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Effect of Seawater Ageing on Fracture Toughness of Stitched Glass Fiber/Epoxy Laminates for Marine Applications

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Abstract: Composite materials are used in various industries such as marine, aircraft, automotive, etc. In marine applications, composites are exposed to seawater, which can affect their mechanical properties due to moisture absorption. This work focuses on the durability of composite materials under the short-term effect of seawater ageing. The specimens were prepared from glass fiber/epoxy using a hand lap-up method and stitched in the z-direction with Kevlar fiber. The specimens were submerged in seawater for 24 and 35 days. A significant decrease in maximum load was found as specimen immersion time in seawater increased. The seawater ageing also affected fracture toughness with a reduction of 30% for 24 days immersion and 55% for 35 days. The ageing also caused the swelling of composites due to moisture absorption, which increased the weight of the specimens. Compared to the dry specimens, the weight of the specimen for 24 days increases to 5.2% and 7.89% for 35 days' seawater ageing. The analysis also showed that due to seawater ageing, the de-bonding rate increased as the number of days increased.

Keywords: glass fiber/epoxy composites; kevlar stitching; seawater ageing; inter-laminar fracture toughness

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1. Introduction

Composite materials have a wide range of applications in various manufacturing industries such as marine, aerospace and automotive, due to their high toughness chemical resistance and light weight [1–5]. Boat hulls, sonar domes, marine building, the waterfront barriers, the offshore structures, propellers and hatch covers are some of the marine applications of composites [6–8]. The exposure of composite materials to seawater for prolonged periods affects the materials' strength and interphase region [9]. The moisture absorption can cause degradation in tensile strength of resin composite material and reduce the bond strength by 15% to 59% [10]. The immersion time in water also decreased the stress property, and affected the Young's modulus and strain of composites [11]. Additionally, moisture absorption makes the material weak, which causes swelling in the material, decreasing its mechanical adhesion, and breaking chemical bonds between fiber and matrix [12]. According to Hodzic et al. [13], water absorption increased the interphase region from 0.5 μm to 2 μm due to which fracture toughness (GI) value decreased. Moreover, composites gained weight by about 8.5–9.4% after placing them in water, seawater and alkaline solution for a long time [14]. Han et al. [15] also concluded that the fracture toughness of the nanocomposite decreased by about 18.5% after seven days of water immersion. Furthermore, flexural strength, glass transition temperature (Tg) and tensile strength of the material decreased by about 9.8%, 2.5% and 13.8% with immersion in seawater for six months [16]. Water absorption also depends on various factors of composite materials, i.e., hydrophobicity, fiber orientation and area exposed due to which mechanical properties are affected [17]. Mourad et al. [12] reported that the tensile strength of glass/polyurethane composite material was decreased by 19% and 31% when placed in seawater at room temperature and 65 °C for one year. E José-Trujillo et al. [18] noted delamination, fibers de-bonding and resin crumbling in the composite due to seawater ageing. Similarly, a detailed overview of the effect of mechanical properties of various type of composite materials, such as carbon fiber-reinforced epoxies and polyetheretherketone (PEEK) composites, was presented by Guen-Geffroy et al. [6]. However, there is limited literature on the use of composite material in the marine application in general and the effect of water absorption on delamination in particular, especially for short-term immersion.

To improve mode I and the interlaminar fracture toughness value of composite material, various techniques like z-pinning, carbon nanotube (CNT), nanoparticles and Kevlar stitching have been developed. Literature has also shown that an increase in mode-I inter-laminar fracture toughness occurred by adding rubber particles [19], and nano-acrylonitrile butadiene rubber in glass fiber/dicyandiamide-cured epoxy [20]. Also, for anhydride-cured epoxy and carbon fiber epoxy, an increase in fracture toughness was observed when nano-silica particles and rubber particles were used in combination [21,22]. Additionally, the CNTs as reinforcement increased the interlaminar fracture toughness about 67% [23]. Also, Rugg et al. [24] investigated that by using short z-pins, an increase in fracture toughness occurred. By z-pinning, an increase in delamination resistance of the continuous fiber composite laminates was also observed by Cartié and Partridge [25].

Different experimental methods, i.e., Mode I, Mode II and end-loaded split (ELS), are established in the literature to measure fracture toughness in composite laminates [6]. The Mode I test method was considered as simplest of all and was used extensively by most researchers [12,13,26,27]. However, it is worth noting that despite the extensive use of composite in various applications, its lower mode-I fracture toughness is still its significant deficiency [28]. An increase in mode I interlaminar fracture toughness is possible when stitching with Kevlar thread [29]. Different stitching techniques include lock stitch, modified lock stitch and chain stitch. Among all these, modified lock stitch has greater damaged tolerance [30].

The stitching of composite laminates with Kevlar, carbon, and glass fiber threads is one way to enhance mode-I fracture toughness [28]. However, the literature studies are mostly focused on moisture absorption effects on laminates, with no stitching for long periods [12]. Therefore, this study investigates the short-term effect of moisture absorption on the interlaminar fracture toughness property of the glass-fiber specimen, stitched in the z-direction with Kevlar fiber at different times under seawater.

2. Materials and Methods

In this work, glass fiber-reinforced composite (E-glass-400 fabric and epoxy) was prepared by a hand layup method. A stepwise detail of sample preparation is explained in Figure 1. The vol. % of fibers used in the specimens ranged from 67% to 70%. The epoxy was prepared from resin (bisphenol A) and hardener (cycloaliphatic amine) available in the market with a product name of Z-epoxy 300. Resin and hardener were mixed in a ratio of 2:1. A total of 24 layers of E-glass fabric of 1 mm thickness were utilized to obtain 6.5 mm-thick double cantilever beam (DCB) specimen as per standard ASTM D5528 [13,31]. In between, 24 layers of Teflon fabric film of thickness 0.3 mm and length of 65 mm were placed in the middle as a crack starter. Vacuum bagging was applied at a vacuum pressure of 10 bars. After the vacuum bagging, the panel was placed in the electric furnace for 2.5 h up to 150 °C. A total of 28 specimens was prepared as per ASTM standard D5528 [31]. The final specimens had a length of 160 mm, a width of 25 mm and a thickness of 6.5 mm.

The specimens were stitched with a thickness of 4.5 mm Kevlar fiber/tape. The stitching was started at 10 mm from the end of the pre-crack. This pre-crack is a short natural crack that propagates as the load is applied to the specimen. The stitching was undertaken in two rows 10 mm apart from each other and 20 mm from the end. The holes for stitching were made through the drill machine with a 5 mm size, as shown in Figure 2a and the final test specimen is given in Figure 2b.

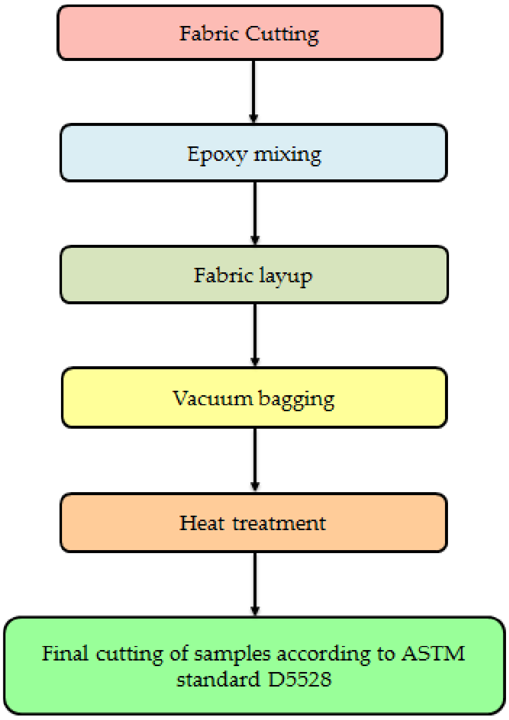

Figure 1. Fabrication steps.

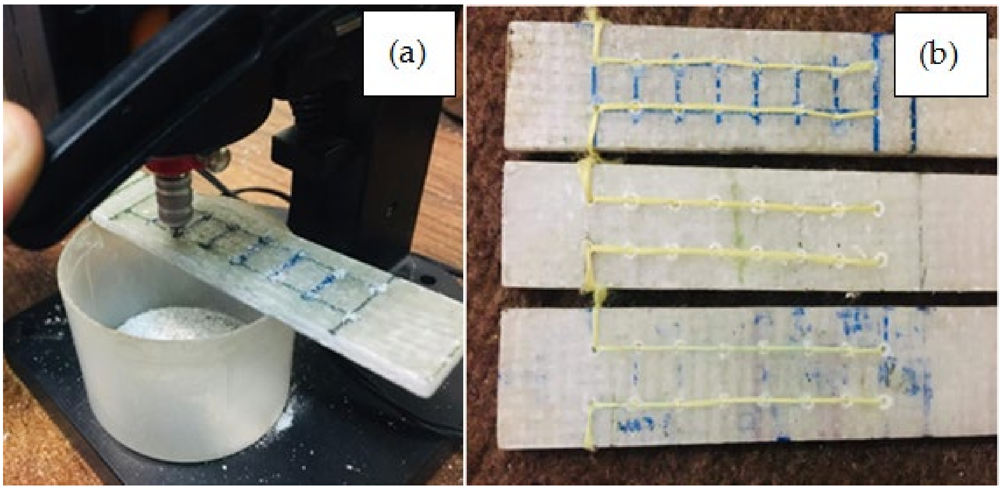

Figure 2. (**a**) Kevlar thread and drilling of the specimen (**b**) stitched double cantilever beam specimen.

The effect of water absorption on the composite laminates was investigated in about liter of seawater at a quiet state. The salinity degree of the water was around 30 ppt with a pH measured of 7.9. The temperature change might affect the strength of glass/epoxy composites laminates [13]; therefore, the ageing was performed at room temperature (25 °C) for 24 and 35 days.

The mode I fracture testing was performed by a universal testing machine shown in Figure 3. The machine has a maximum loading capacity of 50 kN, with a minimum strain rate of 0.005 mm/min and a maximum strain rate of 500 mm/min. The specimens were gripped in the machine with the piano hinges, and tests were conducted at room conditions at a strain rate of 3 mm/min. The delamination increment values were noted after every 10 mm increment against applied load and opening displacement. This type of delamination along the crack path in-between the specimen's points can be easily observed by the naked eye that needs no magnification devices. Therefore, during the trial, the delamination increment was visually observed with a similar approach adopted by Hodzic et al. [13]. During experiments, force and opening displacement data were collected from the machine, and a total of 24 specimens were tested on a universal testing machine. The test was stopped when the specimen delamination reached 80 mm from the opening displacement.

Figure 3. DCB specimen gripped in machine.

The data obtained from the mode I fracture testing was analyzed according to the ASTM standard D5528. The strain energy (GI) was calculated using the modified beam theory given by Equation (1).

$$G_I = \frac{3P\delta}{2ba} \tag{1}$$

G_I is Mode I strain energy release rate, P is applied load, δ is opening displacement, b is the specimen's width, and a is delamination crack length.

After the Mode I fracture testing, the specimens were cut into small pieces with a 5 mm × 5 mm dimension and examined under a scanning electron microscope (SEM) type KYY EM6900 SEM. Cutting was performed using a diamond saw with a similar procedure followed by Hodzic et al. [13].

3. Results

3.1. Loads versus Opening Displacement

Figure 4 shows the force applied versus opening displacement/stroke of the dry, and seawater aged specimens for 24 and 35 days. A low uncertainty was found in the data recorded from the experiment, as shown by error bars, which means an insignificant difference in the data. Results showed the initial linear increase in the load with minimum increase in the opening displacement. The graph's steepness was because of the delamination crack initiation, which resulted in high loads to propagate. The dry specimen's maximum load was 180 N, which decreased to 108 N and 80 N after 24 days and 35 days after seawater ageing. This reduction in load was because of the water absorption that weakened the glass fiber–epoxy bond [12]. The higher amount of water absorption might also cause degradation in the fracture load. The sudden drop in the load variation of the specimens was expected due to the non-homogeneous water distribution that created localized stresses. These stresses acted as regional defects, causing a drop in loads [13]. Furthermore, the peak values observed were associated with initial stitching failure followed by the pullout of the remaining stitches.

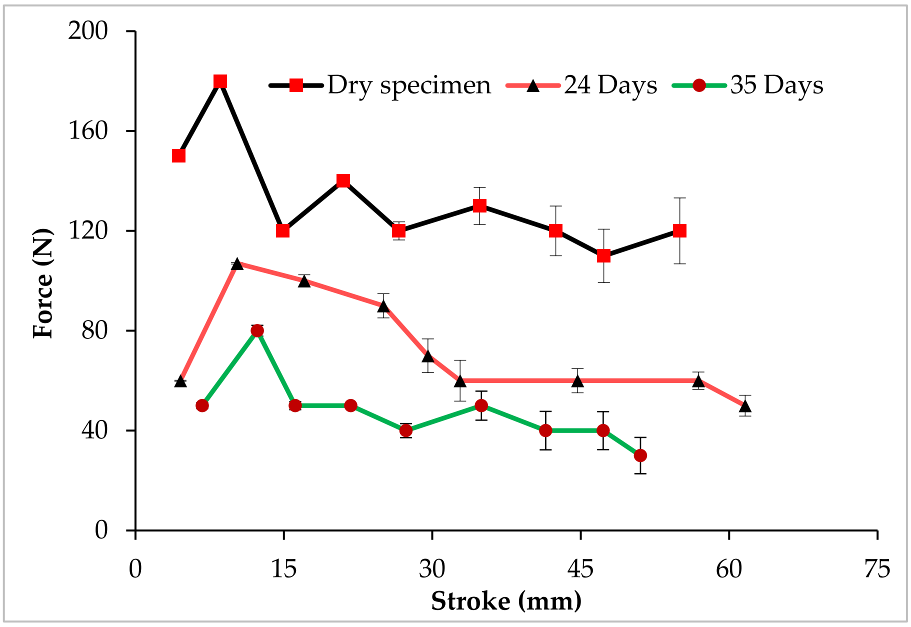

Figure 4. Load versus opening displacement curves of double cantilever beam specimens.

3.2. Inter-Laminar Fracture Toughness

Figure 5 shows that as the water absorption in specimens increases, the fracture toughness values decreased. The fracture toughness value was higher for dry specimens than those aged in seawater. The difference in fracture toughness for the dry and water-aged specimens was smaller at small delamination length, while it increased as delamination length increased. Figure 5 also shows the gradual increase in the fracture toughness values with the crack's increment. Moreover, the initiation value of fracture toughness for 24 and 35 day-soaked specimens was much less than the dry specimens. The seawater decreased the fiber bridging in the adjacent plies of the specimen's laminate during the fracture test, which is the reason for low values of fracture toughness. For 24 day-soaked specimen, the average initiation value of fracture toughness was about 256 J/m^2, while the maximum average value of fracture toughness was about 1385 J/m^2. A similar phenomenon was also observed for the 35 day-soaked specimen where the initiation fracture toughness value was about 346 J/m^2, and the maximum value of 884 J/m^2 was recorded. Therefore, the fracture toughness decreased by 30% for 24 days while a decreased of 55% occurred for 35 days compared to dry specimens because of interfacial degradation for seawater-aged specimens.

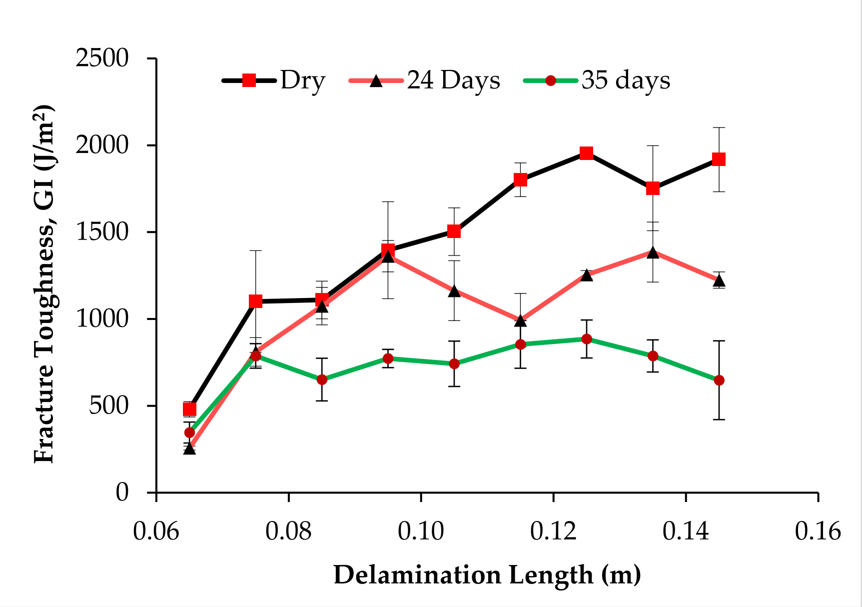

Figure 5. Crack growth curve.

3.3. Fracture Mechanism Analyses and Effect of Water Ageing on Mass

Figure 6 shows the dry specimens with the smooth surface after delamination tests. It was observed that less fiber bridging occurred while some fibers were pulled out from laminates due to which the load was carried out by the epoxy and stitching of fibers. On the other hand, in specimens aged 24 days in seawater, the degradation of specimens occurred as depicted in Figure 7. Epoxy became porous because of moisture absorption in 24 days' ageing due to which more fiber loss occurred than dry specimens. The bonding of fibers and epoxy was weakened, and small bits of epoxy were scattered on the surface. However, after 35 days of ageing in seawater, high chunks of epoxy were formed, and the surface became rough, as shown in Figure 8. The water caused pits on the fracture surface, and the epoxy breakage was approximately glass-like breakage due to an increase in the brittleness of the epoxy. Therefore, the bond between fiber and epoxy became poor after water absorption, which was justified by the lower fracture toughness values.

Moreover, both the dry and seawater-aged samples were measured by weight with a similar procedure followed by Hodzic et al. [13]. The weight of the dry specimens was about 38 g, after 24 days' ageing in seawater, the weight increased up to 40 g, which was about 5.2% of the dry specimen. Also, for 35 days of seawater ageing, the weight was increased to 41 g, which was about 7.89% of dry specimen. This increase in weight revealed the increase in water absorption with time due to which swelling up of the composite material occurred, and hence it de-boned easily [32].

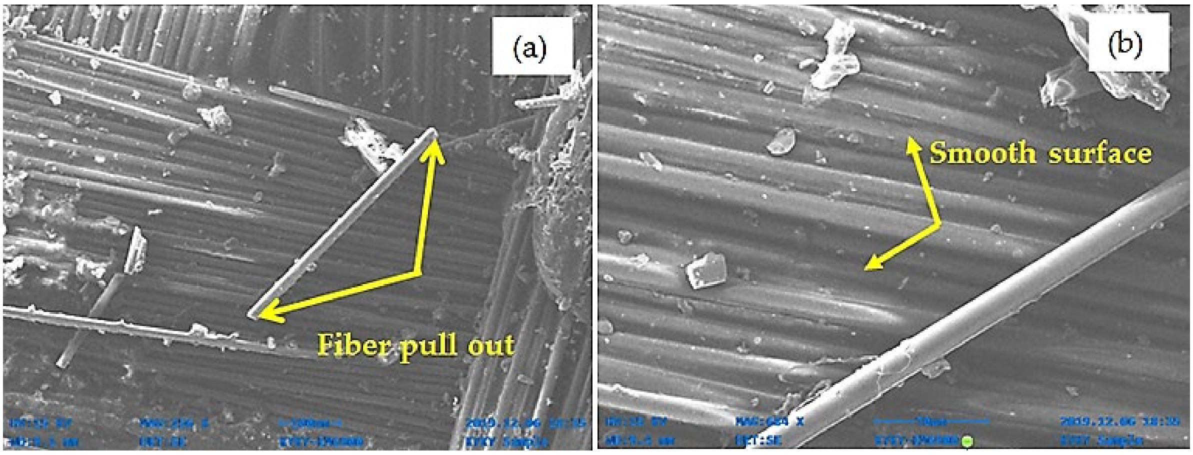

Figure 6. Scanning electron microscope (SEM) images of dry specimens with magnification: (**a**) 256× and (**b**) 684×.

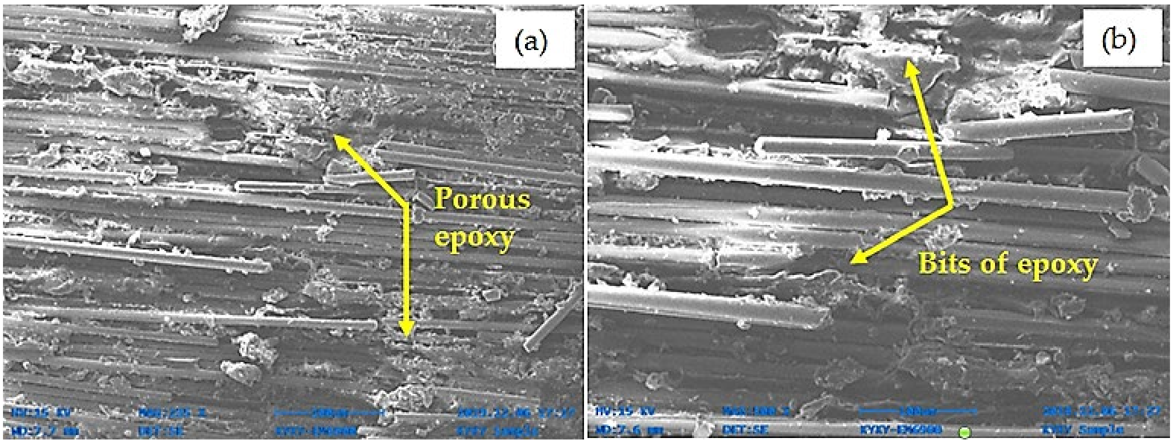

Figure 7. SEM images of 24-day water-aged specimens with magnification: (**a**) 235× and (**b**) 500×.

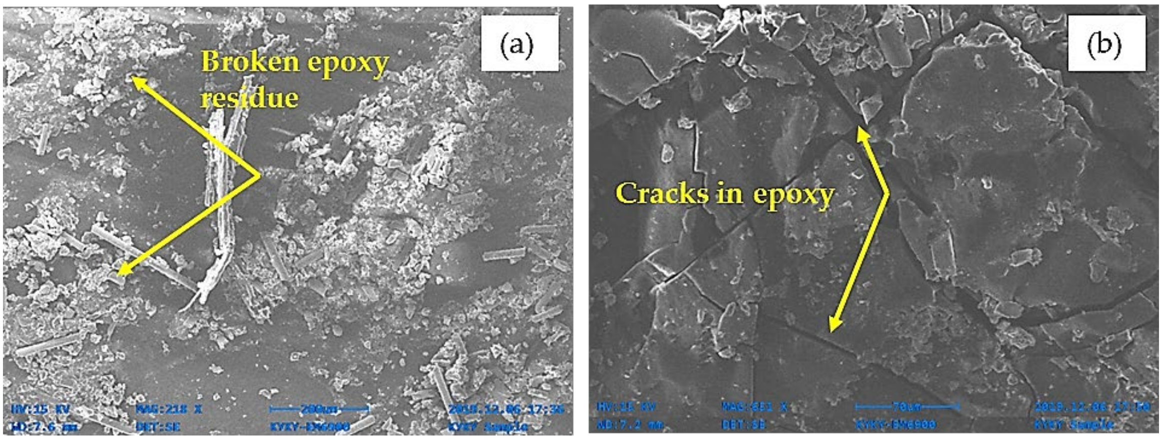

Figure 8. SEM images of 35-day water-aged specimens with magnification: (**a**) 218× and (**b**) 651×.

4. Conclusions

In this work the effect of seawater on stitched glass fiber epoxy was investigated. It was concluded that seawater had a significant effect on the fracture toughness of stitched glass fiber epoxy due to it being soaked in seawater for 24 days and 35 days. Experimental results showed dramatic changes in all the specimens. After immersion in seawater, due to moisture changes in composites, a decrease in the fracture toughness was found. The initial energy in mode-I became low, and fracture toughness decreased up to 30% and 55% for 24-day and 35-day specimens, respectively, compared to dry specimens.

Accordingly, swelling of the composites occurred due to moisture absorption causing an increase in weight of the specimens. The weight increase of 5.2% for the 24-day and 7.89% for the 35-day specimens was observed compared to the dry specimen. Cracks initiated easily, and interfaced bonding became weak because of the moisture absorption. Additionally, the analysis showed that due to seawater ageing, the de-bonding rate increased as the number of days increased.

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