the modulus for CFRP initially decreased and ultimately the reduction is also negligible. It was opined that the weight reduction after peak water uptake is due to hydrolysis and loss of small molecules, but the modulus did not change much for the period of study (145 days). However, the flexural strength of GFRP was seen to reduce considerably, by about 33% but that for CFRP did not change significantly. The performance of the CFRP in sea water aging was seen to be much superior to the GFRP based on polyester resin.

Loos et al. [40] studied hydrothermal effect on USP-based GFRP using distilled water and saturated NaCl solution at 32°C and 50°C. The authors observed that at 32°C, the weight increase is continued with time till saturation value of 3.5–3.6% on 100 days and remained constant thereafter (till 150 days) when immersed in distilled water. For immersion at 50°C, the weight change was having a negative slope after about 50 days. Similar observations were also made by Fraga et al. [41], who studied hydrothermal aging and its effect on interlaminar shear strength and dynamic mechanical properties of GFRP made from isophthalic-acid-based USP with styrene as cross-linker. After 12 days exposure in water at 80°C, the weight change showed a negative slope indicating release of silane coupling agent (sizing of fiber) and also small organic molecules due to hydrolysis of the resin at the elevated temperature. The shear modulus was reduced by about 50% for the composite at 80°C at the end of the study period (1000 h). The glass transition did not change significantly, and the dynamic modulus increased by about 30% but flexural modulus reduced by about 25% at 80°C after about 400 h but stabilized thereafter till 1000 h of study.

Although an USP made of isophthalic acid and neopentyl glycol meets the requirement as a marine-grade resin, as its water resistance is much better than the other USPs, but on a comparison with epoxy resin and vinyl ester resin, the strength of the USP is quite lower, which necessitates a thicker section of a component, say hull of a boat, and consequently there is a possibility of more defects, enhanced water ingress, and faster damage.

5. Diffusion of water in thermosets and FRP

The design of a marine structure is fully dependent on the mechanical properties of the candidate material in various modes. In addition, it must consider the environment in which the object has to perform. Therefore, there is a third consideration of timescale of the service. A very simple example is a static beam under a constant bending load in a building that should carry the load for a long period, for instance, 2–4 decades. Therefore, the design input must be the properties of the material after aging for that service period in the atmospheric environment, especially moisture, carbon dioxide, ultraviolet ray, oxygen, and ozone. While it is not possible to have a data for such a long period for designing an object, it is best to make a prediction of the extent of degradation/aging and degraded properties after a target period of service. This simulation is quite difficult because all environmental and load conditions cannot be simultaneously considered in the mathematical predictive equations. However, a preliminary knowledge or previous study might help in deciding the conditions of fastest degradation due to aging effect. For example, it is known that polypropylene degrades in sunlight due to UV much faster than any other environmental conditions. Therefore, the service life is better decided upon aging under UV of varying intensity.

For marine structures and vessels, the most important considerations to decide the service life are sea water aging, fatigue due to vibration, constant load, and also degradation due to microbial activities. Cyclic sorption-desorption along with a pre-stress was studied by Burla [42], which gave more information on the repeated sorption phenomenon of the cloisite 10A nanocomposites of epoxy, vinyl ester, and unsaturated polyester.

Atmospheric aging due to ozone, UV, etc., is also important for the objects or part of the structures above the water line. In all the factors, sea water aging is most severe because of dissolved salts and alkalinity. The pH of sea water is about 8.3 on an average, and it also contains chlorides, bromides, iodides, sulfates, and carbonates of sodium, magnesium, potassium, calcium, and also traces of heavy metals such as Iron, manganese, cadmium, lead etc. Therefore, diffusion of sea water, and the effect thereof, is the most relevant study for deciding the degradation in mechanical properties of FRP for marine application. It is well known that the extent of sea water uptake and its effect is quite different from potable water or industrial process water.

5.1 Fickian model: constant diffusivity

The diffusion phenomenon in pure thermosets and corresponding FRPs can be generally described by a fundamental theory of diffusion by Fick's Law:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (1)$$

where C is the instantaneous concentration of the diffusing molecule, D is the coefficient of diffusion, commonly called the diffusivity, t is the time, and x, y, z are the three Cartesian coordinates.

Considering only unidirectional diffusion of sea water in a thin panel, (thickness less than 2% of length and breadth), Eq. (1) can be solved to obtain a fractional mass gain (G) at any instant " t " [43]:

$$G = \frac{M_t}{M_\infty} = 1 - \sum_{j=0}^{\infty} \frac{8}{(2j+1)^2 \pi^2} \exp \left[-\frac{D(2j+1)^2 \pi^2 t}{h^2} \right] \quad (2)$$

where M is the mass, suffixes indicate at any time “t” and the final value, D is diffusivity, j is a simulation factor, h is the thickness. The parameter j actually refines the output more for higher value. For example, $j = 10^6$ gives more accurate result than $j = 10^5$.

The diffusivity can be directly calculated from a simple experiment of water uptake by a panel till saturation, using the following equation:

$$D = \frac{\pi}{16} \left(\frac{M_t/M_\infty}{\sqrt{t}/h} \right)^2 \quad (3)$$

If M_t/M_∞ is plotted against $\sqrt{t}$, D is obtained from the slope of the initial linear portion of the water absorption curve.

Eq. (1) can be approximated as [43]:

$$G = 1 - \exp \left[-7.3 \left(\frac{D_x t}{s^2} \right)^{0.75} \right] \quad (4)$$

If the sample is exposed to the sea water on both sides, then $s = h$ (thickness of the panel), if one side is insulated by an impermeable coating, then $s = 2h$.

Rearranging Eq. (4) we can get the time required to attain a certain water content due to unidirectional steady-state diffusion in a thermoset and FRP as:

$$t = \frac{s^2}{D_c} \left[-\frac{1}{7.3} \ln(1 - G) \right]^{1/0.75} \quad (5)$$

Eq. (5) is used for predicting the time required to attain any level of water uptake for different thicknesses (s) in cases of a structure with varying contour where the thickness varies sectionwise, and it might not be possible to carry out experiments with all such thicknesses. Typical examples are marine boats, elliptical underwater objects, composite valves in pipelines carrying water, etc. Shen and Springer [44] showed a similar calculation with 12.7 mm thick panel subjected to moisture exposure.

The one-dimensional diffusion equation is valid for thin panels, where the diffusion from edges is not significant. In case of pure thermoset plaques, the edge effect is not very important, but FRP composites are anisotropic materials and hence the edges are to be protected. This is ensured in FRPs by applying the thermoset resin coating on all edges of the panel. However, there can be an edge correction too, to be more precise on unidirectional mass transfer, provided the sample is homogeneous in diffusivity in all directions [43]:

$$D_c = D_z \left(1 + \frac{h}{l} + \frac{h}{w} \right)^{-2} \quad (6)$$

where D_z is the measured diffusivity and D_c is the edge corrected value and l , w and h are length, breadth, and thickness of the panel.

5.1.1 Example

Figure 1 shows an example of water diffusion data for an epoxy GFRP composite of dimensions $l = 100$ mm, $w = 100$ mm, and $h = 4$ mm experimentally determined and a theoretical value calculated by Eq. (4). The Diffusivity calculated from the M_t vs $t^{0.5}$ was corrected for edge error using Eq. (6). The Fickian model clearly does not validate the experimental data, hence the diffusion process might have either more than one diffusive process as the water ingress progresses or there can be an effect of molecular rearrangement in the epoxy thermoset due to absorbed water.

In order to determine the time required for water absorption to the extent of 90% of the saturation for a 12 mm thick FRP panel, assuming identical conditions, Eq.(5) is used and the time calculated as:

$$t = 30,944\text{ h} = 4.58\text{ years}$$

The life prediction can be done on the basis of the minimum strength required by a designer of the FRP item. Suppose a minimum Flexural strength of 175 MPa is required for the designer to design an underwater vessel hull. The service life of an epoxy-GFRP hull of 12 mm thickness is to be predicted.

Taking the same FRP composition, the laboratory flexural strength data at various times of sea water aging was observed at 35°C for 10,000 h, and **Figure 2** shows the combined data of fractional water absorption and flexural strength with time. The flexural strength measured in 3-point bending test of the original, cured GFRP at 20°C was about 238–245 MPa.

From the source data of **Figure 2**, it is known that the fraction of saturation is 95.4% corresponding to the flexural strength of 175 MPa. Therefore, time required for the 12 mm thick panel at 0.954% saturation as calculated using Eq. (5) is:

$$t = 2397\text{ days} = 80\text{ months at a sea water temperature of }35^{\circ}\text{C}$$

$$t = 2397\text{ days} = 80\text{ months at a sea water temperature of }35^{\circ}\text{C}$$

The above solution of prediction is obviously approximate, as the theoretical curve is not in exact agreement with the experimental data till 7500 h (300 days). However, the theoretical prediction of the diffusion curve in **Figure 1** shows better agreement at longer period of exposure. In addition, considering the good fit in **Figure 2** for the fractional saturation (M_t/M_{∞}) vs. $\log(\text{time})$, with $R^2 = 0.9786$, over the data range of 10–416 days of lab experiment, the data pair of Flexural strength of 175 MPa and 0.954 fractional saturation is fairly accurate compared with experimental value of 0.933 fractional saturation for same strength.

In a different approach, the diffusion-related life estimation can be realized if a time-temperature superposition is done from the data of sea water absorption and a functional property such as strength vs. immersion time at different fixed temperatures of the sea water. In an isothermal analysis with one temperature, the slow relaxation of larger segments of a thermoset polymer ($T_g > \text{ambient}$) is not realized in their contribution to the diffusion and other related properties in long-time aging behavior. There is a slow and continuous physical aging of the matrix at any

Figure 1.
Typical experimental data and corresponding Fickian model prediction.

Figure 2.

Flexural strength and fraction of saturation with immersion time in artificial sea water for an epoxy-GFRP at 35°C.

temperature, even below the glass transition. The water absorbed reduces the T_g and if the test temperature is near the modified T_g , the rate of physical aging is enhanced, which may become significant after a long time for a composite of long service life, say more than a decade. It is possible to accommodate such physical process and its effect on properties by resorting to time-temperature superposition principle, since a property at a particular isothermal temperature after a period of aging is same for a different period of aging at another isothermal temperature. This is achieved by shifting the data of an isotherm to another reference isotherm. In classical theory, this relation can be Arrhenius expression as:

$$\tau = \tau_0 e^{E_a/RT} \quad (7)$$

where t is the relaxation time of the polymer segments. Eq. (7) is applicable for high temperatures above glass transitions since the exponential rise in relaxation time is possible when the movement of a segment or a molecule is not hindered by neighboring species. As the polymer is cooled below glass transition, the mobility is hindered by a close approximation of neighboring segments or molecules, and thus the above equation is not valid. In the glass transition region, the relaxation time would change by several decades on even one degree rise in temperature. A rather different expression is Vogel-Fulcher (VF) equation, which is somewhat valid even near glass transition [45]:

$$\tau = A e^{\frac{B}{T-T_0}} \quad (8)$$

However, the value of the constants A , B , and T_0 would change as the temperature is lowered near T_g when more densification of the molecules would take place.

Williams, Landel and Ferry [46] relate the temperature-dependent events such as viscosity, relaxation time, or relaxation frequency with change in fractional free volume of the molecule or segments. The fractional free volume changes linearly with temperature. Accordingly, the relaxation time-temperature relationship is given as the famous WLF equation:

$$\log a_T = \log \left(\frac{\tau}{\tau_g} \right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (9)$$

where $\log(a_T)$ is the shift factor, C_1 and C_2 are constants, T_g is the glass transition temperature, and if it is the reference temperature, then $C_1 = -17.44$ and $C_2 = 51.6$, valid till a test temperature of $T_g + 50^\circ\text{C}$, and these values are -8.86 and 101.6 respectively at any other reference temperature up to $T_g + 50^\circ\text{C}$, and this is valid till a test temperature up to $T_g + 100^\circ\text{C}$.

However, the best process of superposition is to shift the isotherms graphically in a data plot of the property (say strength) vs. time.

A typical t - T superposition is shown for a limited time of 8 months as an example to demonstrate the predicted value of a property after aging in sea water. The raw data was plotted in **Figure 3** as a flexural strength vs. time as isotherms at only 20°C , 30°C , 40°C , and 50°C and graphically shifted to the reference temperature 20°C , to predict the value of the strength at longer time than experimental time as an example. For a comprehensive study, longer period and more importantly, higher range of temperature should be used for a prediction at much longer period.

Subsequently, the shifted data are plotted as a master curve with a reference temperature of 20°C as shown in **Figure 4**. The best fit of the shifted data is approximately a second-order polynomial expression here. However, for a long period, the property will vary with the logarithm of time. The shift factors corresponding to the temperatures 30°C , 40°C , and 50°C were used to calculate new time (t_{new}) at the reference temperature of 20°C by following simple equation:

$$\log(t_{new}) = \log(t_{test}) + \log(a_T) \tag{10}$$

The process of determination of shift factor from a graphical shifting is described in Ref. [47]. For example, shift factor $\log(a_T)$ of 50°C is 0.301 , and if we take test time at 8 months, then

$$\log(t_{new}) = 0.9031 + 0.301 = 1.2041, \text{ therefore, } t_{new} = 16 \text{ months.}$$

This means that the strength at 50°C after 8 months of sea water aging corresponds to 16 months aging in sea water at 20°C . The shifted values can be approximately described by a polynomial fit:

$$\sigma_f = -0.0238t_{new}^2 - 4.0t_{new} + 222.72 \tag{11}$$

where σ_f is the flexural strength in MPa and t_{new} is in months.

Figure 3.
Isotherms of flexural strength vs. time of immersion of a GFRP based on epoxy resin.

Figure 4.
Master curve for 20°C reference temperature: epoxy-GFRP aging in sea water.

The polynomial fit can be used for determination of the property at extended period too. Therefore, the strength is calculated with Eq. (11) for longer period than the shifted data. **Figure 5** shows the data up to 50 months. The result is obviously an approximation, but gives one the idea of range of the degraded property (strength) for a long exposure time. The validation of the data is not possible unless an experiment is done for the similar period.

Similarly, 10 months data on water uptake by an epoxy-GFRP were studied at limited temperature range of 20°C, 30°C, 40°C, and 50°C. The data were plotted as isotherms and graphically shifted to the reference temperature 20°C. The shift factors were determined, and subsequently new time was obtained using the method already described, and a master curve of water uptake predicted at longer time was obtained. The plot is shown as **Figure 6** here only from 20 months of aging onward till 90 months.

A correlation of these two master curves for prediction of long-term properties as water uptake and flexural strength can be made with some approximation, in this case, because of the limitation of data.

Let us take strength and diffusion data at 48 months from **Figures 5 and 6** respectively. At 48 months, the Flexural strength is 85.6 MPa (calc.) and Water uptake is 6.61% (calc), at a sea water temperature of 20°C.

The example of evaluation of long-term property and water diffusion shown above does not simulate an actual FRP item. In practice, the thicknesses for under-water structures are much higher due to load requirements. Moreover, multiple

Figure 5.
Extrapolation of the master curve for longer period.

Figure 6.
 Long period prediction of water uptake constructed by graphical t - T shift.

types of mats, chopped fibers, fabric with various weaving styles are used in thick composites where FEM analysis is resorted to design the layers.

An approach can be made for life estimation by calculating the diffusion time using Eq. (5) for an FRP of actual size and thickness from the laboratory experiment at different temperature of sea water aging with respect to time. Once a data table is made of $M_t\%$ vs. time for the actual size at various isothermal aging temperatures, the data can be used to obtain a graphically constructed master curve following a time-temperature superposition principle for a reference temperature, which is the actual sea water temperature of that geographical region. Since the composites often show dual Fickian behavior or non-Fickian behavior, the data for only long-term study can be taken from the master curve for a good fitting equation. The probability of error is minimized in this process, as graphical shift does not need any assumption such as glass transition temperature, values of activation energy, or the WLF constants, etc. However, a careful experimental determination of the value of diffusivity is required, which is a most critical parameter.

In experiments on diffusion, the panel thickness plays an important part. Although there is an edge correction method available, but it is best to use thin panels of maximum 4.0 mm thickness and edge sealing by a marine-grade vinyl ester resin tissue coat and gel coat of 1.0 mm thickness each. Number of layers of the fabric should be restricted by using fairly thick quality fabric and mats, but not very thick to make the resin infusion difficult. Nevertheless, similar materials such as the resin, curatives, catalysts, and type of mats and fabrics as actual FRP item would be best for a realistic prediction of service life.

5.2 Dual-stage diffusion

After observation of many experimental results on water diffusion process in thermosets and composites, it is certain that the diffusivity is not unique for a case and may vary according to the behavior of the polymer as the process of water ingress progresses. The water diffused in a polymer acts as a plasticizer to change the relaxation process, resulting in swelling, and also initiates some chemical reactions. Karter and Kibler [48] offered a theory that the water absorption is described by a simple diffusion with sources and sinks of diffusing water molecule and that the absorbed water is divided into mobile and strongly bound phases in the polymer. There is a continuous migration from mobile to bound phase and the reverse. There is an equilibrium of this interchange of bound and mobile water. The theory is somewhat similar to Langmuir theory of adsorption-desorption. Considering the

probabilities of the interchange of bound and mobile water molecules, the relative mass gain is given by the authors as:

$$\frac{M_t}{M_\infty} = 1 - \frac{\gamma}{\gamma + \beta} e^{-\beta t} - \frac{8\beta}{\pi^2(\gamma + \beta)} \sum_{n=0}^{\infty} (2n+1)^{-2} e^{-k(2n+1)^2 t} \quad (12)$$

where γ is the probability per unit time that a mobile H₂O molecule becomes bound, and β is the probability per unit time that a bound H₂O molecule becomes mobile. The units of both are time⁻¹.

The constant k is given as:

$$k = \frac{\pi^2 D}{h^2} \quad (13)$$

When the exposure time is short, an approximate equation can be used as follows:

$$M_t = \frac{4}{\pi^{3/2}} \left(\frac{\beta}{\gamma + \beta} M_\infty \right) \sqrt{kt} ; \quad 2\gamma, 2\beta \ll k ; \quad t \leq 0.7/k \quad (14)$$

Hence, $\beta/(\gamma + \beta)$ can be calculated from the slope of a plot of M_t/M_∞ vs. $t^{0.5}$. and for a long exposure period, so that kt is much larger than 1. The following approximate equation can be used:

$$M_t = M_\infty \left[1 - \frac{\gamma}{\gamma + \beta} e^{-\beta t} \right] ; \quad 2\gamma, 2\beta \ll k ; \quad t \gg 1/k \quad (15)$$

Eq. (15) can be rearranged, and after taking logarithm, it becomes:

$$\ln \left(\frac{M_\infty - M_t}{M_\infty} \right) = \ln \left(\frac{\gamma}{\gamma + \beta} \right) - \beta t \quad (16)$$

Eq. (16) represents a straight line with $-\beta$ as the slope of the curve and the intercept would give the value of γ , once β is calculated.

5.2.1 Example

A GFRP based on USP and chopped glass fiber is exposed to artificial sea water at 45°C for 8400 h. The size of the laminate was 80 mm × 12 mm × 4 mm ($l \times w \times h$), and the maximum water uptake was about 4%. The approximate equation Eq. (15) for long-term prediction was used for evaluating the parameters β , γ , and k from the time-dependent absorption data. The values are:

$\beta = 0.0004 \text{ h}^{-1}$, $\gamma = 0.00233 \text{ h}^{-1}$ and $k = 1.82 \times 10^{-05} \text{ h}^{-1}$. The corrected diffusivity (D_c) calculated at the initial slope was $2.95 \times 10^{-11} \text{ m}^2/\text{h}$.

Figure 7 shows the experimental data and the predicted data of absorption for long-term approximation considering a period beyond 2000 h as the long term.

5.3 Dual Fickian model

Due to the time-varying process of moisture absorption, it is assumed that instead of one constant diffusivity, two diffusivities can be used to describe the long-term water uptake, provided that there is no loss of small molecules as a product of hydrolysis and subsequent leaching out of the experimental panel. The

Figure 7.
Long-term water uptake data: experimental and Eq. (15).

initial diffusivity D_1 is determined by the initial slope, and the second diffusivity D_2 is determined by the subsequent part with a distinctly different slope taking only the linear portion. The water uptake is the summation of mass increase for both the diffusivity and the total mass increase M_t at any given time t is given by:

$$M_t = \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D_1(2n+1)^2 \pi^2 t}{4l^2}} \right) M_{1\infty} + \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D_2(2n+1)^2 \pi^2 t}{4l^2}} \right) M_{2\infty} \quad (17)$$

where $2l$ is the length of the diffusion path (=thickness of the panel), and $M_{1\infty}$ and $M_{2\infty}$ are fractions of final mass uptake M_{∞} .

A similar expression is a modified Jacob-Jones model [43, 49, 50]:

$$M_t = M_1 \left\{ 1 - \exp \left[-7.3 \left(\frac{D_1 t}{b^2} \right)^{0.75} \right] \right\} + M_2 \left\{ 1 - \exp \left[-7.3 \left(\frac{D_2 t}{b^2} \right)^{0.75} \right] \right\} \quad (18)$$

Here, $M_{\infty} = M_1 + M_2$, and $b = \text{thickness} = 2l$ of Eq. (18) above.

Comparing Eqs. (17) and (18), it is more convenient to use the latter, although the equation is an approximate one.

5.3.1 Example

The same water diffusion data of Example 5.1.1, which did not show good fit using the Fickian model with one diffusivity, is tested for the dual Fickian model, taking modified Jacob-Jones expression as in Eq. (18). The diffusivities were calculated as $D_1 = 2.25 \times 10^{-9} \text{ m}^2/\text{h}$ and $D_2 = 7 \times 10^{-10} \text{ m}^2/\text{h}$. The theoretical and experimental data are plotted in **Figure 8** below. The resulting theoretical prediction is more accurate compared with simple Fickian model (**Figure 1**).

5.4 Diffusion relaxation models

In some models, apart from initial diffusion process of Fickian type, relaxation of the polymer chain segments is also considered, as the water ingress progresses. The water has a plasticizing effect, and hence the relaxational phenomenon, which involves segmental motion of macro-Brownian type, increases with the progress of

Figure 8.
Dual Fickian model fitted to experimental data of example 6.1.1.

diffusion. The relaxation process in a polymer is related to the slow rearrangements of the chain segments and therefore, distribution of the free volume in the polymer, considering large number of different sizes of the segments in the network. The diffusion and relaxation were combined in a single model by adding the relaxation terms to a classical Fickian diffusion model. The two diffusion processes were assumed to be independent of each other. The mass uptake at any time interval, t , is given by:

$$M_t = M_d(t) + M_{R\infty}(1 - e^{-rt}) \quad (19)$$

where r is a relaxation parameter (inverse of time), M_d is mass uptake for initial phase, calculated by classical equations of diffusion, and $M_{R\infty}$ is the saturation water content due to segmental relaxation process.

The above model is only applicable where the relaxation process is approximately commensurate with the experimental timescale, since a short-term experiment may not result in actual effect of segmental motion and relaxation of a thermoset, which has a very high relaxation time at the experimental temperature.

6. Nanocomposite

Nanometric-sized materials are presently used as reinforcing fillers with polymers. The nanoparticles are defined as those that has at least one dimension below 100 nm. Due to the tiny size, the nanoparticles have very high surface area compared with volume, and hence, their force of attraction with a polymer is much higher compared with common fillers. In addition, the shaped nanoparticles such as rods, platelets, stacked layers, fibers, etc., impart good resistance to diffusion of gas and liquids in polymers.

Needless to say that the intermolecular forces between the nanoparticle and the polymer much depend on homogeneity and polarity. The force of attraction may be Van der Waals, hydrogen bond, polar attraction, dipole-dipole, etc. Some fillers also form covalent bonds too. The secondary valence bonds are physical bonds and are reversible, unlike the covalent bond, which is a chemical bond. Most common nanoparticles are carbon nanotubes, nanorods, nanofibers, graphene and graphene oxide, clays such as montmorillonite, layered silica, nano particles of minerals such as nano titanium dioxide, nano ceramics, etc.

6.1 Common nano fillers

Nano carbons are chemically modified, for example, —COOH functionalized to improve physical bonding with polymers. The reinforcing effect of single-wall carbon nanotube (SWCNT) is much higher than multiwall tubes (MWCNT) because of higher specific surface area.

Graphene and graphene oxides are a new class of plate-type reinforcing nanoparticles, having layer of single graphitic plates, can be physically bunched as 3–8 layers. Graphene is an allotrope of carbon whose structure is a single planar sheet of sp² bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The graphene can have a spacing of 0.3–0.5 nm between two platelets. Graphene is purer form of carbon, having no organic impurities or functional groups attached, hence their bond with polymers is less intensive than other allotropes of carbon nanoparticles. However, synthesis of graphene from graphite/carbon leads to graphene oxide, which is more polar and can have better bonding with polar resins, which are used for FRP.

Clays are layered silicates, with complex crystal structures. There are different naturally occurring clays such as bentonite, which is kind of rock, mixture of different minerals, including smectite (2:1 layered clay), montmorillonite (dioctahedral), hectorite, (tri-octahedral). The clays are organically modified, for example, ion exchanged with quaternary alkyl ammonium salts, to allow an oligomer molecule to enter in the clay gallery, thus intercalating or even exfoliating the clay. Cloisite is a class of montmorillonite clay, commercially available in various hydrophobicities, and is in the order: Cloisite 15A > 20A > 25A > 10A > 93A > 30B > Cloisite Na⁺. Typical clay gallery spacing in montmorillonite (Cloisite) is about 1–1.9 nm depending on their structure, and the spacing is increased upon modification and is further exfoliated or intercalated when a low-molecular-weight polymer enters the clay gallery. Typical surface area of a montmorillonite nanoclay of 75–150 nm transverse size is approximately 750 m²/g.

6.2 Processing of polymer nanocomposites

However, for processing the nanoparticles with an epoxy/unsaturated polyester/vinyl ester oligomer is not easy because of high agglomeration of the nano particles, causing inhomogeneity. In fact, carbon nanotubes cannot be homogeneously mixed with epoxy oligomer beyond 1% without adding any solvent.

Common processing methods are:

1. Ultrasonication: it is effective in low-viscosity fluids. Generally, 40–50 kHz ultrasound is used in a bath containing the polymer mixed with a solvent. It improves dispersion of the nanoparticle by decreasing aggregates or even separates the nanoparticle. For example, SWCNT is mixed with epoxy using dichloromethane as a solvent.
2. Introducing surfactant: composites containing as little as 1 wt% surfactant-dispersed MWCNTs have better homogeneity, resulting in improved interaction between nanoparticle and matrix.
3. Chemically functionalizing the nanoparticle: nanoclays or MWCNTs are organically modified/functionalized leading to an improved dispersion in thermoset forming oligomers such as epoxy, unsaturated polyester, or vinyl ester.

Figure 9 shows a general process flow of polymer-nanocomposite preparation, using ultrasonication. As an example, an epoxy resin with clay is shown here with appropriate processing parameters.

For FRP nanocomposites, it is better to use a pre-bound process rather than mixing the nano material in the resin—which may cause processing difficulties. In this process, the nanoparticle is dispersed in a solvent and sprayed onto the dry fiber mat laid on a steel mesh fitted with a vessel. A vacuum at the bottom of the vessel extracts the gaseous and fluid part and facilitates drying of the mat. Typical parameters for such process for thermoset-MWCNT-based FRP are:

- MWCNT: 1% in acetone
- Air pressure for spray: 0.3–0.4 MPa
- Vacuum: 0.25 atm (absolute)
- Drying after spray: 12 h at 120°C

Figure 10 shows a schematic diagram for the pre-bound process of FRP-nanocomposites.

6.3 Water diffusion in nanocomposites

The barrier property is a function of cross-link density of the thermoset. The free volume for such densely cross-linked network is small, and the chain segments are very stiff. These two factors resist the penetrant transport in the matrix. Since the glass transition temperature is far higher than ambient, the thermoset can be described as an amorphous material trapped as a frozen mass below its glass transition. The dependence of diffusion on cross-linking is reflected in nonlinear behavior and also wide range of diffusivities reported in literature for rigid thermosets and FRPs based on these.

Thermoset nanocomposites were studied by many researchers to observe the effect of inclusion of nanoparticles in highly cross-linked networks, such as epoxy, USP and VE.

Figure 9.
A typical process for polymer-nanocomposite using ultrasonication.

Figure 10.
 A typical arrangement for pre-bound process.

Epoxy-amino functionalized carbon nano fiber (CNF) composite was studied by Prolongo et al. [51] and concluded that the CNF effectively controlled the extent of unbound free water, which fills the nano-voids, without swelling (type-I water). However, the final water uptake was not much different than FRP without CNF. Balgis et al. [52] studied MWCNT and milled carbon (spherical graphite and chopped micron scaled carbon fiber) in epoxy resin and found that the dynamic modulus improved by addition of these reinforcements by about 8%. The uptake of water was slow, and the ultimate water was reduced by 12% compared with the neat epoxy resin, and after hydrothermal aging, the dynamic modulus was marginally changed from 2900 MPa to 2700 MPa, but the glass transition temperature changed by about 10–11°C.

Maheshwari et al. [53] studied the effect of nano silica on sea water diffusion of unsaturated polyester resin nanocomposites at varying temperatures (40–60°C) and salinity (0–25%). The effect of inclusion of 3% nano silica in distilled water reduced the saturation water uptake from 0.65 to 0.52% approximately, at ambient temperature, while for a 4% saline water, which is slightly more saline than sea water, the saturation with 3% nano silica is about 0.46%, compared with neat USP at 0.6%. Their study also showed a gradual decrease in saturation of water in nano silica content. See et al. [54] used a organically modified montmorillonite (OMMT) clay treated with a modification agent known as X-treatment using an organically reactive dispersion agent (commercially restricted) in unsaturated polyester resin to make a gel coat with improved barrier property against water immersion/moisture diffusion. It is seen that the moisture uptake increased upon addition of 1% OMMT from 1.74% for without clay to about 2.17%, and with a X-treated OMMT, the figure is about 1.9%. The study clearly shows that the inclusion of the OMMT nanoclay did not reduce the ultimate water uptake, nor it could improve upon glass transition compared with the neat resin after moisture saturation, but the diffusivity was reduced by about 25–30%, and the saturation time is same as the neat resin coating. The life extension by formation of the clay-nano composite cannot be expected to be significant. Shah [55] used two different types of surface-treated OMMT with vinyl resin and studied water diffusion and its effect on properties of the resin-clay nanocomposite. The study indicated similar result as reduction of diffusivity but not the ultimate water uptake and no significant difference in glass transition.

Burla [42] studied the absorption-desorption cycles of water in Cloisite 10A nanocomposites of epoxy, polyester, and vinyl ester thermosets at various values of

relative humidity and immersion in water at 25°C under a tensile stress to the extent of 17% of their ultimate tensile strength. Although the diffusivities were reduced upon in addition of the clay, but the ultimate extent of water uptake did not reduce and the time to reach saturation was not improved.

The nanocomposites in all above cases were seen to be non-Fickian in diffusion and in most cases had slightly higher moisture uptake at saturation. This is possibly due to the bound water molecule at the surface of the clay, which is more hydrophilic due to more —OH groups present in the clay compared with that in the resin. A study on fractional free volume and nano hole size distribution was done by Patil et al. [56] with epoxy-Cloisite 10A clay nanocomposites. The authors used Positron Annihilation Lifetime Spectroscopy (PALS) to determine the subnanoscopic free volume in the nanocomposite. The fractional free volume decreased with clay incorporation, but at higher loading, the decrease did not follow a simple linear mixing rule with respect to the volume fraction of the clay, but the reduction was more. This is possibly due to more interaction of the clay with the resin. PALS results showed strong (repulsive) interactions between the clay and the epoxy matrix at lower clay concentrations, which decrease at higher clay concentrations due to the clay-intercalated structure. However, the nanohole size distribution showed an interesting feature. The nanoholes became smaller in size, but the size distribution broadened with respect to nanohole volume beyond the original maximum nanohole volume. There was a net increase in total void volume, although average nanohole volume reduced from 0.075 nm³ to about 0.05 nm³ on incorporation of 7.5% cloisite 10A. The reduction of size and increase in overall hole volume are, of course, a function of the clay-resin interaction, for example, in this case it was repulsive.

A study was done by Rath et al. [57] with USP-Cloisite 15A nanocomposites on the reason for reduction of mechanical properties with increase in clay loading. PALS technique was used to find the free volume change on incorporation of the clay. It was seen that clay loading caused an increase in fractional free volume, suggesting a lower chain packing efficiency in these intercalated USP/clay nanocomposites. This could be a reason for higher or at the most similar water uptake on saturation by the clay nanocomposites.

7. Effect of microbial activities on FRP properties

Microorganisms in sea water can settle on structures, such as on metals, FRPs, and on almost all materials. The microbes form a very thin layer of viscoelastic nature as micro-fouling, quite adherent, and this layer is commonly termed as a slime. The slime formation on a substrate can take place within few days of immersion, as there are enormous amounts and varieties of microbes in the sea.

The slime facilitates the settlement of macro-organisms, which is termed as macro-fouling, and most common fouling macro-organisms are bryozoans, barnacles, mollusks, polychaete and other tube worms, zebra mussels, etc. The size of macro foulants is quite large, could be few centimeters even. The slime formation and macro-fouling are highly undesirable for marine vessels and structures, because of many reasons such as evolution of corrosive gases such as hydrogen sulfide, hydrogen, etc., due to metabolism of the organisms, surface roughness of vessels due to macro-fouling, thereby increasing the drag on movement substantially. FRPs are equally vulnerable to such settlements and degradation due to microbial settlement. There are many microbiological studies on the effect of microbes on various materials immersed in sea water. A brief discussion and most important findings are given here for FRP composites.

Little et al. [58] studied the adhesion of the slime on substrates. Gu et al. [59, 60] reported microbial growth and degradation of glass and carbon fibers upon penetration of fungi into the resin matrix. Organic additives to fibers, such as plasticizers and surfactants, may provide nutrients for microbial growth and ultimate degradation as reported by Upsher [61]. Glass fibers are more vulnerable.

Wagner et al. [62] examined carbon fiber-reinforced epoxy (T-300) and a glass (S-2) and carbon fiber (T-300) vinyl ester exposed to microbial culture for 161 days, to study the possible microbiologically influenced degradation. Composites, resins, and fibers were exposed to various microbes including hydrogen producing and sulfate-reducing bacteria (SRB). All types of bacteria colonized surfaces, preferentially on irregularities such as scratches and fiber disruptions. SRB degraded the organic surfactant on glass fibers. Tensile strength of a CFRP of epoxy was reduced on exposure to SRB. The SRB mixed culture did not degrade neat vinyl ester. Degradation of the organic surfactant on glass fibers due to the microbes was observed. Hydrogen-producing bacteria appear to have disrupted fiber-vinyl ester resin bonding with gas production. The study indicated that it is essential for marine application to screen the FRPs against various microbes of sea water before designing the structure.

8. Conclusion

Application of fiber reinforced composites based on thermosets is increasing as the cost and availability of fuel increase with time. This is simply because a lighter marine vessel has the fuel efficiency much higher than metallic vessels. For static RCC construction too, a simple outer jacket of a composite can protect a concrete pillar of off-shore structure for quite a longer period than an exposed RCC. The undersea pipelines are the other areas of potential use of carbon-vinyl ester composites. Nano-carbons can effectively improve the toughness of such items.

A large number of studies are already done to examine the efficacy of using FRPs for use in marine environment considering the chemistry of the matrix resins and relevant properties. Similarly, various fibers were also investigated by many researchers. Recent advancement is focused at incorporation of nanofillers of different chemistry and forms such as nanotubes, fibers, rods, spherical, platelets, etc.

The composites studied so far are widely varying in the resin-fiber ratios, forming sequence, and processing methods. Therefore, the results of each study cannot be fully generalized, but a broad conclusion on quantitative figures of merit can be made for each polymer-fiber combination.

A very general conclusion on durability in marine environment is that vinyl ester resin with carbon fiber is the best choice for applications in static structures, high strength ship components, and commercial speed boats where durability and weight reduction are important. However, for naval ships and submarines, for use in superstructures, the CFRP composites have a problem of radar reflections similar to metallic structures. Modern-day stealth ships exclusively use GFRP since it is radar transparent material (RTM). CFRP is only used in radar absorbing structures (RAS). Internal areas of the vessel can be made with CFRP for better strength and hence reduced weight. However, GFRP has slightly more damping capability than CFRP, which is stiffer. The SONAR Dome can be made with glass fiber or carbon fiber, also with hybrid fiber system. CFRPs are electrically more conductive than GFRP, and hence it is better to use GFRP as inside layers to avoid electrical problems for securing the transducer arrays.

Most studies on durability of FRPs reported so far are either using moisture, or distilled water or artificial sea water, but very rarely natural sea water has been

used. Artificial sea water does not simulate the natural sea water. The variations in types of microbes across the world are so much that a result of durability study in sea water at Mumbai coast in India is not applicable in a coast of the United States. There are no comprehensive reports on effect of microbial activity and effect of sea water constituents both considered together to decide a service life of an FRP.

To determine service life of an FRP in marine water, it is required to use the panels immersed in actual sea water using a raft and periodically observing the change in water uptake, chemical groups, mechanical strength, dynamic mechanical properties, surface restructuring, glass transition, etc. Mathematical models commonly used may not be directly applicable for considering the influence of all unforeseen parameters of the sea, but a functional property such as bending strength/modulus can be monitored with time. The data can be superimposed with the similar value of the property with that from a simultaneous laboratory experiment at different temperature as is normally done. The time-temperature superposition will be better used in such cases with graphical shift method to avoid any assumptions. Although the microbe activities are not mapped in temperature scale in such method, it is fairly accurate since the microbe activity is constant due to approximately constant sea water temperature and salinity. The study must be done for at least two cycles of breeding of microbes. This means that the experiment may be only for at least 12 months. Vinyl-ester-based GFRP and CFRP are therefore required to be studied to observe the effects of sea water chemistry and microbiological activity to decide the service life.

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