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REVIEW PAPER

Review on Efforts to Improve the Mechanical Performance of Fiber-Reinforced Polymer (FRP) Composites Under the Marine Environment

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Abstract Fiber-reinforced polymer (FRP) composite material has predominant applications in the marine environment over traditional materials because of its superior mechanical properties, design flexibility, high strength-to-weight ratio as well as notable resistance to corrosion. These properties are very well supported by FRP composite materials in various applications in the marine environment. However, exposure to the harsh seawater environment causes a significant deterioration in the FRP composite material properties, which also has an impact on the reliability of the composite structures. Seawater absorption is one of the most critical parameters affecting the mechanical properties of FRP composites and needs to be analyzed for its specific performance testing in the marine environment. This review paper aims to give a comprehensive summary of the most significant approaches for improving the mechanical performance of FRP composites by reducing damage mechanisms caused by moisture absorption during seawater aging and also discusses suggestions for future research.

Keywords Fiber-reinforced polymer (FRP) composites · Seawater exposure · Degradation · Moisture absorption · Mechanical properties

Introduction

In order to effectively meet the demands of sustainable development, the maritime construction industry has undergone constant modification and enhancement, resulting in a requirement for more durable, corrosion resistance, less labor-intensive and service-intensive products at a competitive cost. The technology of fiber-reinforced polymer (FRP) composite materials in the maritime sector is now matured and time has come to develop the use of the next generation of composite materials to improve the cost-effectiveness and performance of marine structures and their components [1]. The use of FRP composite materials, especially glass fiber and carbon fiber, in marine vessels is expected to increase in the coming years for a variety of applications including decks, bulkheads, hatch covers, propellers, propulsion shafts, pipes, pumps etc. Also, other marine machinery equipment's/parts, as well as components of structure for tidal turbine blade applications in maritime renewable energy [2–4]. This has happened because of the desirable properties of FRP composite material that reflects the best substitute over the traditional materials used in marine industry [4–6]. Glass fibers are most preferable materials over the carbon fiber because of its higher cost; also, the structures made entirely of carbon fiber are not easily affordable. As a result, ship designers are fascinated by the usage of hybrid composite laminates consisting of glass and carbon fiber-reinforced polymer (HFRC) [7]. The hybrid composite laminate is helpful in significantly reducing the weight of marine components. This results in significant fuel savings and decreased greenhouse gas emissions in ships which are supportive in boosting the cargo carrying capacity, optimize performance life cycle, and lower maintenance costs due to a better barrier to corrosion [4, 8]. But, unfortunately, the FRP composite materials are susceptible to marine environment like moisture, temperature, UV radiation, seawater aging etc. which results in significant decrease in durability and performance of FRP when exposed to long durations [5, 9, 10]. Of all the factors, seawater aging is the most serious due to

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alkaline nature and dissolved salts. The absorbed seawater has a major impact on the mechanical properties of composite materials. The molecules of the matrix polymer come into contact with the water molecules results in generation of cracks in matrix, pitting, hydrolysis, fiber breakage, plasticization, fracture, delamination and fiber/matrix debonding [9, 11]. The most pertinent study is therefore one that examines moisture absorption and how it affects the mechanical properties of FRP composites used in marine applications.

The properties of marine FRP composites shall be deteriorated during their lifespan due to the antagonistic corrosion environment due to the alkaline nature of seawater, resulting in the deterioration of mechanical properties [3, 12]. In order to improve the mechanical performance of FRP composites under marine environment, it is seen that majority of the researchers have covered different approaches such as coating on fiber surfaces [13], hybridization in fiber and matrix with or without nano-filler [14, 15], and interply rearrangement [16]. But these individual approaches are used in isolations which minimize the moisture absorption up to certain level. Therewith, there is an opportunity to study the behavior of FRP composites in the aggressive marine environment to reduce moisture absorption under the influence of seawater by combining several approaches. Therefore, this review paper specifically aims to explore the appropriate approaches that can reduce the damage mechanisms caused by moisture absorption and improve the mechanical performance of FRP marine composites. It will also identify and discuss the knowledge gap by comparing results published in various references. Based on this review, the future research works required to improve the mechanical performance of the FRP composites in the marine environment are mentioned.

The review article is structured as follows: Section one presents the introduction, Section two describes the state of research on the degradation of FRP composites and the mechanism of moisture absorption and diffusion in the marine environment; Moving on, Section three discusses the current literature approaches to improve the mechanical properties of FRP composites in marine applications. Section four contains comprehensive discussions and conclusions, encapsulating insights for future research direction.

Degradation of FRP Composites Under Marine Environment

In the marine environment, the use of FRP composite material is rising exponentially. During the service life, some FRP components are directly or indirectly exposed to seawater. But they are especially vulnerable to the seawater environment, which results degradation in mechanical performance owing to physical degradation that is plasticization and swelling of matrix and chemical degradation that is matrix hydrolysis, interface hydrolysis and fiber degradation. These types of degradation would cause new damages and accelerate advancement of the damages inside composite [5, 13, 17, 18]. The standard requirements set in the marine industry are temperature, seawater, chemicals and various radiations such as UV and microwave as environmental conditions that need to be considered when evaluating the environmental impact on the mechanical performance of FRP composites. However, the moisture absorption due to seawater aging has major influence on the mechanical performance of FRP marine structure. The schematic representation of the environmental degradation of fiber-reinforced polymer composites due to seawater as shown in Fig. 1. The detailed literature review was carried out which provides in depth information associated with followings aspects:

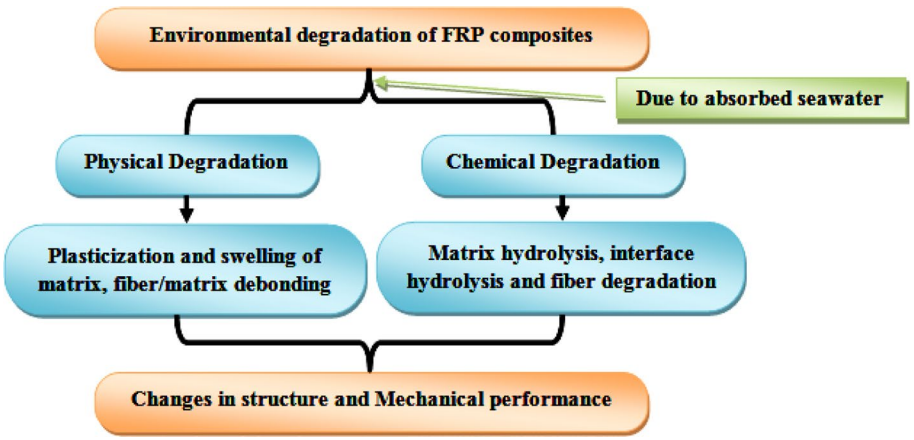

Fig. 1 Schematic representation of the environmental degradation of fiber-reinforced polymer (FRP) composites due to seawater aging

Seawater Aging

The composition of seawater is a major factor affecting the aging behavior of FRP composites for marine applications. The most profuse ions concentration dissolved in the seawater is presented in Fig. 2. Oceanographers use salinity to assess the total salt content of seawater. But the salinity can also be used to directly estimate the concentrations of the major ions in seawater. The salinities of open seas are about 35 parts per thousand contains approximately 35 g of salt and 965 g of seawater. For typical marine applications, a pH value of seawater is within the range 7.5–8.4 [12], because of seawater contains the combination of more free hydrogen and hydroxyl ions. For marine applications, seawater temperatures typically range from 5 to 50 °C [18]. FRP composites are directly or indirectly exposed to particular seawater media conditions for an extended period of time in marine applications, resulting in degradation. This happens because of hydrogen and hydroxyl ions permeation into the fibers and these ions gradually replace the sodium ions that were previously present. Due to the replacement of ions, the mismatched strain may introduce cracks into the fiber surfaces. The saline water solutions may hydrolyze the glass siloxane groups accelerating the defect formation. Failure of FRP composites may occur in the interfacial region because of chemical reactions or plasticization, when seawater penetrates the interfaces. Furthermore, the different salt ions found in seawater (e.g., NaCl, $MgCl_2$) attempt to breakdown the bonding between carbon and hydrogen in the epoxy resin and attach to the carbon. This also induces the strain in the matrix due to a change in the dimension of the atom [19].

Moisture Absorption and Diffusion Mechanism

FRP composites are composite materials that contain fibers as reinforcement in a thermoset polymer resin matrix. When FRP composites are used in seawater environments, moisture absorption is a problem, leading to matrix plasticization and swelling. Moisture absorption causes large residual strains in multi-directional laminate because swelling of composite lamina due to restricted in the fiber direction. Usually, the moisture rate increases with the increase in immersion time for a longer period [21]. Moisture absorption affects the material's glass transition temperature at elevated temperature [22]. The mechanical properties of the FRP composite can deteriorate by moisture diffusion with three main mechanisms: first mechanism: the diffusion of water molecules into micro gaps between polymer chains, second mechanism: capillary transport into the gaps and defects at fiber-matrix interfaces, and third mechanism: swelling effects, the lead to the formation of tiny cracks in the matrix. Seawater absorption mechanism is shown for the three different FRP composites namely, plain glass fiber composite, carbon fiber composite and hybrid fiber (glass fiber/carbon fiber)-reinforced polymer composite (HFRC) by secluded pores/voids and capillary movement shown schematically in Fig. 3. In hybrid composites in particular, the path of water diffusion is redirected or blunted by the alternative fiber layer, resulting in a reduction in the overall water diffusion of the composites. The reduced seawater uptake of hybrid composites is attributed to the strong bonding of the interface between the different layers of fibers and thus the matrix, resulting in water uptake being halted by uneven swelling during seawater aging. Good interfacial

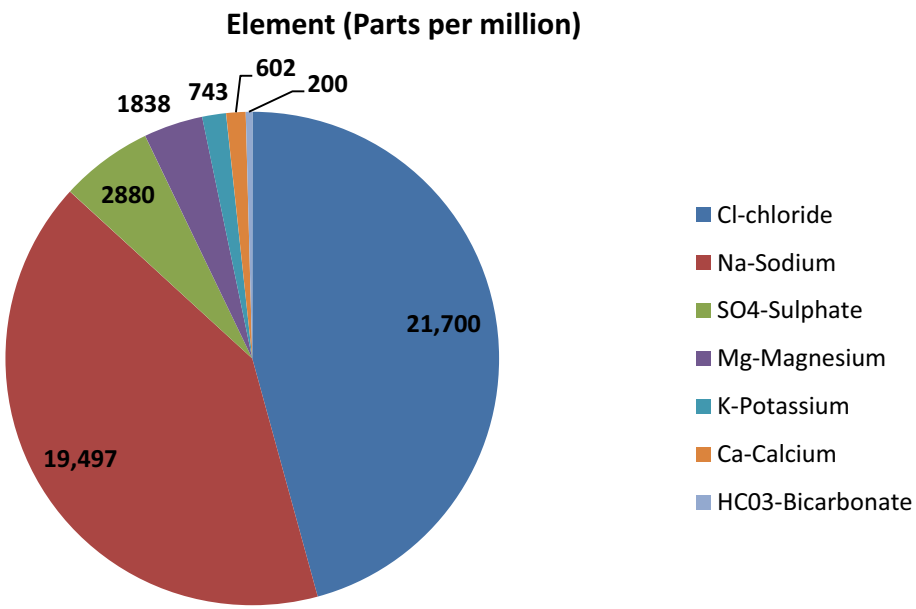

Fig. 2 Ion concentration dissolved in the seawater [20]

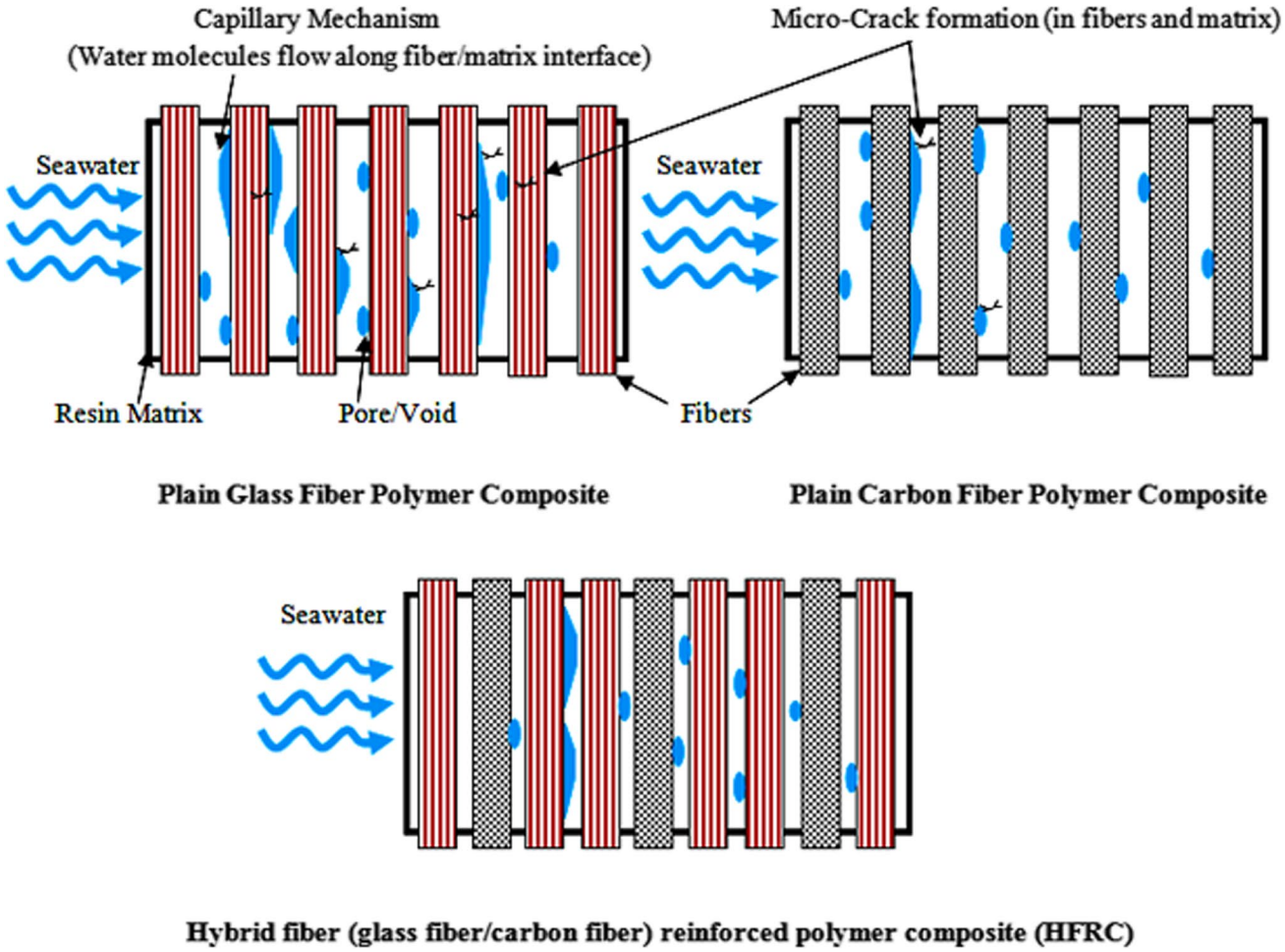

Fig. 3 Seawater absorption mechanism in fibrous-reinforced polymers (FRP) composites [16]

bonding also reduces the tendency for seawater uptake by capillary movement [16]. The interface is the most critical part and plays a crucial role in deciding the overall performance of FRP composites in marine structures.

The study of moisture absorption is conducted by researcher using the ASTM D 570 [23] and ASTM D 5529 standard [24] by immersing composites in liquid medium and then removing and weighing them at each time interval until saturated. Both standards illustrate in detail the structure and methodology of gravimetric tests to assess the diffusion properties of plastics and polymer composites. Researchers applied seawater (natural or artificial seawater) as aging immersion medium for moistures study in order to understand the marine environmental exposure. However, in order to predict the long-term behavior of FRP composites for the marine environment, the salt concentration of laboratory-made artificial seawater must be similar to that of natural seawater. Seawater composition according to ASTM D1141 standard [25] is shown in Fig. 4. The percentage of moisture absorption after each period is

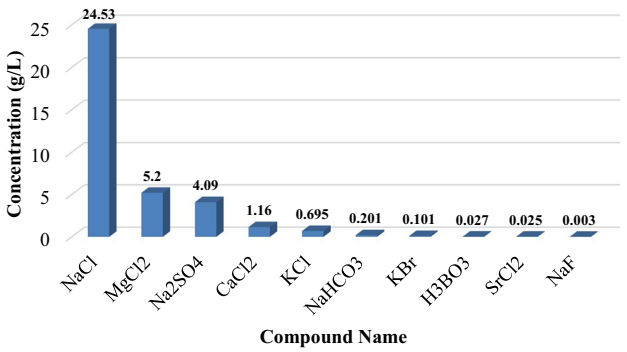

Fig. 4 Standard substitute for seawater as per ASTM D1141 [25]. :

expressed as the weight gain of the sample as a function of time, as mentioned in Eq. (1) [26].

$$M_t(\%) = \frac{(W_t - W_0)}{W_0} \times 100 \quad (1)$$

where M_t is the percentage of moisture absorption after each interval of time; W_0 is the weight of the dry sample (before seawater immersion) and W_t is the weight of the wet sample at time t (after seawater immersion).

(**Note:** Chlorinity of the substitute artificial seawater = 19.38 and Ph value (after adjustment with 0.1 N NaOH solution) = 8).

From the analysis of moisture absorption results, Fick's law of diffusion is used to understand the moisture absorption behavior of the FRP composite. Fluid diffusion in FRP composite materials is typically anisotropic. Diffusivity in the fiber direction is more quickly than in the transverse direction. The moisture diffusivity or diffusion coefficient (D) can be calculated using moisture absorption curve, using Eq. (2) [13].

$$D = \pi\left(\frac{h}{4M_\infty}\right)^2\left(\frac{M_2 - M_1}{\sqrt{T_2} - \sqrt{T_1}}\right)^2 \tag{2}$$

where h is the sample thickness, M_∞ is the weight of the saturated sample and M_1 and M_2 are the moisture absorptions at time T_1 and T_2, respectively

A similar kind of procedure is used by researchers for the assessment of long-term performance. The influence of seawater on mechanical performance and behavior of FRP composite materials by determining the mechanical properties with the final comparison of the dry and weight specimen. Eventually, this is a time-consuming procedure. Accelerated test methods were developed to shorten the test time required. [12, 27, 28]. In the laboratory experiments, moisture diffusion in the FRP composite material is achieved by subjecting it to either a natural or a hygrothermal aging test. The natural aging test is conducted by immersing the material in seawater at room temperature, whereas, the hygrothermal aging test is a phenomenon of an accelerated aging in which the moisture diffusion rate is increased by immersing the materials at high temperature [5]. The wet glass transition temperature of typical marine composites is likely to be positioned between 60 and 80 °C. When FRP composite structures are exposed to temperatures above the glass transition temperature (T_g), the matrix material softens and interlaminar bonding is reduced [9]. Therefore, it is suggested to raise the temperature from 45 to 55 °C that could be an appropriate way to accelerate the conditioning process further [18]. This method is based on the principle of heating the water to create a faster diffusion process, thus reducing the time required to reach the water saturation of the material. Testing takes place in aging chambers under controlled environments with monitored parameters such as temperature, humidity and UV radiation. Table 1 shows an overview of recent studies on the influence of the seawater environment on the degradation of FRP composites. There is consensus in the reported literature that seawater can significantly degrade the properties of FRP composite materials.

The effect of seawater environment on FRP composites resulted in a considerable reduction in durability and performance after exposure for longer durations. The composition of seawater and environmental temperatures are two critical factors influencing the aging behavior of FRP composites used in marine applications. However, the absorbed seawater has a major impact on the mechanical properties of FRP composites. The seawater molecule is in contact with the matrix polymer molecules resulting matrix cracking, pitting, hydrolysis, fiber breakage, plasticization, fracture, delamination and fiber/matrix debonding [11]. A study of moisture absorption and its effect on mechanical properties under the effect of marine environment as seawater aging process was carried out by researchers both on glass fiber and carbon fiber-reinforced polymer composites. Idrisi et al. [29] made an attempt to investigate the mechanical properties on E-glass epoxy composite. It was concluded that the degradation mechanism accelerated at elevated temperature that is 90 °C results in fiber/matrix debonding. In this research study, samples were aged for 360 days in seawater (natural seawater) at different exposure temperatures (23 °C, 65 °C and 90 °C). Seawater absorption was increased at 23 °C and 65 °C, while it decreased at an elevated temperature of 90 °C. Tensile strength was reduced by 1% and 9%, respectively, with a slight change in elastic modulus of the sample immersed at 23 °C and 65 °C, respectively. Conversely, at 90 °C, the tensile strength decreased significantly to 7%, with the modulus of elasticity increasing significantly. Another study of composites by Vizentin et al. [30] reported that glass fiber with epoxy and polyester with three different build configurations, e.g., unidirectional with longitudinal fiber orientation (UD_0), multi-directional (0/90)s and (0/45/90)s, were conditioned in a real seawater environment. The result showed reduction in tensile strength at various levels depending upon the layup configurations and also the mass gain because of seawater moisture absorption and development of microorganism on the composite laminates. However, glass fiber polyester composites with [0/45/90]s layup showed the utmost resilience to the seawater environment. Recently a study of Gunoz et al. [31] instigated some important mechanical properties that is hardness and density values of glass fiber epoxy composite pipes under the effect of seawater (natural seawater). The specimens were subjected to high salinity seawater aging (Mediterranean seawater) for the period of 30 days, 60 days and 90 days. The result showed that changes in mechanical properties of specimen that is increase in hardness value due to the epoxy damage and increase in density value due to deviation in fiber volume ratio.

Padmaraj et al. [26] studied the influence of aging on the fatigue performance of quasi-isotropic glass fiber epoxy

Table 1 An overview of state-of-the-art studies on the effect of seawater environment on degradation of FRP composites

S.N.	References	Types of specimens		Approach	Types of conditioning			Accelerated test	Moisture absorption (↑-Increase and ↓-decrease)	Mechanical property (↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp			
1	Idrisi et al. [29]	Glass fiber	Epoxy	Elevated temperature of seawater environment	Natural seawater	360 days	23 °C, 65 °C and 90 °C	AT	↓ at elevated temperature and ↑ at 23 °C and 65 °C	Significant ↓ in tensile strength elevated temperature
2	Goran et al. [30]	Glass fiber	Epoxy and polyester	Three different layup configuration such as unidirectional (UD_0), multi-directional (0/90)s and (0/45/90)s	Real seawater	180–365 days	Sea temperature 10–14 °C	–	↑ in moisture absorption	↓ in tensile strength
3	Gunoz et al. [31]	Glass fiber	Epoxy	GFRP pipes with a winding angle of ± 55	Natural seawater	30, 60 and 90 days	25 °C	–	↑ in moisture absorption	↓ in mechanical properties
4	Padmaraj et al. [26]	Glass fiber	Epoxy	Quasi-isotropic laminate at different temperature condition	Artificial seawater	180 days	Ambient, sub-zero and humid environment	–	↑ in moisture absorption	↓ in fatigue properties
5	Padmaraj et al. [28]	Glass fiber	Polyester	–	Artificial seawater	60 days	–	AT	↑ in moisture absorption	↓ in mechanical properties
6	Pavan et al. [32]	Glass fiber	Epoxy	Stacking sequence [0°/90°/+45°/−45°]s	Artificial seawater	150 days	Sub-zero and ambient temperatures	–	↑ in moisture absorption at ambient temperatures	Reduction in tensile strength
7	Chakravarty et al. [22]	Glass fiber	Epoxy	18ply Glass fiber layup, glass transition temperature	Natural seawater	60, 120, 180, 240, 300 and 360 days	Room temperature	–	↑ in moisture absorption	↓ in mechanical properties.as the immersion period increases
8	Oguz et al. [33]	Glass fiber	Epoxy	Specimens with different length/width (L/w) ratios	Artificial seawater	42 days	25 °C and 70 °C	–	Higher ↑ in moisture absorption for increase in L/w ratio	–
9	Cavasin et al. [34]	Glass fiber	Epoxy	New evaluation testing tool for long term exposure of seawater	Artificial seawater	365 days	25–80 °C	–	Higher value of diffusion kinetics as the temperature rises	Not reported in paper

Table 1 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Accelerated test	Moisture absorption (↑-Increase and ↓-decrease)	Mechanical property (↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp			
10	Garcia-Espinel et al. [35]	Glass fiber	Polyester, vinyl ester and epoxy	Long term effect on composites	Natural seawater	65, 210 and 810 days	Ambient temperature	–	Epoxy-based glass fiber composites become stabilized after attaining the moisture saturation level	↓ in flexural properties of epoxy and vinyl ester-based glass fiber composites
11	Boisseau et al. [36]	Glass fiber	Epoxy	Long term behavior	Natural seawater	912 days	60 °C	–	↑ in moisture absorption as the duration increases No significant effect on fiber type	↓ in quasi-static mechanical properties
12	Mourad et al. [37]	Glass fiber	Epoxy	Specimens immersed in Arabian Gulf seawater for long term duration (High contents of ion concentration)	Natural seawater	2700 days	Room temperature, and 65 °C	–	Gradually ↑ in moisture absorption due to long term immersion time at higher temperature	Higher ↓ in in tensile strength at higher temperature
13	Mourad et al. [20]	Glass fiber	Epoxy	Specimens immersed in Arabian Gulf seawater (High contents of ion concentration)	Natural seawater	90, 180 and 365 days	Room temperature (RT) and 65 °C	–	Gradually ↑ in moisture absorption due to long term immersion time at higher temperature	No major changes in tensile strength and modulus for initial period ↓ in tensile strength.by small amount after 90 days
14	Mungamurugu et al. [38]	Glass fiber	Unsaturated polyester, epoxy resins and vinyl ester	Long term effect of seawater on different matrix composites	Artificial seawater	360 days	At various temperatures	–	Less amount of ↑ in moisture absorption in vinyl ester-based composites	Minor amount of percentage ↓ in flexural strength for vinyl ester-based composites compared to others

Table 1 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Accelerated test	Moisture absorption (↑-Increase and ↓-decrease)	Mechanical property (↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp			
15	Kennedy et al. [39]	E-glass or E-CR glass	Epoxy or vinyl-ester	(±45°/90°/0°)s Quasi-isotropic layup, long term seawater effect	Natural seawater	912 days	30–40 °C	AT	Lowest moisture absorption in both the epoxy and vinyl-ester composites	Decrement in static failure strength in vinyl-ester/E-glass composites Significant decrease in fatigue strength
16	Hassan et al. [40]	Glass fiber	Epoxy	Stitching of glass fiber by kevlar thread	Natural seawater	24 and 35 days	RT	–	Higher amount of ↑ in moisture absorption	↓ in interlaminar fracture toughness
17	Guen-Geffroy et al. [41]	Carbon fiber	Epoxy	Unidirectional stacking sequence	Natural seawater	120 days	60 °C	AT	↑ in moisture absorption at saturation level	↓ in interlaminar shear strength
18	Guen-Geffroy et al. [42]	Carbon fiber	Epoxy	Unidirectional stacking sequence	Natural seawater	105 days	60 °C	AT	↑ in moisture absorption	Changes in fracture toughness property
19	Gargano et al. [43]	Carbon fiber	Vinyl ester	Explosive blast loading on composite laminate	Artificial seawater	90 days	30 °C	–	↑ in moisture absorption	Significantly↓ (20–30%) in the mechanical properties because of plasticization
20	Li et al. [44]	Carbon fiber	Epoxy	Variations of properties	Artificial seawater	120 days	Room temperature	–	↑ in moisture absorption almost linearly at the beginning after that it became stable	Initially ↓ trends of tensile strength then after recovered Significantly ↓ in the bending strength ↑ in the longitudinal-transverse shearing strength
21	Prabhakar et al. [45]	Carbon fiber	Vinyl ester	Edges of the specimens were sealed with vacuum-sealant tape	Artificial seawater	120 days	Room temperature	–	↑ in moisture absorption	↓ in fatigue life of seawater saturated specimens

Table 1 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Accelerated test	Moisture absorption (↑-Increase and ↓-decrease)	Mechanical property (↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp			
22	Li et al. [46]	Carbon fiber	Epoxy	Different temperatures and NaCl concentrations of seawater	Artificial seawater	210 days	50–70 °C	–	↑ in moisture absorption	Rapid ↓ in tensile strength during the first 90 days
23	Li et al. [47]	Carbon fiber	Epoxy	Seawater temperature and NaCl concentration	Artificial seawater	210 days	70 °C	–	↑ in moisture absorption	↓ in interlaminar shear strength
24	Hong [48]	Carbon fiber	Epoxy	Long term hygrothermal aging effect	Natural seawater	Upto 547 days	Ambient, 66, 93, 121, 149,177, 204, 232, and 260°C	–	↑ in moisture absorption	↓ in short beam shear strengths
25	Koshima et al. [21]	Carbon fiber	Epoxy	Stacking sequence [(0°/90°)/(±45°)]s, [(0°/90°)/(±45°)]2s	Natural seawater	100, 225 and 385 days	20 °C	AT	↑ in moisture absorption	↓ in mechanical properties
26	Nandagopal et al. [49]	Carbon fiber	Epoxy	Synergetic effect of the layup sequence, stress ratio and hygrothermal aging	Natural seawater	30 and 90 days	60 °C	–	Progressively ↑ in moisture absorption for constrained laminate specimens	↓ in fatigue properties of the unconstrained laminate
27	Tual et al. [50]	Carbon fiber	Epoxy	Long term behavior of different carbon epoxy composites	Natural seawater	100, 225 and 385 days	60 °C and 80 °C	AT	↑ in moisture absorption at higher temperature	↓ in tensile strength and interlaminar shear strength
28	Ghabezi et al. [51]	Glass fiber, carbon fiber	Epoxy	Hygrothermal aging effect	Artificial seawater	270 days	Room Temp and 60 °C	AT	↑ in moisture absorption at higher temperature	Significantly ↓ in tensile and shear strengths of glass fiber epoxy composites Conversely, the more ↓ in flexural properties of carbon fiber composites than glass fiber composites

Table 1 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Accelerated test	Moisture absorption (↑-Increase and ↓-decrease)	Mechanical property (↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp			
29	Ghabezi et al. [27]	Glass fiber, carbon fiber	Epoxy	Layup sequence and orientation of fibers	Artificial seawater	1552 days (carbon fiber composite) and 370 days (Glass Fiber composite)	Ambient temp and 60 °C	AT	↑ in moisture absorption	↓ in tensile strength and flexural strength
30	Jose-Trujillo et al. [52]	Glass and carbon fiber	Epoxy, vinyl ester and polyester	Different fiber and matrix types	Artificial seawater	50 days	40 °C	AT	↑ in moisture absorption for epoxy-based composites	Substantial ↓ in strength of epoxy and polyester-based composites
31	Boisseau et al. [53]	Glass and carbon fiber	Epoxy, polyester	Long term durability effect, different fiber orientation	Natural seawater	240 days	50 °C	–	↑ in moisture absorption for Glass fiber epoxy composite	Positive effects resulted in fatigue properties of carbon epoxy composite

laminates. The samples were aged for 180 days in seawater (artificial seawater) at ambient, sub-zero and wet conditions. The results showed that the growth of fatigue damage depends on the aging conditions and the percentage of moisture content. Similarly, recent studies focus on aging of composite structures in seawater (artificial seawater); Padmaraj et al. [28] studied the mechanical properties of fiberglass-polyester composites for a maximum duration of 60 days using an accelerated aging test. The results of the tensile and impact tests showed that the deterioration in maximum strength value was reduced by 23% and 41% for samples aged 60 days in seawater compared to dry samples. Similar trends in flexural properties, namely a 50% reduction, were observed at the initial 20 days immersion time due to a higher rate of water absorption and higher swelling of the composites. The rate of change in flexural properties should be significantly influenced by moisture absorption. Flexural strength decreased by 72% for 60 days aged samples compared to dry samples. Pavan et al. [32] conducted a study on quasi-isotropic glass fiber epoxy composites immersed in artificial seawater for 150 days at ambient and sub-zero temperatures. The moisture absorption profile at ambient temperatures, the composites absorbed 13.22% seawater to equilibrium, but the greatest seawater absorption at equilibrium was 2.61% for conditions below zero degrees. According to study the result revealed that plasticization reduces tensile stress by 27%, whereas failure in the composite is mainly caused by fiber failure and cracks in the reinforcement/resin interface. To understand the influence of the marine environment on the glass transition temperature and composite weight of fiberglass-epoxy composites, a study by Chakravarty et al. [22]. The results showed that the glass transition temperature deteriorated and the weight of the composite samples increased. Mechanical properties such as interlaminar shear strength (ILSS), stress and strain at break, and Young's modulus also deteriorate with increasing immersion time. Another study of glass fiber epoxy composites specimen immersed in seawater (artificial seawater) at 25 °C and 70 °C temperatures for 42 days with the approach of different length/width (*L*/*w*) ratios by Oguz et al. [33] showed the higher water absorption for increase in *L*/*w* ratio at elevated temperature. Similarly, a study of Cavasin et al. [34] investigated the evolution glass fiber epoxy composites properties under the effect of seawater (artificial seawater). The result reported the alteration in material properties for higher value of diffusion kinetics with increasing the temperature that is 25–80 °C. Moisture absorption behavior was not completely Fickian for the period of 365 days. Garcia-Espinel et al. [35] investigated the mechanical properties of marine engineering structures made of polyester, vinyl ester and epoxy-reinforced glass fibers under the influence of seawater conditioning over a period of 65, 210 and 810 days. The results revealed that the flexural properties of epoxy and vinyl ester-based glass fiber composites deteriorated. But the degradation in flexural and tensile strengths of epoxy-based glass fiber composites become stabilized after attaining

the moisture saturation level, which indicated that epoxy resin could be safely used for structural design. There is no significant change noted in fatigue life of epoxy-based glass composite either in seawater environment or air. Furthermore, the epoxy matrix composite was suggested to be use in marine structures because of no biodegradation impact on mechanical performance of FRP composites. A study of various glass fiber epoxy composites exposed to seawater by Boisseau et al. [36] showed a reduction in quasi-static mechanical properties by 40–56% and a change in bending mode from compression to tension due to seawater (natural seawater) absorption over longer periods of aging. The strength loss was due to changes in the matrix and the fiber/matrix interface. The fiber type does not have a significant impact on the absorption of saline water. The long-term effects of seawater in the marine environment on E-glass epoxy and E-glass polyurethane were examined by Mourad et al. [37]. The specimens were conditioned in seawater (natural seawater) for the period of 2700 days at room temperature resulted in a minor change in strength. On the other hand, after 1800 days of immersion in seawater at a higher temperature of 65 °C, strength decreased by 47% and remained practically stable until 2700 days (90 months). In his previous research [20] on similar glass epoxy composite material exposed to seawater (natural seawater) for the duration of 360 days at room temperature (RT) and 65 °C, respectively. A little decrement in the tensile strength that is from 794 N/mm^2 (control value) to 788 N/mm^2 and 749 N/mm^2 was recorded for glass epoxy composite. In addition, it was reduced by 19% and 31%, respectively, in seawater at RT and 65 °C over the same exposure time. Another study by Mungamurugu et al. [38] evaluated the long-term performance of glass fiber-reinforced polymer composite by measuring the amount of moisture absorbed and the reduction in mechanical properties over a 360-day period in a seawater environment at different temperatures. Three commonly used polymers with different chemistry such as unsaturated polyester, epoxy resins and vinyl ester were included in this study. Specimens were aged in seawater (artificial seawater) at temperatures including sub-ambient as well as elevated temperatures below the glass transition temperature. The result showed that vinyl ester plaques and composites absorbed less moisture and also showed less reduction in flexural strength compared to unsaturated polyester and epoxy systems. An investigation by Kennedy et al. [39] into the effects of water saturation on the fatigue of glass fiber-reinforced polymers used in the structures of ocean energy. Using an abstemiously accelerated aging process, quasi-isotropic samples with an epoxy or vinyl ester matrix were reinforced with E-glass or E-CR glass and aged in seawater (natural seawater) for up to 913 days. The Hassan et al. [40] studied short-term effect of moisture absorption on the durability of the sample of stitched glass fiber epoxy composite laminates for 24 and 35 days under seawater (natural seawater) at room temperature. The samples were sewn in the z-direction using Kevlar fibers. The study showed that the absorbed seawater increased the weight of the specimen which resulted in swelling of the composites and reduction in interlaminar fracture toughness that is 30% for 24 days and 55% for 35 days due to seawater aging.

A study on the impact of seawater on epoxy-based carbon fiber composites were investigated by Guen-Geffroy et al. [41]. In this experiment, the performance of interlaminar shear strength was evaluated by considering the unidirectional stacking sequence approach. The specimens were immersed in seawater (natural seawater) at 60 °C temperature for the period of 120 days. The result showed that fracture resistance was reduced for the saturated mode I and mode II specimens as compared to dry specimens. Other study of Guen-Geffroy et al. [42] examined the fracture toughness carbon fiber-reinforced epoxy composites exposed to seawater (natural seawater) at 60 °C temperature for the period of 105 days. The result reported that changes in fracture toughness property because of effect of seawater and due to physical aging during the accelerated test. Even for worst case scenario, epoxy-based carbon fiber composites showed the 70% retention of its initial fracture characteristics. In the further study, the impact of seawater absorption on the explosive air blast reaction of a woven carbon fiber vinyl ester composite laminate was identified by Gargano et al. [43]. These types of composite laminates are used for submarines, naval ships, submersibles vessels and offshore structures. The composite panels were immersed in seawater (artificial seawater) for 90 days with the temperature maintained at 30 °C. The result showed that under explosive loading, carbon fiber vinyl ester laminate degrades the polymer matrix and the fiber/matrix interphase region, leading to greater deformation and damage. The absorbed seawater degraded the polymer matrix and the fiber/matrix interphase, resulting in a decrease in compressive, flexural and interlaminar shear properties. These properties were significantly lowered (20–30%) because of plasticization. Another study of epoxy-based carbon fiber polymer composite immersed in seawater (artificial seawater) for the period of 120 days at room temperature by Li et al. [44] showed initially decreased trends of tensile strength then after recovered and significantly decrement reported in the bending strength however with an enhancement in the longitudinal-transverse shearing strength. The increment in moisture absorption was recorded almost linearly at the beginning of the immersion after that it became stable. In another work carried out by Prabhakar et al. [45], flexural fatigue life and damage mechanics of woven carbon-vinyl ester composites under both dry and seawater circumstances were reported. The tests were performed with a displacement-controlled sine wave with a frequency of 1 Hz in three-point bending. These samples were aged in seawater (artificial seawater) at room temperature for a soaking time of 140 days while ensuring moisture saturation. Seawater saturation in carbon-vinyl ester composites

reduced the fatigue life of saturated samples by up to 62% compared to dry samples across all strain ranges. Plasticization of the vinyl ester matrix caused by seawater saturation is responsible for reducing the fatigue life of these composites. Li et al. [46] studied the static and dynamic mechanical properties of carbon fiber-reinforced polymer composites in seawater environments (artificial seawater) over a period of 210 days. The findings demonstrated that aging duration and ambient temperature have an impact on tensile strength. Tensile strength degrades rapidly during the initial aging phase. As the aging process progressed, this decline was gradually slowed. The rapid deterioration during the first 90 days can be caused by debonding of the fiber/matrix interface and delamination induced by moisture absorption and swelling. The study indicates that the concentration of NaCl had no effect on the elastic modulus. However, it is affected by the Poisson's ratio. Another study by Li et al. [47] studied the interlaminar shear behavior of carbon fiber epoxy composites exposed to seawater. For 210 days, the laminate specimens were submerged in seawater (artificial saltwater) at 70 °C. The ambient temperature has a significant impact on the moisture diffusion coefficient and moisture absorption content. The results reported that the shear strength increases in initial period but after gaining the maximum amount of moisture absorption it decreases. This is brought on by the damage to interface characteristics and the release of curing shrinkage stress. The degradation of interlaminar shear strength is because of damaging the fiber/matrix interface. A study on the impact of long-term seawater (natural seawater) on the specimens of carbon epoxy composite by Hong [48] exposed thermally to ambient, 66 °C, 93 °C, 121 °C, 149 °C, 177 °C, 204 °C, 232 °C, and 260 °C for the period up to 547 days. The outcome demonstrated that a maximum weight rise in seawater was mostly caused by a poorer diffusion coefficient because mass loss through the leaching of organic species was greater than mass uptake through sorption of salts. The interlaminar shear strength of short beam were resulted declination at a different temperature. By considering the approach of unidirectional stacking sequence reported by Koshima et al. [21], the effect of long-term that is 100 days, 225 days and 385 days in seawater (artificial seawater) immersion at 20 °C resulting the deterioration of the fiber/matrix interface. The result indicated declination in the fiber/matrix interface load transmission efficiency with reduction in mechanical properties of plain-woven carbon fiber-reinforced polymer composite laminates. Similar to this, a method of combining the stress ratio, layup sequence, and hygrothermal aging on carbon fiber epoxy composite laminate submerged in seawater (natural seawater) at 60 °C for period of 30 and 90 days investigated by Nandagopal et al. [49]. This investigation indicates that hygrothermal aging at both stress ratios caused the unconstrained laminate's fatigue characteristics to deteriorate.

According to study on long-term behavior of different carbon epoxy composites subjected to seawater (natural seawater) aging at different temperatures using accelerated aging tests conducted by Tual et al. [50]. For tidal turbine blade applications, carbon fiber epoxy composites are synthesized using three distinct techniques: prepreg autoclave, resin transfer molding, and vacuum infusion. Results reflected that seawater absorption affects tensile strength and interlaminar shear strength (reduced by 20–30%) because of the matrix plasticizes and the fiber/matrix interface deteriorates. Due to the evolution of glass transition temperature throughout aging process, weight gain at higher temperature (60 °C and 80 °C) was elevated than the lower conditions. The thickness and orientation of the composite have a minor impact on water diffusion, which is unaffected by the specimen's geometry. A recent study by Ghabezi et al. [51] studied the hygrothermal degradation of carbon fiber and glass fiber epoxy composite laminates in marine environments. The specimens were immersed in seawater (artificial seawater) at room temperature and an elevated temperature of 60 °C for a period of 180 days. The results revealed that the degradation mechanism with the change in mechanical properties persists even after the saturation point has been reached in both composite laminates. Another study on the long-term performance of carbon fiber epoxy composite and glass fiber epoxy composite laminates in a seawater environment conducted by Ghabezi et al. [27]. Using accelerated aging test in seawater (artificial seawater) for the period of 45 days at 60 °C temperature resulted reduction in tensile strength (10.67%) and flexural strength (7.7%) of carbon fiber epoxy composite, respectively. In the event that glass fiber epoxy composites experienced a decrease in tensile strength (21.3%) and flexural strength (8.62%). At room temperature, similar decreases in mechanical characteristics have been noted. The long-term behavior of these composites on the basis of service condition was also predicted by using Arrhenius degradation theory. Similar reinforcement along with carbon and glass fiber used as composite laminate immersed in seawater (artificial seawater) for the period of 50 days at 40 °C by Jose Trujillo et al. [52] showed that substantial strength loss due to seawater aging on composites with epoxy and polyester matrices. Also reported great amount of moisture absorption in epoxy-based composites compared to vinyl ester-based composites. The comparative study of fatigue behavior investigated by Boisseau et al. [53] on three different composite materials differs by fiber orientation, fiber/matrix type, and manufacturing process. The glass/epoxy, carbon/epoxy and glass/polyester composite samples were immersed in seawater (artificial seawater) at 50 °C, resulting in the carbon epoxy composite being the best compared to the other materials achieved results. An effect of seawater aging on FRP composite materials leading to failure in marine application as shown in Fig. 5. During

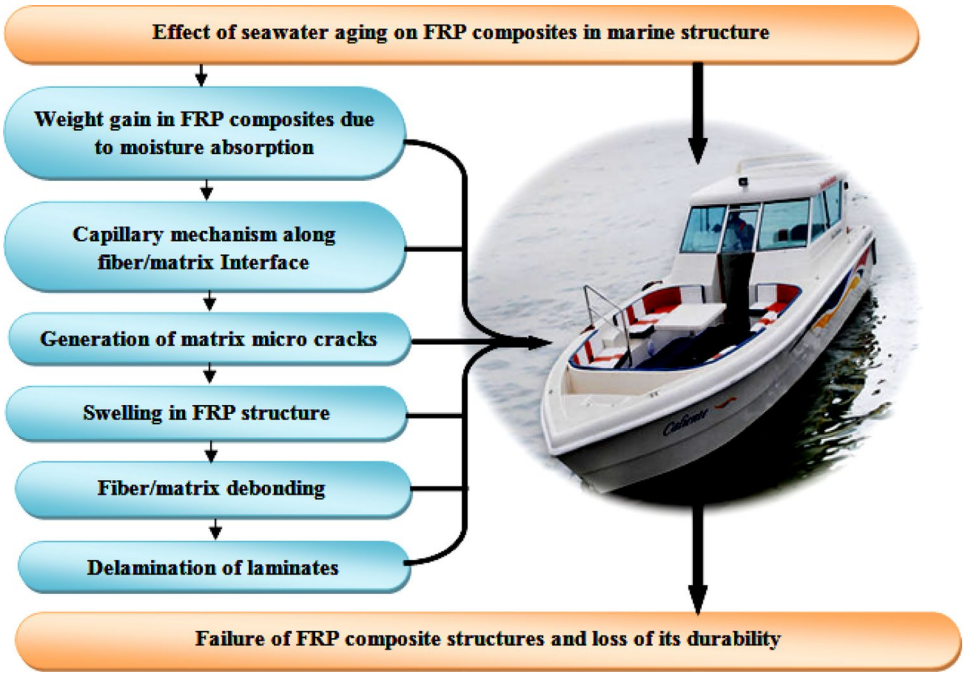

Fig. 5 Failure of FRP composite structure under the effect of seawater aging in marine application

the service life of FRP material system, all these defects that originated at a small point and progressed as cracks resulting in unexpected failures and durability loss.

Approaches for Improving the Mechanical Properties of Polymer Composites in Marine Application

The properties of marine FRP composite are deteriorated throughout the span of their service life due to the very corrosive environment caused by seawater's alkaline composition. Previous research has explored key approaches such as coating of fiber surfaces, hybridization in fiber and matrix with or without nanofiller, and interlayer rearrangement to improve mechanical properties under the influence of seawater. These approaches are helpful for reducing and controlling the damage mechanism in FRP composites caused by seawater moisture absorption. Table 2 shows an overview of studies on improving the mechanical properties of polymer composites in marine application with most significant approaches.

Coating on Fiber Surface

Coating on fiber surface plays a vital role in improving the interfacial performance of fiber and matrix. Different types of coating like ester, polyurethane, gel coat and epoxy etc. have been used in naval structures and marine environments to increase the durability of composites. In the recent, nanofiller coatings like silica-based coating, graphene oxide, alumina, nano-clay, and carbon nanotubes (CNTs) or hybrid coatings has caught more and more attention in the improvement of interfacial modified technology. So far, different methods have been described in the literature about incorporation of carbon nanotubes (CNTs) on surface of fibers, matrix polymer or both by using chemical vapor deposition [76], dipping [77], polymer sizing [58], electrophoretic [78] and spray coating deposition [79]. Among these methods, deposition by spray coating is the simplest method for applying and dispersing nanomaterials onto substrates. The key benefits of this technique include potential industrial scale, ease of processing, and relatively inexpensive tooling. It is also one of the most effective methods now a day for integrating CNT in the preparation of composite laminates that are useful for improving the flexural properties, fracture properties, and impact resistance properties even though under the effect of seawater aging [13, 54, 79].

A study of depositing 0.25 wt% multiwall carbon nanotubes (MWCNTs) onto all ply interfaces of glass fiber epoxy composite using a spray coating technique investigated by Rodriguez-Gonzalez et al. [13]. The outcome demonstrated that the wet glass fiber epoxy laminate's favorable impact on its moisture absorption behavior, mode II interlaminar fracture characteristics, and improvement of the G_{IC} was around 50% greater than that of the neat laminate at dry conditions. Another study by Rubio-Gonzalez et al. [54] examined the effects of coating unidirectional glass fiber fabrics with 0.75 wt% MWCNTs using a spray coating technique and resin (epoxy or vinyl ester) aging in seawater. The specimens were immersed in seawater (artificial seawater) at 60 °C for 83 days. The result stated that retention in the

Table 2 An overview of studies on improving the mechanical properties of FRP composites in marine application with most significant approaches

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
Coating															
1	Rodriguez-Gonzalez et al. [13]	Glass fiber	Epoxy	0.25 wt% MWCNTs deposition on interfaces of all ply with Spray coating	Artificial seawater	163 days	70 °C							√	↓ in moisture absorption behavior and ↑ in mode II interlaminar fracture properties
2	Rubio-Gonzalez et al. [54]	Glass fiber	Epoxy/vinyl ester	0.75 wt% MWCNTs deposition on interfaces of all ply with Spray coating	Artificial seawater	83 days	60 °C						√		Retain the moisture absorption and greater amount of energy absorption in MWCNTs coated composites
3	Rodriguez-Gonzalez et al. [55]	Glass fiber	Epoxy	MWCNT (0%, 0.25%, 0.50%, 0.75%and 1 wt%) with spray coating	Artificial seawater	55 days	63 °C			√					Gradual ↑ in moisture absorption with immersion time ↓ in flexural properties
4	Rodriguez-Gonzalez et al. [56]	Carbon fiber	Epoxy	Deposition of MWCNTs, RGO, and hybrid combination of MWCNT/RGO at the middle plane interface with Spray coating	Artificial seawater	55 days	70 °C							√	Positive effect on their behavior moisture absorption and (mode I/mode II) interlaminar fracture properties

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
5	Mansouri et al. [14]	E glass fibers	Epoxy	Gel coating	Natural seawater	At different duration 2 days, 30 days and 365 days	At different temp.40 °C, 60 °C and 80 °C			√					Higher ↑ in mechanical properties with ↓ of coefficient of diffusion for woven composite with gel coated aged in seawater
6	Mamalis et al. [57]	Carbon fiber e (5 °C, F0E & 60E)	Epoxy (powder)	Coating of fiber sizing agent (0.3%, 7% and 1wt%)	Natural seawater	90 days	50 °C					√			↓ in the moisture absorption for modified composites Significantly ↓ in flexural strength due to hydrothermally seawater aging
7	Gargano et al. [58]	Carbon fiber	Vinyl ester	Coating of fiber sizing agent	Artificial seawater	210–900 days	Room temperature	√	√	√		√		√	↓ in the moisture absorption ↑ in the mechanical property due to strong bonding between the fibers and polymer matrix

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
8	Yu et al. [59]	Carbon fiber	Epoxy	Silane coating and MWCNTs modified silane coating on the surfaces of carbon fibers	Artificial seawater	120 days	50 °C				√				↑ in interlaminar shear strength with ↓ in the moisture absorption for modified composites
9	Gibhardt et al. [60]	E-glass fiber	Epoxy	Silane coating on E-glass fiber	Natural seawater	62 days	50 °C				√				Major ↓ in fatigue life due to ↑ in the moisture absorption under accelerated test
Hybridization															
1	Ulus et al. [15]	Basalt fiber	Epoxy	Hybrid laminates with 2 wt% of Halloysite nanotubes (HNTs)	Natural seawater	180 days	Room temperature					√		√	Remarkably ↑ in the fracture performance with an addition of HNTs in epoxy
2	Komorek et al. [61]	Glass fiber and woven carbon fiber	Epoxy	Glass and carbon fiber hybrid laminates	Natural seawater	36 days	15 °C			√			√		↑ in the flexural strength for hybrid type of reinforcement as compared to others ↓ in the Impact strength

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
3	Bal et al. [62]	CNT	Epoxy	CNT (0.5, 0.75, and 1 wt%) hybridization, dispersion method by ultrasonication	Natural seawater	180 days	30 °C			√					↑ in flexural strength of 0.5% CNT than others with ↓ moisture absorption Maximum ↓ observed for all specimens from the second month to the fourth month due to ↑ of moisture absorption
4	Bal et al. [63]	Glass fiber	Epoxy	Partially Aligned CNT (0.5, 0.75, and 1 wt%) hybridization, dispersion method by ultrasonication	Natural seawater	180 days	30 °C			√					↑ in flexural properties and glass transition temperature for 0.75 wt% of CNT with ↓ moisture absorption

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
5	Saha et al. [64]	Functionalized MWNT	Epoxy	Functionalized MWNT (0%, 0.50%, 0.75% and 1 wt%) hybridization, dispersion method by ultrasonication	Natural seawater	180 days	Room temperature			√					Least moisture absorption with least ↓ in properties in all aspects with 0.75 wt% of CNTs composites
6	Anandet al. [65]	Glass fiber	Epoxy	0.5 w% graphene oxide (GO) hybrid composites	Natural seawater	270 days	30°			√					↑ in flexural strength ↓ seawater absorption in GO modified composite than the neat GE composite
7	Garg et al. [66]	Glass fiber	Epoxy	MWCNTs alignment hybridization, dispersion by ultrasonication, restriction of water through specimen edges	Simulated seawater	121 days	Room temperature			√					↑ trends in flexural strength, ILSS, and elongation at break with immersion of time for the specimen Significantly minor equilibrium water content and diffusion coefficient

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
8	Imran et al. [67]	Carbon fiber	Epoxy	1–3 wt% of nano-clay	Simulated seawater	180 days	Room temperature		√						↑ in the compression properties ↓ in moisture absorption
9	Silva et al. [68]	Carbon fiber	Epoxy	Modification of matrix by natural reinforcement that is cork powder	Seawater	90 days	Room temperature and 60 °C						√		Minimum ↓ in impact strength for cork-filled modified epoxy laminates ↓ in moisture diffusion between the cork/matrix interfaces
10	Nayak et al. [69]	Glass fiber	Epoxy	Different concentration of nanofillers − 0.1 wt% of Al_2O_3 and 0.1 wt% of TiO_2 hybridization	Natural seawater	40 days	70 °C			√		√			↓ in the moisture diffusion coefficient ↑ in residual interlaminar shear strength and flexural strength

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
11	Swami et al. [70]	Glass fiber	Vinyl ester	Vinyl ester mixed with SiO_2 and silicon oil filler	Artificial seawater	56 days	Room temperature	√		√					Positive ↑ in tensile strength and flexural strength with minimum ↓ in moisture absorption due to synergistic effect of nano-filler
Interply rearrangement															
1	Jesthi et al. [16]	Glass fiber, carbon fiber	Epoxy	Symmetric interply stacking sequence of carbon and glass fiber, glass to carbon fiber ratio by weight is 72:28	Natural seawater	90 days	Room temperature	√		√			√		Greater ↑ in flexural strength with minimum moisture absorption
2	Jesthi et al. [71]	Glass fiber, carbon fiber	Epoxy	Plain glass, plain carbon and a hybrid composite $[G_2C_2G]_S$	Natural seawater	90 days	Room temperature	√		√			√		↓ in mechanical properties (tensile strength, flexural strength and impact strength) of hybrid composites $[G_2C_2G]_S$

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
3	Tcherbi-Narteh et al. [72]	Glass fiber, carbon fiber	Epoxy	Different profiles of carbon and glass fiber [5C-3G-5C] and [2G-9C-2G]	Artificial Seawater	120 days	Room temperature			√					Least amount of seawater absorption in [2G-9C-2G] hybrid composite ↓ in flexural strength but slight ↑ in flexural modulus and ↓ in glass transition temperature (Tg) for all composites
4	Abd El-baky [73]	Glass (G)–polypropylene (P)	Epoxy	Interply stacking sequence of glass (G)-polypropylene (P) fibers	Natural Seawater	350 days	Room temperature						√		Controlling of moisture absorption rate and impact performance
5	Nandagopal et al. [49]	Carbon fiber	Epoxy	Layup sequence: Unconstrained $[0_6]$, and constrained $[\pm 45/03]_S$ laminates	Natural seawater	30 days and 90 days	60 °C			√					↓ in the flexural strength due to ↑ in moisture absorption

Table 2 (continued)

S.N.	References	Types of specimens		Approach	Types of conditioning			Mechanical performance							Findings -Moisture absorption—(↑-Increase and ↓-decrease) and -Mechanical property—(↑-Improvement and ↓-deterioration)
		Fiber	Matrix		Environment	Days	Temp	T	C	FLX	F	ILSS	I	ILFT	
6	Oguz et al. [74]	Glass fiber, aramid fiber	Epoxy	Stacking sequence of glass fiber and aramid fiber $[G_3A_3]_S$, $[A_3G_3]_S$	Natural seawater	42 days	25 °C and 70 °C			√			√		↓ in flexural strength of hybrid composites ↓ in impact strength of all composites by ↑ in temperatures
7	Muralidharanl et al. [75]	Carbon, glass fiber	Epoxy	Stacking sequence of (C5G4)	Natural seawater	50, 150, and 300 days	20 °C, 40 °C., and 60 °C	√							Gradually ↓ in tensile stress retention for the increment in the time period due to ↑ in moisture absorption

Note:Tensile testing = T, Compression testing = C, Flexural testing = FLX, Fatigue testing = F, Interlaminar shear strength = ILSS, Impact testing = I, Interlaminar fracture toughness = ILFT

moisture absorption along with resulted higher absorbed energy in MWCNTs coated composites because additional failure modes including bridging, pull-out, and breaking have developed. Similarly, by using the spray coating techniques on the glass fiber epoxy composite laminates by (0.25 wt%, 0.50 wt%, 0.75 wt% and 1 wt%) multi-walled carbon nanotubes (MWCNTs) under the effect of seawater investigated by Rodriguez-Gonzalez et al. [55] indicated that reduction in their flexural mechanical properties. The specimens were immersed in seawater (artificial seawater) at 63 °C for a period of 55 days. The flexural modulus, flexural strength, and elongation at break in wet specimens without MWCNTs were reduced by 17%, 14%, and 18%, respectively. This was happened mainly due to the changes in the matrix leading to plasticization and swelling, resulting in fiber/matrix interface degradation /Matrix performs interface in the composite. Except for the 0.75 wt% MWCNT, the results for wet specimens with MWCNTs showed a similar downward trend. It was also found that when composite laminates were treated with MWCNTs, the diffusion coefficient and saturation values increased moderately. In another study [56], the deposition of MWCNTs, RGO, and hybrid MWCNT/RGO combinations at the midplane interface of carbon fiber epoxy composites was investigated using a spray coating technique. The specimens were immersed in seawater (artificial seawater) for the period of 55 days at 70 °C resulting in an improvement of G_{IC} and G_{IIC} by 39% and 4% for MWCNTs, 53% and 8% for RGO and 57% and 13% MWCNT/RGO hybrid combination, respectively. Similarly, mixed short fiber/fabric composite laminates with and without a gel coating under the influence of hygrothermal aging by Mansouri et al. [14] demonstrated a higher value of Young's modulus, yield strength and ultimate stress of woven composite with gelcoat aged for different periods of time and at different temperatures. This sample, whose surface is covered with a gel coat, is better protected from the seawater environment (natural seawater), which helps reduce the diffusion coefficient. Another recent study of study Mamalis et al. [57] conducted under seawater (natural seawater) aging on mechanical properties of unidirectional carbon fiber-reinforced epoxy composites containing fibers with coating of three different (0.3%, 7% and 1 wt%) and powder epoxy resin. The result revealed that reduction in the moisture absorption for modified composites and higher degradation in fiber/matrix interfacial strength due to greater amount of sizing for the period of 90 days at 50 °C. Similarly, Gargano et al. [58] examined the effect of two types of coating of fiber sizing agents with chemically compatible and without chemically compatible carbon fiber vinyl ester composite under the effect of seawater. The both the laminates were immersed in seawater (artificial seawater) for up to about 210 and 900 days, respectively. The results showed that the rate of absorption and the maximum amount of seawater absorbed at saturation were significantly reduced by the sizing coating to allow for strong bonding between the fibers and the matrix of the composites. The interfacial strength was reduced more by the incompatible sizing agent (~60%) than the compatible agent (~40%). A study of Yu et al. [59] investigated the interlaminar shear strength property with an strengthened bonding between interfaces and fiber/matrix stability for the period of 120 days of seawater (artificial seawater) aging at ambient temperature. A study by Yu et al. [80] investigated the interlaminar shear strength property of nanofiller-modified carbon fiber epoxy composites for strengthening the interfacial bond and fiber/matrix stability under seawater (artificial seawater) for a period of 120 days at ambient temperature. The outcome of the study showed an increase in interlaminar shear strength of 14.5% and 26.3% for silane coatings and multi-walled carbon nanotubes (MWCNTs)-modified silane coatings on the surfaces of carbon fibers, respectively. On the other hand, silane coating of E-glass fiber epoxy composite laminate under the effect of seawater (natural seawater) investigated by Gibhardt et al. [60]. The result indicated that major reduction in fatigue life of 50% for unidirectional glass fiber-reinforced epoxy matrix laminates for the period of 62 days at 50 °C by using accelerated test.

Hybridization in Fiber and Matrix with or Without Nanofiller

A cutting-edge method for creating FRP composites, hybridization blends two or more fibers from several groups in a single matrix to control desired qualities. Fabrics can now be customized to meet individual needs due to the hybridization approach. With a single type of reinforcement, it might be challenging to achieve balance and more desirable qualities but the hybridization approach provided this opportunity. With this approach, composites made from glass and carbon fibers in the polymer, so-called hybrid fiber-reinforced polymer composites (HFRC), exhibit higher strength and lower weight compared to simple glass fiber-reinforced polymer composites [81]. With the advent of nanotechnology and the consequent advancement of a new class of materials called nanomaterials, it has been found that the integration of these materials into composites that is nano-hybrid composite can boost the different properties of composites [80, 82].

The characteristics of composites are significantly influenced by different types of nano-filler materials. Modification of the matrix with a new type of nanofiller, namely halloysite nanotubes (HNTs), which acts as a barrier against saline water absorption and to improve delamination resistance without affecting thermal properties such as glass transition temperature of marine composites [15], and having good fire retardancy [83]. HNTs, a novel class of nanofillers, have recently attracted study interest as a means

of enhancing the mechanical behavior and performance of polymers [84, 85]. Ulus et al. [15] reported remarkable improvement in the fracture performance that is around 43% increase using 2 wt% of Halloysite nanotubes (HNTs) in the modification of epoxy without fiber. After 6 months of seawater (natural seawater) aging period, the hybrid composite (HNT modified epoxy with basalt fiber) improved by 52% and 34% in interlaminar shear strength and mode I interlaminar fracture toughness values compared to neat composite. The application of HNTs in FRP evidenced to be an effective means of improving the delamination resistance of marine composites under the influence of seawater aging. In the same context, Komorek et al. [61] investigated that hybrid laminates with glass and carbon reinforcement (HFRC) resulted in a 19% increased flexural strength relative to glass reinforcement. The hybrid laminates were immersed in the seawater (natural seawater) for the period of 36 days at 15 °C. Natural aging and exposure to seawater have little effect on flexural strength, and impact loading also results in an overall strength loss of 33%. By using the same hybridization approach in CNT-based epoxy composite containing 0.5 wt%, 075 wt% and 1 wt% of MWCNT conducted by Bal et al. [62] an immersing the specimen for the duration of 180 days in seawater (natural seawater) at 30 °C. The results showed a maximum degradation occurred in all specimens from 60 to 120 days and flexural strength of 0.5 wt% MWCNT in seawater was less deteriorated (that is 61%) than others. It was found that the swelling of epoxy matrix which causes wrapping of matrices around CNT. Another study [63] was performed by the same researcher on the mechanical properties of nanocomposites filled with different filler contents; 0.5% by weight, 0.75% by weight and 1% by weight of CNT in epoxy resin appeared in sea water (natural sea water) and kept at a constant temperature of 30 °C for 180 days. For 0.75 wt% CNT loading recorded minimum decrease in flexural properties and glass transition temperature value with less moisture absorption. Similar results were also found in the study by Saha et al. [64] reported. In the same vein, Anand et al. [65] conducted hybrid composites of glass fiber and modified epoxy resin with 0.5 wt% graphene oxide (GO) immersed in seawater (natural seawater) at 30 °C for 270 days. The study reported that seawater absorption is lower compared to pure glass fiber epoxy composite and also showed an improvement in flexural strength and modulus by 13% and 18%, respectively. Garg et al. [66] selected reinforced glass fiber epoxy composites with pristine or amino-functionalized carbon nanotubes. These samples were immersed in seawater (artificial seawater) for a period of 121 days and showed better results with significantly lower equilibrium water content and diffusion coefficients due to the high resistance and water-repellent properties of CNTs. In comparison with both pure CNT composites, the mechanical performance of carbon nanotube-based composites with amino functionalization has generally responded better to the seawater aging environment. In another investigation conducted by Imran et al. [67] used the small amount nanofillers such as nanoclay of 1–3% by weight in carbon epoxy composites. It was concluded that the improvement in mechanical performance and the reduction of 0.39% of moisture absorption for 2 wt% nanophased composites due to better interfacial bonding between the fiber and matrix even in seawater (artificial seawater) for a period of 180 days. Similarly, recent research by Silva et al. [68] on carbon fiber epoxy composite laminate with a modification of matrix by natural reinforcement that is cork powder, for a duration of 180 days under seawater (artificial seawater). The findings demonstrated that moisture diffusion between the cork/matrix surfaces was slower as a result of the longer and more complicated routes created by the cork particles. Additionally, cork-filled modified epoxy laminates exhibit a smaller variation in maximum load and recovered energy than carbon epoxy composite laminates. The cork powder acts as an impermeable barrier. Another investigation on the synergistic effects of nanofillers in the glass fiber epoxy composite specimen were exposed to seawater (natural seawater) at 70 °C for 40 days presented by Nayak et al. [69] decreased the water diffusion coefficient by 12% in comparison with the control and other nano-FRP composites. This study used nanofillers with a concentration of 0.1 wt% Al_2O_3 and 0.1 wt% TiO_2. The result reported that the increment in residual flexural strength by 19% and interlaminar shear strength by 21%. With the further increase in concentration of nanoparticles, the flexural strength as well as interlaminar shear strength has been reduced. This can be due to nanoparticle agglomeration and the generation of more pores/voids in nanocomposites. Similarly, a recent study by Swami et al. [70] on the synergistic effect of nanofiller like silicon dioxide and silicon oil into the vinyl ester matrix reinforced with glass fibers composite laminates exposed in seawater (artificial seawater) for a long-term duration of 56 days. Modified composite laminates showed an advancement in tensile and flexural behavior after aging in seawater. Silicon dioxide and silicon oil fillers provided good interfacial bonding and adhesion between fiber and resin.

Interply Rearrangement

One of the important approach, interply rearrangement or stacking sequence of hybrid composite is having the greatest benefits for design optimization in order to achieve improvement in the mechanical properties. A study of Jesthi et al. [16] investigated the effect of stacking sequence on glass fiber/carbon fiber hybrid composites by emerging in seawater (natural seawater) for a period of 90 days at room temperature resulted the highest flexural strength of 462 N/mm^2

with minimum seawater absorption as compared to plain glass fiber-reinforced polymer composites during seawater aging. This property facilitates in the fabrication of the ship's frames and outer body, as well as other marine structures. Also showed the highest impact strength value of $[GCG_2C]_s$ composite compares to the other composite.

Another study with similar aging conditions in seawater for the stacking sequence of $[G2C2G]_S$ hybrid composites was investigated by Jesthi et al. [71]. The result showed deterioration in the tensile strength by 6.4%, the flexural strength by 11.2% and the impact strength by 11.1% of the hybrid composites $[G_2C_2G]_S$ compared to the dry state. On the similar approach, hybrid composites of carbon/E-glass fabrics conducted by Tcherbi-Narteh et al. [72] immersed in seawater (artificial seawater) for 120 days at room temperature, profile of (5C-3G-5C) hybrid composites had highest weight gain while the profile (2G-9C-2G) hybrid had the least absorption. While the flexural strength decreased for all composites, there was slight increase in the flexural modulus. The failures were caused by fibers/matrix under compression on one side and tension on the other of the composite laminate. The investigation of glass-polypropylene fiber-based reinforced epoxy hybrid composites conducted by Abd El-baky [73] an immersing the specimen in seawater (natural seawater) for the duration of 350 days at room temperature. The results showed that a percentage of seawater absorption can be effectively prevented by improving impact performance by altering hybrid arrangement, ply stacking order, and fiber ratio. Another study was investigated by Nandagopal et al. [49] on carbon fiber-reinforced polymer composite material with layup sequence of constrained $[\pm 45/0_3]_S$ and unconstrained $[0_6]$ laminates under the effect of seawater (natural seawater) conditioning for a period of 30 days and 90 days at 60 °C temperature. The investigation revealed a deterioration in the flexural and fatigue behavior of both the constrained and the unconstrained laminates. A study of glass/aramid/epoxy hybrid composites with an interply arrangement of $[G_3A_3]_S$ and $[A_3G_3]_S$ exposed in seawater (natural seawater) for 42 days at 25 °C and 70 °C temperature by Oguz et al. [74] showed a reduction in flexural strength and impact strength by gaining the water uptake rates of hybrid composites with rising temperatures. Another study of Muralidharanl et al. [75] indicated that gradually reduction in tensile stress retention of carbon fiber/glass fiber FRP hybrid composite immersed in seawater (artificial seawater) for the period of first 50 days then progressively reduction in remaining period of 150, and 300 days at temperatures of 20, 40, and 60 °C, respectively.

Discussion and Conclusions

A comprehensive review of experimental studies investigating the mechanical performance of FRP composites for marine applications subjected to seawater aging and its degradation mechanism has been performed. In addition, efforts taken through the most significant approaches for improving the mechanical performance with reducing and controlling the damage mechanisms caused by moisture absorption under the effect of seawater were discussed. The reported experimental studies have aided in the development of solutions to improve the mechanical performance and moisture absorption behavior of FRP composites and, more importantly, provided useful future directions for the study. Based on the findings of these studies, the following some major points are summarized here.

- The majority of studies show that epoxy resin is the most commonly used polymer matrix in FRP composites for marine structural applications, along with reinforcement elements such as glass fibers or carbon fibers. The epoxy resin serves as a binder for reinforcement and charge transfer to the fibers; also protects fibers from harsh seawater environments.
- The most preferred FRP composite is glass fiber-reinforced epoxy composite for marine applications due to its cost-effectiveness. On the other hand, it is more prone to seawater aging, which degrades long-term mechanical properties due to fiber/matrix interface failure caused by hydrolysis and plasticization of the resin matrix.
- In order to overcome the problems of glass fiber epoxy composites caused by seawater aging, carbon fiber epoxy composites are being replaced because of their excellent mechanical properties (rigidity and strength) as well as excellent fatigue and corrosion resistance. However, carbon fiber epoxy composites are restricted due to their poor cost-effectiveness.
- One of the options is to apply carbon fibers instead of glass fibers which improve the mechanical performance in the marine environment. However; the structures made entirely of carbon fiber are not affordable due to their high cost. As a result, ship designers are captivated by the usage of hybrid composite laminates consisting of carbon and glass fibers.
- In order to predict the long-term behavior of exposed FRP composites, the salt concentration of the artificial seawater used in the laboratory needs to be similar to that of the natural seawater to target the marine environment.
- The main factor affecting the mechanical performance of FRP marine structure is moisture absorption due to seawater aging. The studies indicate that a number of complex mechanisms act on the three components of the FRP composite, namely the fiber, the matrix and the fiber/matrix interface. Most researchers have studied the effects of seawater aging on these components in isolation.

- The amount of moisture absorption in seawater aging is majorly through the matrix reinforcement and therefore, the need of proper selection of matrix is required to achieve the better toughness characteristics.
- The majority of studies show that the moisture absorption process due to seawater aging in FRP composite materials follows the Fickian mechanism in which the relaxation rate is much higher than that of diffusion, even quite a few studies show a non-Fickian mechanism in which the rate of relaxation is approximately same as the rate of diffusion. Therefore, the study of moisture absorption behavior is essential for the newly developed FRP composites with potential use in marine structures.
- The degradation mechanism of FRP composite materials used in marine structures can be accelerated by the long exposure time, elevated ambient temperature and salinity of the seawater solution. Therefore, it is important to first thoroughly understand the concept and behavior of the degradation mechanism of FRP composites exposed to seawater.
- Degradation of FRP composites under seawater aging can occur through a combination of different damage mechanisms such as cracking within the matrix, pitting, hydrolysis, breakage of fibers, plasticization, fracture, delamination, and fiber/matrix detachment. However, studying aging in a seawater environment is often difficult. Therefore, the damage mechanism is complex and requires simplification.
- Moisture diffusion of seawater into FRP composites creates complex damage mechanisms that result in degradation of overall mechanical properties such as tensile and flexural strength, fracture toughness and interlaminar shear strength (ILSS) and affect the behavior of FRP composites. Therefore, the effect of moisture absorption on the mechanical performance of FRP composites subjected to seawater aging is a subject of investigation.
- To improve the mechanical properties of FRP composites in marine applications, the main approaches have been reported in previous studies, e.g., B. the coating of fiber surfaces, the hybridization with and without nanofiller and the interply rearrangement. Many researchers have applied these approaches in isolation to reduce and control the mechanism of damage caused by moisture absorption of FRP composites.
- The degradation of FRP materials due to seawater was controlled by providing the coating on fiber surfaces before the fabrication of FRP materials. The coating on the fiber surface plays a vital role in improving the interfacial performance of fiber and matrix. Furthermore, FRP composites are more resistant to seawater and have sufficient strength.
- A positive improvement in the overall mechanical properties was achieved by effectively preventing the absorption of seawater considering the interply rearrangement or the stacking sequence of hybrid composites. This approach offers the greatest benefits for design optimization without additional costs to achieve mechanical performance improvement of FRP composites.
- The significant improvement in mechanical properties by reducing the moisture absorption when aged in seawater of FRP composites can be achieved by the addition of a small amount of nanofillers compared to traditional FRP composites in marine applications. The nanofiller material improved fiber-matrix adhesion while increasing the lifespan of the materials.
- In order to overcome some of the limitations of individual nanofiller in FRP composites, a novel strategy of the synergistic effect of nanofillers is introduced in the modification of fibers, matrix, or both the constituents of FRP composites used in a marine application.
- The majority of researchers reported that nanofillers at higher weight fractions are difficult to disperse and the agglomerates could serve as sites of stress concentration, thus declinations in the mechanical properties of FRP composites.
- This comprehensive review will help to identify the importance of nanofillers, appropriate concepts and methodologies for manufacturing a superior and reliable hybrid FRP composite material for long-term marine applications.

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Declarations

Conflict of interest The authors declare that there is no conflict of interest.

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