



Effect of Marine Environmental Conditions on Physical and Mechanical Properties of Fiber-Reinforced Composites—A Review

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Abstract Fiber-reinforced polymer materials are finding their increasing importance as structural material in marine, civil and aerospace applications. The durability and potential applications of these structures are influenced by the susceptibility to working environments. The ease of prediction of degradation of mechanical property becomes cumbersome due to the heterogeneity of constituent materials and non-standardized weathering conditions. This review article presents a study of long-term performance behavior of composite structures exposed to moisture, temperature, ultraviolet radiation and alkaline solution. Reduction in modulus due to increasing temperature, swelling of polymers due to moisture absorption and scission or alteration of polymer structures are either due to the attack of chemical mediums or ultraviolet rays observed in polymer composites during their service life.

Keywords Moisture absorption · Alkaline solution · Ultraviolet radiation · Degradation

Introduction

Composite is the heterogeneous materials containing combination of two or more materials having different physical and chemical properties. Composite materials take the advantage of higher properties of fiber and matrix materials to achieve higher mechanical performance in the required plane [1, 2]. Desirable properties like high strength to weight ratio, corrosion resistance, design flexibility, low cost, durability, chemical resistance of fiber-reinforced polymer (FRP) composite materials show that they are the best alternative for the traditional homogenous materials in automotive, aerospace and marine industries and in civil construction applications [1, 3–5]. The mechanical behavior of a FRP composite is dependent on the orientation of fiber, stacking sequence, strength and modulus of reinforcement and matrix material, chemical stability, manufacturing process and the interface bonding between the fiber/matrix to enable stress transfer [6, 7]. Further, the composite structure provides design flexibility to the material by allowing change of the composition, orientation, volume fraction of constituent materials to achieve desired properties in a required direction.

The marine industry is one of the largest consumers of FRP materials. Since the mid 1980's use of composite materials extensively increased in marine structures and global industry expects a growth rate of 5.8% per year as an alternate material for the traditional materials which are subjected to galvanic corrosion [8, 9]. Marine environment is posing a greatest challenge among the researchers to select a suitable material for structural applications. There is a scope for extensive research in the long-term structural performance, sustainability and durability of materials. For marine applications, understanding the performance, properties, process ability and sustainability in harsh

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climatic conditions have received much attention in the recent past [10–12]. It is possible to enhance the durability and integrity of composite materials in various service conditions by altering the constituents; i.e., fiber, type of matrix, interface between matrix and fiber [7, 13]. Life of marine composites largely depends upon the environmental conditions and greatly influenced by various working environments. During the service life of marine composites, these structures and components are subjected to various environmental conditions like temperature, high humidity, alkaline and ultraviolet (UV) light environments [3, 7, 14].

Unfortunately, polymeric composite materials are susceptible to moisture and temperature and continuous exposure of these materials to such harsh environment leads to the degradation of the mechanical properties of the material. It is necessary to know the durability and life cycle of composites in terms of their mechanical, chemical, thermal properties for the prediction of service life of the structures [15–18]. The main objective of the present study is to understand the effect of moisture, temperature, UV rays and alkali solution on thermoset-based fiber-reinforced composites.

Effect of Environmental Parameters on Durability of Marine Structures

Moisture

FRP materials are extensively used in marine applications such as hulls, masts, funnels, superstructures, air, and fuel storage tanks and propeller shaft [19]. In marine field, moisture absorption is the major parameter behind the degradation of FRP composites. Mechanical behavior of FRP materials purely depends on the structural and physical changes occurring in matrix material during temperature and hygrothermal treatment [20–22]. Continuous exposure of FRP to moisture generates a new phase between fiber and matrix. Absorption of moisture causes plasticization and swelling of matrix material and leads to reduction of interfacial bonding strength between matrix and fiber surface. At elevated temperature moisture intake effects the glass transition temperature of the material [7, 23–25].

Difference in the thermal expansion coefficient at matrix and fiber interface region induces thermal stress in the laminates and results in residual stresses. Because of these, residual stresses and lower interfacial bonding application of load on the material lead to microcrack initiation and propagation between the matrix and fiber interface region. Moisture introduced through these microcracks was distributed in the matrix system by intermolecular diffusion

process. Moisture diffusion process through matrix material was explained with the help of Fick's law of diffusion [26, 27]. As per Fick's Law of diffusion, in the initial period, FRP material shows rapid intake of moisture and reaches to an equilibrium or saturation point. After saturation point polymers show steady and slow moisture intake phenomenon [28]. Moisture absorption phenomenon of FRP mainly depended upon the void content and quality of the composites. Defective or the presence of voids in the material will diverge the moisture absorption phenomena from Fick's law of diffusion and such absorption behavior known as non-Fickian diffusion process [26, 28].

Visco et al. [29] compared the moisture absorption behavior vinylester and polyester-based composite material for a duration of 10 months at a constant temperature 17 °C. During accelerated aging duration both polymers showed unequal gain in moisture because of the structural difference of the polymers. Based on the curing temperature vinylester matrix material established compact intermolecular structure, which was useful to reduce the diffusion coefficient as compared to polyester matrix [30]. The water absorption rate can be controlled by providing silane or polydimethylsiloxane elastomer (PDMS). Experiments conducted by Christos et al. [23], showed evidence of reduction of diffusion coefficient of silane-treated fibers. Study of surface morphology of the aged glass fiber-reinforced polymer in an alkali solution at a temperature of 80 °C a duration of 300 days showed increment 90% in the porosity level. Consequently, GFRP showed rapid intake of moisture and drastically reduced tensile property by 40% [31]. Impact energy absorption property of the polyester resin also influenced by moisture intake. Aging of GFRP specimen for a duration of 30 months at 60 °C showed increment in the quantity of damage under low velocity impact. Studies conducted at 10 J penetrated more damage in the specimen as compared to low energy impact test. Compression test after impact test showed 60% reduction of compressive strength against the duration of aging period [32]. Moisture absorption rate is greatly influenced by operating temperature. Aging of vinylester-based composites for a duration of 28 months also exhibited reduction in after impact compressive strength by 10% [33]. At low temperature polyester matrix material, follow Fickian diffusion process and aging under high temperature (65–90 °C) showed non-Fickian water absorption behavior [32]. A multistage diffusion moisture absorption behavior observed in polyester matrix material at high temperature. Moisture absorption rate of the fiber-reinforced polymers influenced by laminate thickness. Study of aging of 3 mm and 10 mm glass/vinylester, carbon/vinylester, glass/polyester and carbon/polyester in artificial seawater showed deviation for the Fick's law of diffusion. 10 mm thick, specimens showed large deviations as

compared to 3 mm thick specimens. Interlaminar shear strength and flexural strength of both laminates showed 10% degradation as compared to dry specimens [34]. Exposure of vinylester matrix composite material to corrosive fluid also influences the mechanical properties. Concentration of corrosive medium and immersion time drastically influences the performance of the composites. Immersion in corrosive media resulted in the formation of pits and blisters on the surface of the material and as the immersion time increased these zones were converted into swelling zone [3]. Diffusion coefficient of epoxy/carbon composites depended upon the concentration of the aging medium. Seawater immersed specimens exhibited lower diffusion constant as compared to tap water immersion [35–37]. Moisture absorption behavior varies with respect to type of reinforcement. Kootsookos et al. [20] compared the durability of carbon/polyester with glass/polyester under the influence of marine environment. Lower resistance to moisture absorption of glass fibers at the fiber/matrix interphase resulted in larger quantity of moisture uptake by glass fiber-reinforced composites. Liao et al. [38] compared the flexural properties of 0° and 90° oriented glass/vinylester composites aged in water, 5%NaCl, 10%NaCl and at water at 75 °C for a duration of 3000 h. Water absorption curve showed deviations with respect to different aging mediums. Immersion of glass/vinylester composites in NaCl showed resistance to moisture gain as compared to water immersion [39]. Results showed that orientation of fabrics does not have any influence on the moisture absorption behavior [38]. Studies conducted by Xu et al. [40] showed that moisture absorption behavior of composites influenced by relative humidity (RH) and temperature of the working environment. Specimens immersed at 96%RH showed larger gain in moisture level as compared to aging at 40%RH. Water aging of E-glass/polyester resulted in a weight gain of 3.5% and vapor aging of the same showed a moisture gain of 0.3% for the same duration [22, 40].

Ultraviolet Radiation (UV)

Polymer-based composites are widely used as external structural member in aircraft and marine industry. Long-term exposure of external structures to environmental weathering shown large impact on mechanical performance of the FRP structures [41, 42]. The degradation and damage induced in the material will be irreversible, which minimizes the quality and compromise the performance of composite. Exposure to UV lights or photo-oxidative aging of thermoset results in breakage of polymer chains and produces free radicals in the polymers resulting in reduction of molecular weight and extensive degradation of mechanical properties [43]. When composites exposed to

UV environment, UV photons were absorbed by the polymers, which results photo-oxidation reactions [44, 45]. This chemical reaction causes molecular chain scission, which lowers the molecular weight [46]. This reduction in weight causes reduction in matrix strength and heat resistance [43]. It also leads to brittleness of material which results in microcracking of the matrix material. Exposure of epoxy to UV lights leads to reduction thickness of the material because of the evaporation of volatiles and shrinkage [47]. Degradation of mechanical performance of FRP materials depended on UV exposure time, intensity, temperature and wavelength. Combined effect of moisture and UV rays accelerates the formation of microcracks and flaking and pitting in fiber matrix interface [48–52]. Gloss and color of FRP also shown significant changes. In some cases, content of fibers was visible because of photo-chemical degradation of polymers [17, 43, 45]. Photostability of the aramid fibers can be improved by treating fibers with titanium hydrosol. Treatment of aramid fibers with titanium hydrosol will form an UV ray-resistant thin film coating around the fiber surface [53].

Alkaline Solution

The major challenge in marine industry is exposure of FRP structures to alkali solution. The presence of hydroxyl group in the matrix material easily reacts with the alkaline solution. Alkaline solution interacts with the matrix material and not only attacks polymer but also degrades fiber/matrix interphase structure. This degradation mainly due to hydrolysis between matrix and alkaline solution [14, 54–56]. Hydrolysis intensifies on the matrix surface, and there is a chance of formation of shorter and soluble polymeric chains in the alkaline solution. Study of glass fiber/epoxy composites in sodium hydroxide (NaOH) showed that the corrosive environmental significantly affects the flexural strength and flexural modulus. The alkaline solution was more aggressive as compared to acidic solution and promotes the degradation of flexural properties. The surface roughness and resistance of the laminates to repeated low velocity impacts were dependent on the corrosive environment and the exposure time [16]. Alkali aging of glass/epoxy of a duration of for 718 h at 40 °C resulted in loss of elastic modulus by 5% and residual strength reduced by 18% [57]. Immersion of epoxy/flax composites for a duration 365 days in 5% NaOH showed similar trend of weight gain as compared to water-immersed specimen. During initial period of aging in alkali solution, showed rapid weight gain and reaches to a saturation point. The same kind of behavior observed in water absorption test. Mechanical characterization of aged samples showed reduction of tensile modulus and flexural modulus by 36% and 25.2%, respectively [17]. Aging of

epoxy/basalt fiber-reinforced composites in alkali solution resulted in remarkable reduction of tensile and interlaminar shear strength. Higher immersion/aging temperature was resulted in more serious kind of degradation of mechanical properties [5]. Vibration property of the quasi-isotropic glass/epoxy laminates was influenced by the exposure to alkaline solution. The natural frequency of the specimens was depended on amount of moisture gain. Alkali aged specimen showed 10% reduction in natural frequency as compared to pristine specimens [58]. Mechanical properties of thermoset-based materials depend on exposure time, pH level of the solution and operating temperature.

In modern growing composite industry, researchers are working on alternate reinforcement material for carbon, aramid and glass fibers. Basalt fiber is the present choice of material and has high strength, high modulus, high temperature and chemical resistance [59–61]. To identify the suitability of basalt fiber as a reinforcement material for marine and civil application, researchers focused on understanding the durability of basalt composites in different environments. Wang et al. [21] investigated the effect of acid and alkali solution on strength of the basalt/epoxy laminate. Studies showed declination of tensile and flexural modulus in both environment. The durability of basalt fiber in acid environment is very poor and showed higher rate of degradation of mechanical properties. Comparison of moisture absorption behavior of glass/epoxy and basalt/epoxy specimens exhibited same absorption behavior. At saturation point, both the specimens absorbed 15% of moisture. The result indicates that moisture absorption depended upon type of matrix material rather than the type of reinforcement [62]. Immersion of basalt/epoxy laminates in seawater also showed irreversible chemical degradation and physical damage. Penetration of seawater into matrix material promoted breakdown of matrix structures and resulted in deterioration of matrix/fiber interphase [63]. Basalt fiber-reinforced material exhibited relatively strong resistance to corrosion in salt solution than in acid solution. Interaction acid solution with fiber matrix interphase resulted in pitting of fiber surface and also induced chemical changes in matrix material [64]. Comparative study of basalt fiber-reinforced polymer (BFRP) bar in ocean water with simulated seawater showed that the alkalinity is the key factor, which causes the degradation of BFRP. Uncovered BFRP shows more degradation in seawater and concrete-covered BFRP shows more degradation in ocean water. Seawater is moving in ocean, but the laboratory-simulated seawater is static, so the static seawater has higher-pH-value. The alkaline solution density change is an important factor in BFRP degradation [65]. Degradation study of BFRP after 63 days of aging at different conditions like normal-seawater and sea sand concrete(N-SWSSC), high-performance

seawater and sea sand concrete(HP-SWSSC) and alkaline solution with the pH of NSWSSC, 13.4, 12.7 and 12.9–13.1, respectively, showed N-SWSSC solution is most aggressive, HP-SWSSC is least aggressive and alkaline lies in between [66]. Basalt fiber-reinforced polymer/concrete interface under wet-dry cycling in a marine environment had about 45.1% and 65.2%, reduction in the tensile strength and ultimate strain after 360 cycles. And also the ultimate strength and elastic modulus of the matrix material decreased by approximately 27.8% and 64.8% [67]. Flax and flax-basalt composite were exposed to salt-fog environmental conditions for 60 days. Remarkable uptake was found for the flax laminates between 500 and 700 h of aging. Compared to flax, flax-basalt specimens stayed stabilized at lower values of moisture uptake[68]. Fiore et al. [69] investigated durability of two laminates, namely flax (10 layers of bidirectional flax fabrics) and flax-basalt (replacing two external flax layers with two layers of basalt mat) exposed to salt-fog environmental conditions for 60 days. After 15 days of exposition, the hydrophobic properties of laminates decrease. After 60 days of salt-fog exposition, the average thicknesses of flax and flax-basalt samples become 3.39 mm and 3.29 mm, respectively. The swelling thickness of flax and flax-basalt measured they were equal to 15.4% and 5.0% which means that basalt slows down the water absorption. Basalt fibers within polymer metallic and concrete matrices exhibit promising properties. Hence, these fibers have great potential to be the next generation materials for structural application for infrastructure, automotive industry and consumer applications [70].

Temperature

Synthetic fibers such as carbon, aramid and glass were known to be high-temperature resistance materials and will retain most of their mechanical properties at elevated temperature. Since the composite materials made up of combination of matrix and fibers, the exposure to elevated temperature influences matrix-dominated properties rather than fiber-dominated properties. Exposure of polymers near to its glass transition temperature (T_g) in service life leads to degradation of mechanical properties [24, 71–75]. Exposure of composite structures to sub-zero temperature or freeze–thaw cycling also affects the durability of material because of the differential thermal expansion between fiber and matrix interphase. The presence of moisture content in sub-zero temperature also results in swelling of composite structure [76]. Rami et al. [18] compared the tensile properties of glass/epoxy, carbon epoxy and carbon/glass/epoxy at various temperature ranging from 25°C to 250°C. Carbon\epoxy showed 28% reduction in tensile modulus as compared to room

temperature tested specimen. Whereas glass/epoxy and glass/carbon/epoxy hybrid composites tensile modulus degraded by 26% and 9%, respectively. The failure of the specimen categorized into three modes based on the testing temperature. In mode I (100–150 °C) specimen showed by brittle fracture of fibers and same kind of failure observed in room temperature testing. In mode II (200–250 °C) softening of matrix resulted in sheet splitting interlayers of fibers. In mode, III above 300 °C self-ignition and burning of epoxy resulted in rupture of the specimens [18]. Impact energy of glass/epoxy composites was also influenced by operating temperature. Low energy (20 J) impact test conducted at room temperature and at –60 °C has developed equal amount of damage. But as the level of impact energy increased the specimen tested at –60 °C showed catastrophic fiber failure [74]. Exposure of vinyl ester/glass specimens to lower temperature (–60 °C) resulted in improvement in mechanical properties due to the increase in stiffness of the amorphous polymer matrix. At elevated temperature reduction in mechanical properties observed due to change of state in polymer and reaction of degradation [76]. Above critical temperature, (< 300 °C) FRP structures will be subjected to thermal degradation and result in failure of the structures. Systematic accelerated aging test on the bond durability of steel-FRP composite bar (SFCB) and seawater and sea-sand concrete (SWSSC) in a simulated marine environment conducted. After 9 months of aging in a 40 °C seawater wet-dry cycling environment had bond strength reduction by 5% and 26.2% in a seawater immersion at 50 °C environment [77].

Conclusions

In engineering applications, durability and reliability of the structures are critical for safety and economical aspects. The review on durability of marine structures provides the details about the parameters influencing the structural health of FRPs. Moisture absorption is the key parameter influencing the mechanical performance of marine structures. During the initial service life, rapid moisture absorption observed and thereafter reaches to saturation point. The presence of voids, low crosslink between fiber and matrix, diffusion through microcracks promotes the moisture absorption. Moisture absorption with the variation of pH weakens the stiffness and flexural properties of the structures. The rate of degradation of strength mainly depended on exposure time, pH level.

Matrix-dominated failures such as matrix erosion, microcracks and color changes observed under the influence of UV radiation. UV ray intensity, wavelength and angle of exposure and humidity play important role on the

durability of composite structures. Freeze–thaw cycling and exposure to elevated temperature greatly influence the elastic modulus and tensile properties of the FRP structures. Exposure of structures above glass transition temperature (T_g) leads to softening of matrix material and reduces interlaminar bonding. On the other hands, exposure to freezing temperature can cause hardening, microcracking and deterioration matrix/fiber interphase.

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