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ORIGINAL RESEARCH

Durability study of quasi-isotropic carbon/epoxy composites under various environmental conditions

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Abstract

Fibre-reinforced polymer (FRP) composites are gaining more attention for civil, automobile, aircraft and marine applications due to their excellent properties. The present work investigated the effect of ageing on mechanical properties of the autoclave-cured quasi-isotropic carbon/epoxy prepreg composites. The specimens were aged at artificial seawater under ambient, sub-zero (− 15 °C), and humid conditions (70% RH. and 40 °C) for 12 months. The tensile, flexural and impact properties were determined at regular intervals. The gravimetric study revealed that moisture absorption behaviour depended on the medium and duration of ageing condition. The moisture absorption for the quasi-isotropic carbon/epoxy composite specimens followed a non-fickian distribution. The moisture absorption of the carbon/epoxy composite laminate specimens showed an adverse effect on their mechanical properties. The moisture absorption results revealed that composite specimens aged under ambient condition absorbed more moisture compared with sub-zero and humid conditions. It was evident from the results that there was a 36.06% reduction in tensile properties of the composite specimens aged under ambient condition in comparison with pristine specimens. In contrast, the flexural properties were affected largely at sub-zero condition, and the impact properties were largely degraded at humid condition. The failure surface morphology revealed that matrix cracking and inner fibre debonding were the major causes of degradation in mechanical properties.

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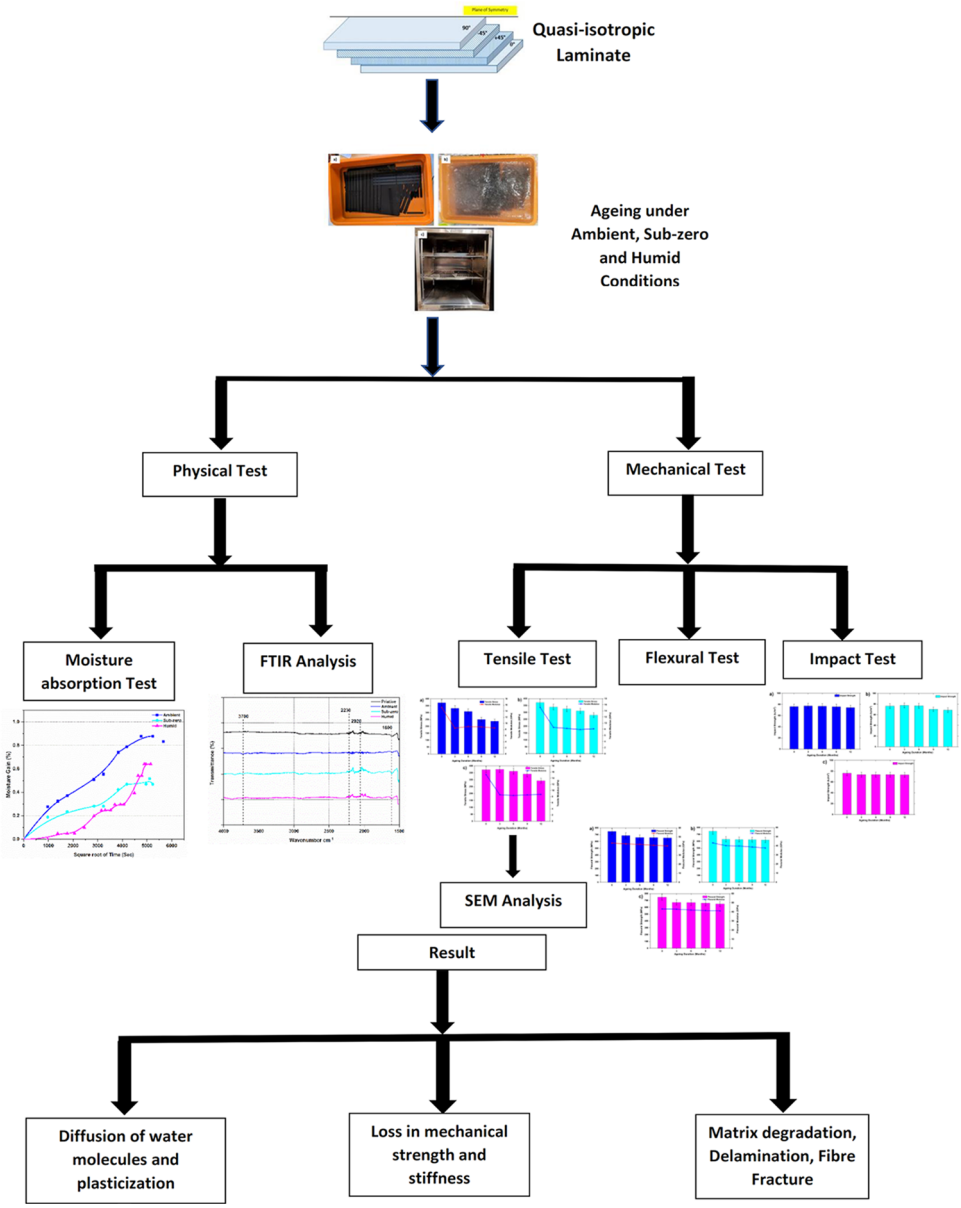
Graphical abstract



Keywords Quasi-isotropic · Prepreg · Autoclave · Seawater ageing · Moisture absorption · Mechanical properties

Introduction

Fibre-reinforced polymer (FRP) composite materials are preferred as a substitute for conventional materials because of their improved physical, chemical and mechanical properties. Owing to enhanced strength-to-weight ratio, corrosion resistance, and fatigue damage tolerance, fibre-reinforced composite materials have a wider range of applications in the aircraft, marine, and civil industries [1–3]. The fibre-reinforced composites are extensively employed in marine applications such as landing craft, personnel boats, shielding of wood hulls, and submarine sonar domes. Since 1980, use of FRP in the marine industries has increased extensively [4].

Glass fibre-reinforced polymer (GFRP) and carbon fibre-reinforced polymer (CFRP) composites are the major composite materials used in the marine industry. The applications of CFRP composites in the marine industry are stiffer hulls, decks, masts, corvettes, propulsion of shafts, rudders and propellers. Using CFRP composites in large marine

applications reduced the hull's weight by 30%. The composite propeller shafts, produced using CFRP laminates, offer better fatigue resistance, avoid corrosion problems and provide better vibration damping and air blast damage resistance [5, 6].

The selection of a suitable combination of matrix and fibres for marine structural applications in hostile environments is challenging among researchers. The durability of FRP under marine conditions mainly depends on environmental factors such as moisture, elevated temperature, and humidity [7]. In real-time, observing the changes in the material behaviour of FRP due to environmental conditions requires more time, owing to which researchers are now mainly focusing on accelerated ageing. Ageing is a process where the materials properties change over time. An ageing study determines the materials behaviour in any type of environments [8]. Depending on the service condition, FRP ageing tests can be chemical, physical, thermal, or a combination of them. Chemical ageing is the process of immersing FRPs in chemicals or water (seawater or distilled water, for example) for a predefined period to observe changes in mechanical and physical properties [9].

Capillary flow and diffusion are the primary mechanisms for the diffusion of water into FRP materials. Capillary flow is caused by flaws in the void, whereas diffusion is governed by molecular configurations. Plasticization and hydrolysis of resins and fibres are induced by moisture diffusion into the matrix phases [10, 11]. Plasticization lowers the fracture strength and viscosity of the polymer-water mixture, and hydrolysis causes debonding between fibres and matrix [12–14]. Thermal ageing is the process of detecting variations in the physical and chemical characteristics of FRP under specific temperature and humidity conditions. The temperature during ageing should be below the glass transition temperature of matrix material. The damage caused by chemical or thermal ageing increases with time, reducing the material strength and leading to failure [15–17].

In recent years, scientists have been focusing on understanding the effects of moisture absorption on the mechanical characteristics of FRP. Zong et al. [18] evaluated the mechanical properties of artificially aged CFRP and GFRP composites. After ageing in tap water at 80 ˚C for three months, moisture content was more in CFRP laminates than in GFRP ones. The increased moisture content was due to the reinforcement weave pattern, which might alter FRP moisture behaviour. Amounts of 11.01% and 15.98% reduction in tensile strength were observed for CFRP and GFRP composites, respectively. The diffusion coefficient for the CFRP specimens aged in normal water was more than that for seawater-aged specimens. This could be due to the higher concentration of dissolved salts in seawater, which prevented water from diffusing by osmosis.

The mechanical properties, such as tensile strength, degraded by 18% in normal water-immersed specimens, whereas it was decreased about 13% for the seawater-aged specimens [19]. The seven-month durability test of the carbon/epoxy specimens in seawater and NaCl solutions showed that moisture absorption was higher in the seawater-aged specimens than those aged in the NaCl solution. The tensile strength of the aged carbon/epoxy specimens decreased by 11.5 percent compared to the pristine specimen [20].

Forty-five days of durability test of the carbon/epoxy and glass/epoxy specimens under artificial seawater showed that glass/epoxy specimens absorbed more moisture than carbon/epoxy specimens. Moisture absorption caused plasticization and swelling resulting in the reduction of glass transition temperature (T_g) in both glass/epoxy and carbon/epoxy specimens. The seawater ageing resulted 7.7% and 3.1% reduction in flexural strength for carbon/epoxy and glass/epoxy specimens, respectively [21]. The flexural property analysis of 30 days seawater-aged carbon/epoxy specimens showed a 23% decrement compared with pristine specimens. The weak matrix-fibre interfacial bonding was the major reason for reducing mechanical properties in the conditioned carbon/epoxy specimens [22].

The moisture absorption behaviour of the carbon/epoxy composites exposed 300 days to saltwater and demineralized water was investigated by Zafar et al. [23]. Specimens aged in demineralized water had a greater equilibrium moisture content than those aged in saltwater. Accelerated ageing of the carbon/epoxy specimens resulted in a 20% degradation of tensile strength compared with the pristine specimens. The hygro-thermal ageing at 70 °C and 90% relative humidity (RH) of unidirectional carbon/epoxy specimens resulted in 41% reduction of tensile strength compared to the pristine specimens.

Askari et al. [24] examined the effect of thermal ageing (between 25 and 100 ºC) on carbon/epoxy laminates. The thermal ageing was carried out for 40 thermal cycles. The results revealed that the exposure of composite up to 40 cycles resulted in improvement in the impact properties. Scanning electron microscopic (SEM) studies showed that delamination and pullout were the primary types of failure observed during the study.

García-Moreno et al. [25] evaluated the effect of thermal ageing on the charpy impact and flexural properties of carbon/epoxy specimens. The thermal ageing below T_g caused an increase in the impact and bending strength. Above T_g, the properties were degraded with the duration of ageing. Dahil et al. [26] investigated the tensile and impact properties of hybrid glass-carbon fibre-reinforced composites. The results revealed that stacking sequence and the numbers of layers affected tensile and impact properties. SEM studies

revealed the existence of surface cracks and matrix fractures after the tensile test.

Deng et al. [27] examined the effect of thermal ageing on the glass fibre-reinforced composite. The thermal ageing was performed in the range of 85 °C to 145 °C. The thermal ageing at that temperature resulted in the decrement of tensile and flexural properties. The higher temperature also caused brittle fractures and the deterioration between the fibres and matrix.

Observations based on previous studies revealed that the moisture absorption of polymer composite increased with ageing duration and temperature. Also, the studies showed that as ageing time increased, mechanical properties of the material deteriorated significantly. Several investigations on moisture absorption and its impact on mechanical properties focussed on unidirectional or angle ply, glass, or carbon epoxy composites. The literature focusing on the effects of moisture absorption and its effect on the mechanical properties of the quasi-isotropic composite laminates was limited.

The current work investigates the effects of moisture absorption on the mechanical properties of the quasi-isotropic carbon/epoxy laminates in marine environment conditions. The artificial seawater ageing investigation was carried out for 365 days in ambient, sub-zero, and humid conditions. The tensile, flexural and impact tests were performed at intervals of 3 months, and the results were compared with the pristine specimens. The thermogravimetric study was conducted to check the thermal stability of the quasi-isotropic carbon/epoxy specimens. The failure surface was analyzed using SEM technique.

Experimental

Materials

In the present work, a quasi-isotropic carbon/epoxy composite was fabricated from a unidirectional carbon fibre prepreg having a thickness of 0.2 mm and an areal weight of 200 gsm was procured from The BHOR Chemicals and Plastics Pvt Ltd, Nasik, India. The prepreg was made from carbon fibre fabric with a density of 1.8 g/cm^3 and a tensile modulus of 240 GPa. Epoxy was used as the prepreg's matrix material, having a tensile modulus of 2.91 GPa and a resin content of 38%.

Methods

The autoclave method was incorporated to fabricate carbon/epoxy laminates with a stacking sequence of $[0°/\pm45°/90°]_s$ as reported else where [28]. The specimens were cut using a water jet cutting machine at Stonemax waterjet cutting. The average laminate thickness was 1.7 ± 0.021 mm. The 30 specimens with a dimension of $80 \times 10 \times 1.7$ mm^3 were weighed using digital balancing equipment having the least count of 0.001gms to determine experimental density. The average experimental density was 1.54 ± 0.041 g/cm^3. The theoretical density was found to be 1.52 g/cm^3 and calculated using the rule of mixtures. By comparing actual and theoretical densities, the void percentage in the fabricated carbon/epoxy laminate was estimated to be 1.31 percent.

Moisture absorption study

The primary aim of the current study is to examine the mechanical behaviour of quasi-isotropic carbon/epoxy laminates in the marine environment. ASTM D1141 standard was used to prepare artificial seawater to replicate the marine environment. The pH value of the prepared artificial seawater was maintained at 8.1. The selected three environments for the ageing process were (i) artificial seawater ageing at ambient temperature (≈ 30 °C), (ii) artificial seawater ageing at sub-zero temperature (− 15 ºC stored in a deep freezer), (iii) Humid conditions (70% RH and 40 ºC in an environmental chamber). The specimens were aged for 365 days.

As per ASTM D5229, the percentage of moisture gain of specimens during the ageing process was evaluated at regular intervals [29] and calculated as per Eq. (1) [30] as follows:

$$M_t\,(\%) = \frac{M_t - M_o}{M_o} \times 100 \tag{1}$$

where M_t is the weight gain and M_o is the initial weight of the specimen (g). The moisture diffusion co-efficient (D_z) at three different ageing conditions was estimated according to Eq. (2) as follows:

$$D_z = \pi \left[\frac{h}{4M_\infty}\right]^2 \left[\frac{M_1 - M_2}{\sqrt{t_1} - \sqrt{t_2}}\right]^2 \left[1 + \frac{h}{L} + \frac{h}{w}\right]^{-2} \tag{2}$$

where M_∞ is equilibrium amount of moisture concentration, M_1 and M_2 (g) are the measured weights at different time periods t_1 and t_2 (s), correspondingly and *L, h,* and *w* are specimens length, thickness, and width (mm), respectively.

Mechanical characterization

To understand the effect of moisture absorption on mechanical properties, a series of tensile, flexural, and impact tests were conducted on aged carbon/epoxy specimens at regular intervals of 3 months. After the ageing period was completed, the specimens were stored in an airtight container. The results of aged specimens were compared with the pristine specimen.

The tensile tests were conducted under uniaxial tensile loading and displacement control mode with a 2 mm/min crosshead speed using a BiSS (India) 50 kN servo-hydraulic machine as per ASTM D3039. The tensile specimens were provided with glass fibre/epoxy end tabs for better gripping and to prevent specimen failure at gripping. The stress and strain at the fracture point were considered as the ultimate values of the carbon/epoxy specimens. The three-point flexural test assesses the carbon/epoxy specimens flexural strength and modulus.

The flexural test was conducted as per ASTM D790 using a UNITECH-9450 (India) UTM of 50 kN capacity with a crosshead speed of 1 mm/min. A rectangular specimen having a dimension of $120 \times 12.7 \times 1.7$ mm^3 with a span length of 87.5 mm was tested. The load vs displacement curve slope was utilized to calculate the flexural modulus.

A charpy impact test was performed to regulate the impact strength and energy absorption as per ISO 179. The testing energy was distributed evenly over the thickness of the specimen. The impact test was conducted using Zwick Roell JB-450I/750I (Germany) impact testing machine with a maximum energy of 25 J at a velocity of 3.809 m/s. In all test conditions, five specimens were tested to get the average tensile, flexural and impact strength of carbon/epoxy laminates.

TGA

Thermogravimetry analysis (TGA) is a technique for measuring the thermal stability of polymers and polymer-based composites. The powdered samples of pristine and aged carbon/epoxy laminates weighing 10 mg were tested to investigate the effect of ageing environment on their thermal stability. TGA was conducted by the TGA-55 (TA Instruments, New Castle, DE, USA) instrument using platinum pans with a resolution of 1 µg and could operate up to 1000 °C. The sample purge flow (nitrogen) was set to 60 mL/min, and the balance purge flow (air) at 15 mL/min. In a platinum pan, the powdered sample was heated to 800 °C at a rate of 10 °C/min.

SEM

The tensile failure surface morphology of pristine and aged carbon/epoxy specimens was analyzed using a SEM with 10 kV excitation voltage. To improve the electrical conductivity, a thin layer of gold sputtering was carried out for a period of 3–5 min on the carbon/epoxy specimens.

Results and discussion

Moisture absorption

The moisture absorption behaviour of carbon/epoxy quasi-isotropic laminates was calculated as per Eq. (1) and the moisture absorption curve for different ageing conditions is shown in Fig. 1.

The moisture content increased with an increase in the exposure period. The moisture absorption rate was found to be higher in the ambient conditions compared with other two conditions. The moisture absorption curve showed non-fickian moisture diffusion behaviour. The specimens aged under ambient and sub-zero conditions showed two-stage non-Fickian distribution. During the initial stages of absorption, a Fickian distribution was followed by non-Fickian distribution. In the first stage, the Fickian distribution response was thermally triggered, and the temperature accelerated the water absorption rate. The second stage can be attributed to structural relaxation creating voids that retain water molecules. The specimens aged under humid conditions followed sigmoidal type non-Fickian distribution attributed to phase void formation and localized ingress of water molecules [31].

The specimens aged in the artificial seawater gained 0.83%, 0.46% and 0.64% moisture in ambient, sub-zero, and humid conditions, respectively. Higher moisture absorption in ambient conditions than in humid conditions is due to the environmental humidity, which is essential in accelerating the water molecule penetration into the polymer matrix. The diffusion of moisture into carbon/epoxy

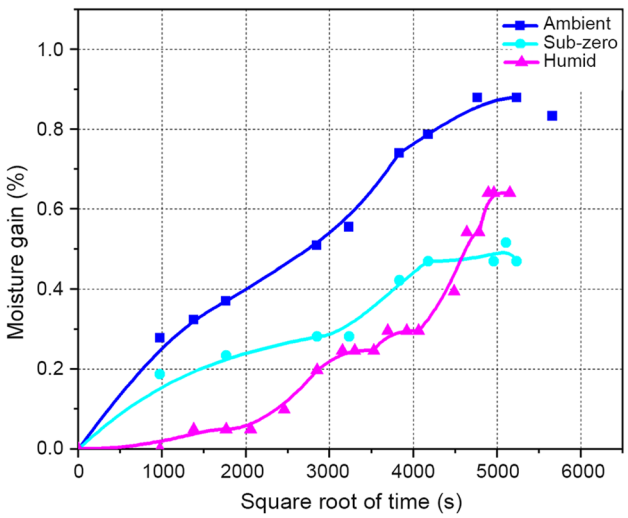


Fig. 1 Moisture absorption curves for carbon/epoxy composite specimens aged under different conditions

specimens is controlled by the activity of water molecules, and it can be further influenced by relative humidity [32].

The water dispersion rate in the composite laminate through the area can be estimated by calculating the diffusion coefficient. The diffusion coefficient of the laminates was calculated according to Eq. (2), and the obtained results are shown in Table 1.

Carbon/epoxy specimens aged under ambient conditions had a greater moisture diffusion coefficient compared with sub-zero and humid conditions. Carbon/epoxy specimens aged in humid conditions had a lower diffusion coefficient. The decrease in moisture content and diffusion coefficient was due to the deterioration of matrix below glass transition temperature. When carbon/epoxy specimens were exposed to a humid condition, the specimens lost weight.

The chemical variations caused in the laminate due to ageing were assessed using the Fourier transform infrared (FTIR) technique. FTIR spectra of aged carbon/epoxy specimens were compared with a pristine specimen that are shown in Fig. 2.

The specimens were scanned in the frequency range of 500 cm^{-1} to 4000 cm^{-1}. The vibration at 3700 cm^{-1} in all three ageing conditions confirms moisture absorption during the ageing process. The broad stretching of the peaks was due to the presence of the hydroxyl groups involved in hydrogen bonding. At 3700 cm^{-1} the intensity of these peaks was low due to a lower moisture absorption percentage compared with Fig. 1. The vibration in the range of 2230 cm^{-1} represented the stretching of C–O bonds. The peak intensity was higher for humid aged specimens than pristine, ambient, and sub-zero aged specimens. When carbon/epoxy specimens were immersed completely in seawater, the lack of oxygen prevented oxidation, and fewer peaks were observed for the specimens aged under ambient and sub-zero conditions. Whereas the presence of oxygen during humid conditions, the oxidation was more, hence showing sharper peaks [33]. The peaks in the range of 2020 cm^{-1} can be characterized by carboxyl group bending.

Effect of ageing on tensile properties

The variation of tensile strength and tensile modulus of carbon/epoxy specimens at pristine and different ageing conditions are showed in Figs. 3 a-c, respectively.

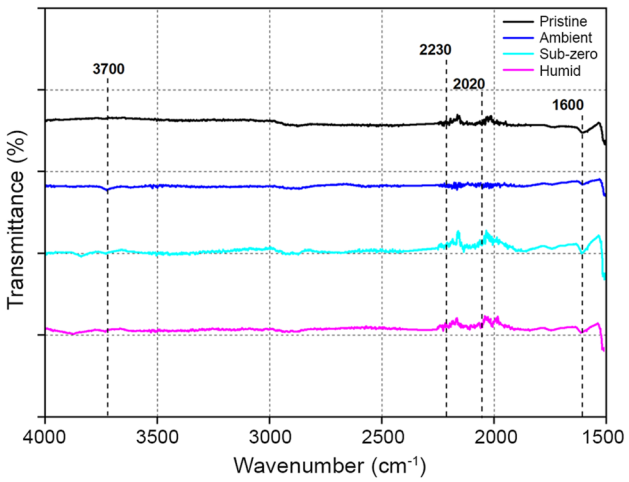


Fig. 2 FTIR spectra of pristine and carbon/epoxy composite specimens aged under different conditions

The pristine carbon/epoxy specimens show an average tensile strength of 372.16 ± 30.51 MPa at tensile strain of 0.0256 ± 0.0017 and an average tensile modulus of 15.7 ± 1.05 GPa. Following 365 days of exposure of carbon/epoxy specimens in artificial seawater, tensile properties were degraded. The specimens aged under ambient conditions showed a significant decrease in tensile properties than the other ageing condition (Fig. 3a). The tensile strength of ambient aged condition showed degradation of 10.84%, 17.08%, 32.73% and 36.06% in 3, 6, 9 and 12 months compared to the pristine specimen's values (Fig. 3a).

The specimens aged under sub-zero conditions for the same period resulted in a degradation of tensile strength of 24.68% compared to pristine value (Fig. 3b). The specimens aged under humid conditions showed degradation of 21.3% compared to pristine value (Fig. 3c). Due to higher moisture content, tensile strength was more degraded in ambient and sub-zero aged conditions than in humid conditions, as shown in Fig. 3b, c. The moisture in the composite diffused through inherent microvoids and microcracks in the composite or might transfer through the fibre-matrix interface. The fibre-matrix interface is susceptible to moisture, thereby reducing the fibre-matrix interfacial adhesion, and as a result, the tensile strength of the composite was reduced [34, 35].

Table 1 Diffusion co-efficient of carbon/epoxy composite specimens

Ageing condition	Moisture content at equilibrium M_∞ (%)	Slope of moisture absorption curve	Diffusion co-efficient D_z (mm^2/s)
Ambient	0.83	0.00021	3.25×10^{-8}
Sub-zero	0.51	0.00009	1.71×10^{-8}
Humid	0.64	0.00012	1.37×10^{-8}

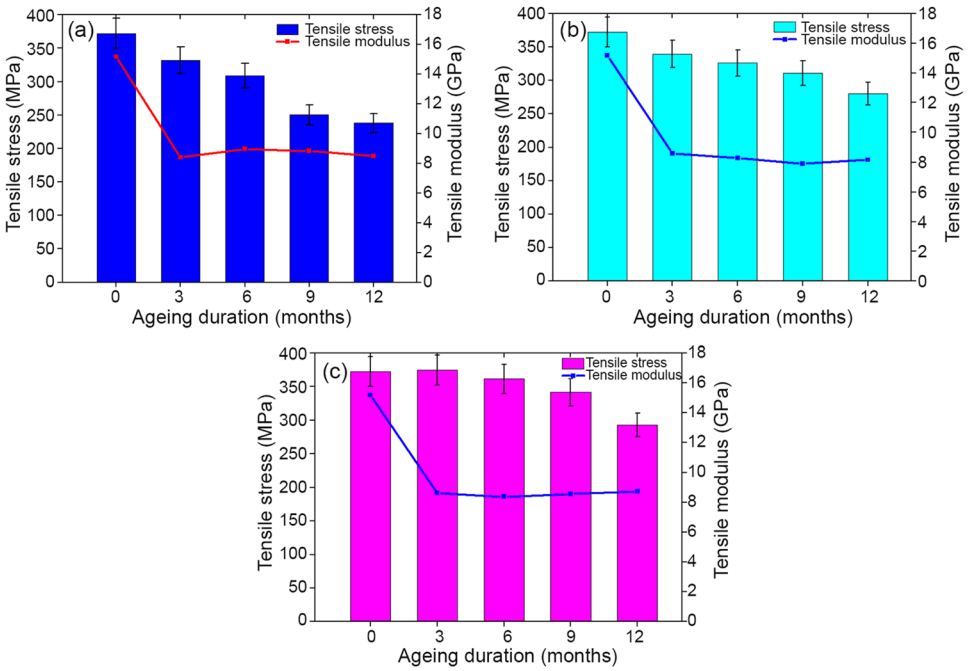


Fig. 3 Variation of tensile properties of carbon/epoxy composite specimens aged at: **a** ambient, **b** sub-zero and **c** humid conditions

The tensile modulus of the specimens aged under ambient, sub-zero, and humid conditions compared to the pristine values showed a higher rate of degradation in the first three months, followed by a steady degradation in the subsequent three months. In the first three months of ageing, from the moisture absorption curve in Fig. 1, a higher percentage of moisture was induced into the carbon/epoxy laminates, due to which modulus showed a rapid degradation. During the further ageing stage, the rate of moisture induced into the carbon/epoxy laminates was lesser and resulted in steady degradation in tensile modulus. The specimens aged under ambient conditions, sub-zero and humid conditions showed reductions of 44.57%, 45% and 45.17% in their tensile modulus, respectively.

In the chemistry of polymer construction, polymer behaviour, hydrogen bonding, and Van Der Walls bonding significantly impact the load-bearing capacity of the polymer composites. As the moisture saturates the composite, hydrolysis and plasticization of the matrix occur, weakening the polymer chains and their bonding. Due to this, the interfacial bonding weakens, and polymer adhesion impaired, resulting in modulus degradation. The chemical reaction between chlorine ions of seawater and ions of carbon fibres also caused severe degradation of the tensile properties of the carbon fibre-reinforced composites [30, 36]. Tensile characteristics deterioration suggested that hygrothermal conditioning reduced the CFRP interfaces quality. Hygrothermal ageing utilizing seawater damaged the strain to fracture fibres within the composites.

Figure 4 a–d show the failure pattern of the specimens under pristine, ambient, sub-zero, and humid conditions. The failure in the carbon/epoxy composites was a combination of matrix and fibres failures [20]. The fibres oriented in 90° direction showed brittle failure. The fibres oriented with ± 45° directions resulted in fibres pullout and matrix cracking. The change from fibre-dominated material resistance to matrix-dominated material resistance caused the ± 45° orientations to lose strength more quickly than 0° fibres. The fibres in 0° orientation in the loading direction showed fibre breakage. With further ageing time (3 months), the delamination between the layers occurred, resulting in pullout of the fibres. The main reason behind

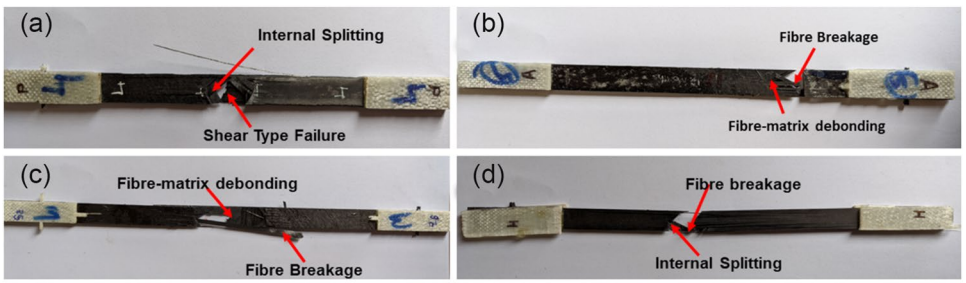


Fig. 4 Failure pattern of tensile composite specimens for: **a** pristine, **b** ambient, **c** Sub-zero and **d** Humid Conditions

such phenomenon was a degradation of the fibre-matrix interphase. As the ageing period increased, delamination became more intense, leading to the catastrophic failure of the CFRP specimens.

Effect of ageing on flexural properties

The flexural test of the aged carbon/epoxy specimens is favourable over tensile loading as it subjects the specimen to bending, tension, compression, and shear. The variation of flexural strength and flexural modulus of carbon/epoxy specimens under different ageing conditions are showed in Figs. 5 a–c.

The pristine carbon/epoxy specimens showed a flexural strength of 748.91 ± 14.82 MPa and a flexural modulus of 43.22 ± 3.67 GPa. However, the immersion of carbon/epoxy specimens in seawater for 12 months resulted in a decrement in flexural properties (Fig. 5a). The specimens aged under sub-zero condition showed a significant reduction in flexural properties compared with the pristine, ambient, and humid conditions (Fig. 5b). The flexural strength of specimens aged under sub-zero conditions decreased by 17.21% compared with the pristine specimen values. In contrast, flexural strength dropped by 8.21% and 13.21% in ambient and humid conditions, respectively. In the initial phases of moisture absorption, the carbon/epoxy specimens absorbed moisture rapidly, thereby reducing the internal stress, due to which the flexural strength decreased quickly.

Due to the high moisture and sub-zero temperature environment, the plasticization and swelling of the matrix occur, resulting in decreased flexural strength of carbon/epoxy specimens [37]. Under sub-zero conditions, the frozen water molecules entered these voids, making the material more brittle. The flexural modulus of the aged composite resulted in a steady degradation compared to the pristine specimen value (Fig. 5b). The flexural modulus degraded by 7.03% in sub-zero, 0.68% in humid and 1.2% in ambient conditions. It was observed that the reduction in flexural properties in seawater-aged carbon/epoxy specimens was due to the weakening of the bond between the epoxy matrix and carbon fibre leading to the failure of the carbon fibre at the outer surface. The interaction between O–H groups and fibres created hydrogen bonding is the cause of the low resistance.

Further, the moisture absorption resulted in poor interphase adhesion, thereby reducing the flexural properties of the specimens. Two modes of failure were observed during the flexural testing; the first crack initiation was heard before the total rupture of the specimen, indicating that breakage of matrix material was followed by delamination and fibre-matrix debonding, followed by tensile fracture of the specimens. The general failure during flexural tests was included tensile, compressive and shear resulting in matrix failure, delamination, fibre failure and fibre matrix debonding [38, 39].

Effect of ageing on impact properties

The variation of impact properties of carbon/epoxy specimens under different ageing conditions is shown in Figs. 6 a–c.

The pristine carbon/epoxy specimens showed an impact strength of 75.04 ± 5.87 kJ/m^2. It was evident

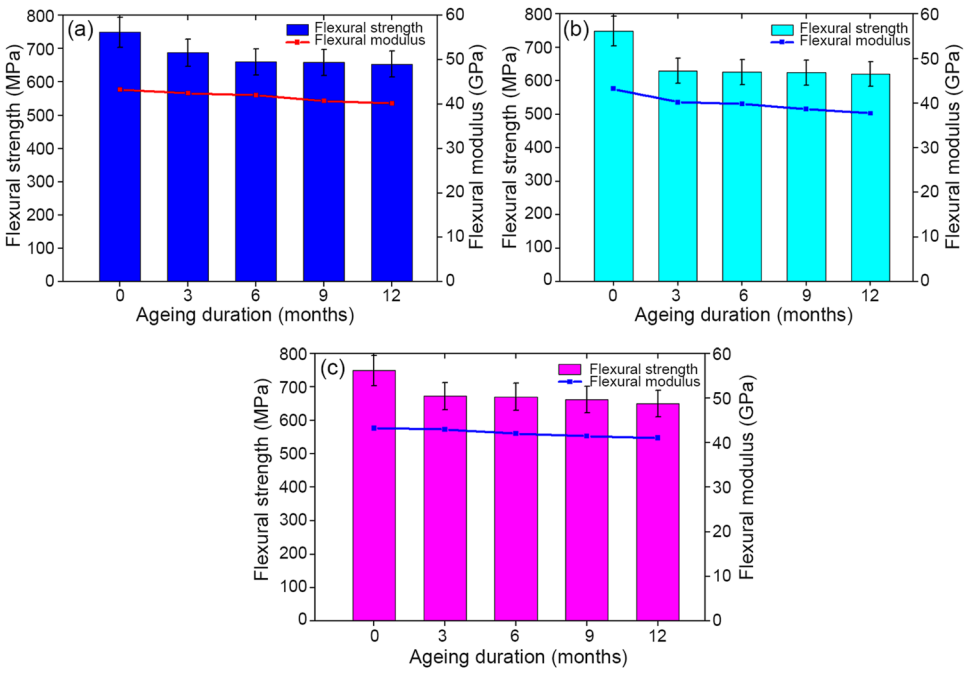


Fig. 5 Variation of flexural properties of carbon/epoxy composite specimens aged at: **a** ambient, **b** Sub-zero and **c** humid conditions

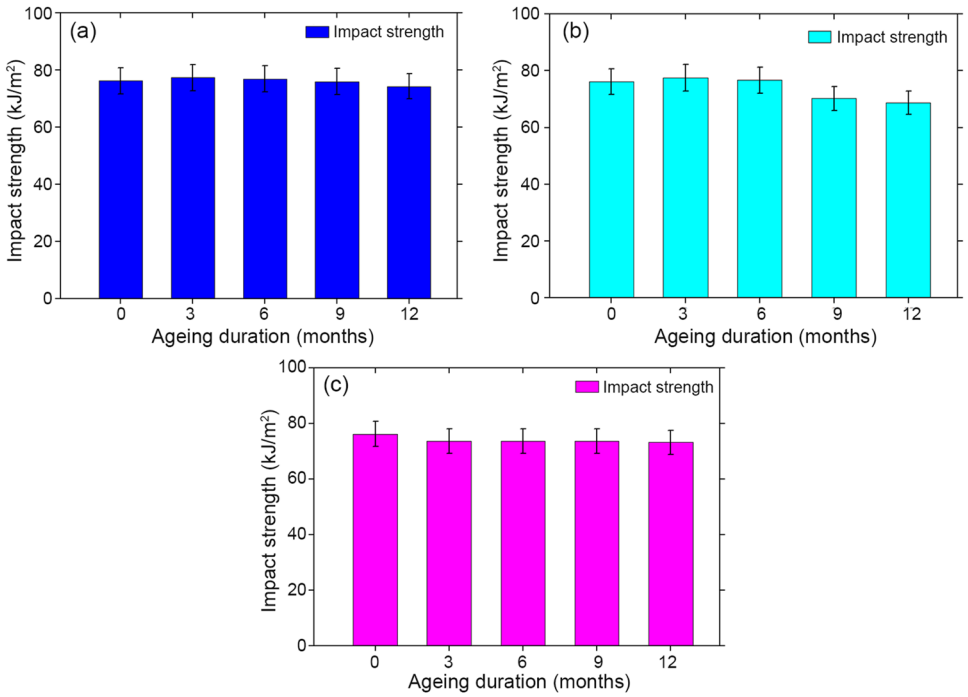


Fig. 6 Variation of impact properties of carbon/epoxy composite specimens aged at: **a** ambient, **b** Sub-zero and **c** humid conditions

that seawater immersion of carbon/epoxy specimens for 12 months reduced the impact strength. It was apparent from the experimental results the impact strength was directly related to stacking sequence, temperature, and ageing process. Energy absorption and impact strength were reduced due to the brittleness of the carbon fibre and matrix. The specimens aged under humid conditions showed a decrease of 6.39% compared with the pristine specimen value. Due to the higher temperature under humid conditions, the carbon/epoxy specimens absorbed more moisture, reducing the energy absorbed and the impact strength.

For specimens aged under ambient and sub-zero conditions, impact strength increased in the first six months, followed by a steady degradation in the final ageing period. During ambient and sub-zero ageing, the moisture ingressed into the polymer matrix increased free volume, thereby reducing T_g and making the material ductile. The increased flexibility resulted in plasticization, thus requiring higher energy to break the specimen [40]. At the end of ageing, the specimens aged under ambient and sub-zero conditions showed a reduction of 3.96% and 8.48% in impact strength, respectively. The impact properties were reduced mainly due to the absorbed moisture causing the plasticization, which weakened the fibre matrix interphase [41, 42]. During the impact testing, along with brittle fracture and fibre breakage, matrix cracking and delamination-dominated failure were observed in the carbon/epoxy specimens.

Thermogravimetry analysis

The thermogravimetric study was conducted on quasi-isotropic carbon/epoxy composites to measure their thermal stability. The thermal analysis of the carbon/epoxy composites started with heating up to 800 ˚C at a constant heating rate. The variation of thermogravimetry curves of carbon/epoxy specimens under pristine, ambient, sub-zero, and humid conditions are showed in Figs. 7 a–d.

Bhor prepreg A45 was the epoxy used in the prepreg preparation. The thermogravimetry analysis on A45 resin showed that decomposition occurred when the temperature reached 150 °C, but from Fig. 7, it can be observed that the thermal stability of A45 epoxy resin was increased after incorporating carbon fibres in both pristine and aged composites specimens.

The thermogram can be characterized by $T_{D,}$ representing the temperature at which 2% weight loss occurred and where the decomposition started. T_{10} represents the temperature where 10% weight loss occurs, *SDR* is the threshold value of rapid decomposition, where rapid decomposition of resin starts, and R_{500} represents the remaining residue after 500 °C. For pristine specimens in Fig. 7a, 2% weight loss was noted in the range of 235 °C, where epoxy started to degrade. The T_{10} was observed at 380.6 C, *SDR* around 390 °C, and the epoxy degraded rapidly. As the temperature reached 500 °C, the epoxy in the composite had degraded completely, and only the fibres remained.

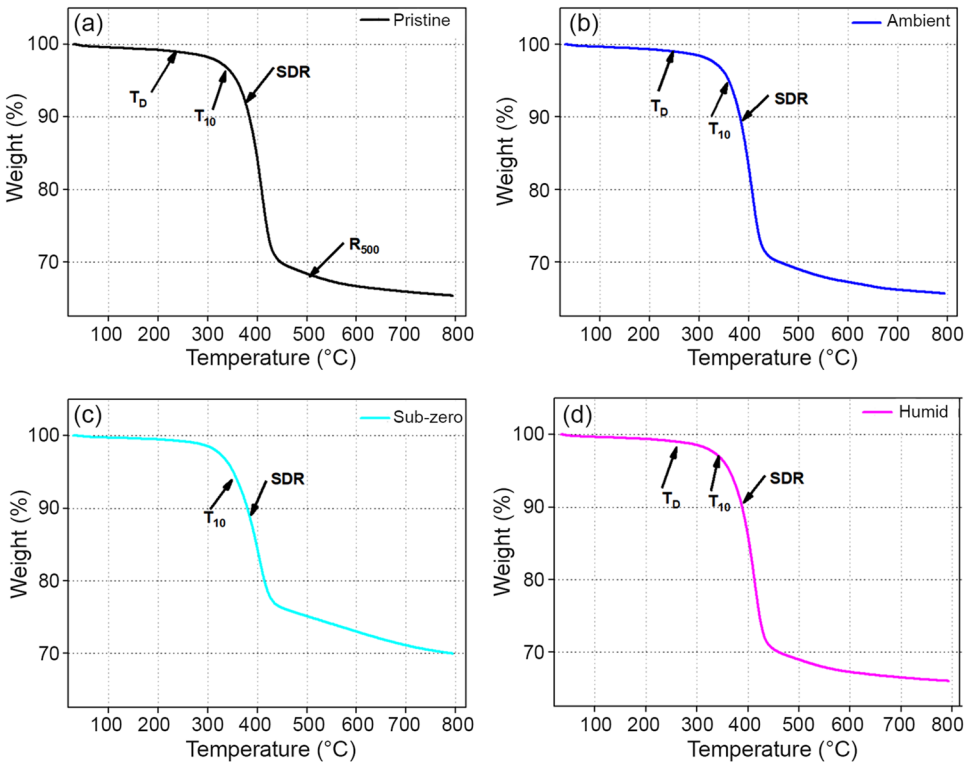


Fig. 7 Thermal behaviour of carbon/epoxy composite specimens at: **a** pristine, **b** ambient, **c** sub-zero and **d** humid conditions

For ambient conditioned composite specimen shown in Fig. 7b, the 2% weight loss was observed at a temperature of around 249 °C. The increment was due to the water molecule entering the matrix material, which changed the chemical composition of epoxy. The 10% weight loss was observed at around 378 °C, and the rapid degradation started at around 392 °C.

For sub-zero conditioned composite specimen (Fig. 7c), T_D was increased to 274 °C compared with those specimens at pristine and ambient conditions. The 10% reduction and standard value of rapid decomposition were observed around 375 °C and 395 °C, respectively. For composite specimen under humid condition (Fig. 7d), the decomposition of epoxy started around 260 °C. But for composite specimen aged in all conditions, the epoxy entirely deteriorated at the temperature around 500 °C.

Failure surface evaluation

The failure pattern of the pristine and aged composite specimens was examined using SEM technique. Figure 8 a–d show the failure patterns of tensile tested specimens under pristine and ambient, sub-zero, and humid aged conditions.

The fracture morphology of the pristine and aged specimens showed that fibres debonding was the typical mode of the failure. The SEM micrographs of tensile fractured pristine specimen shown in Fig. 8a revealed that fibres breakage was neat, indicating a better fibre-matrix interface. In addition, the presence of residual matrix flakes around the fibres surfaces indicated good fibre-matrix adhesion.

After the immersion of carbon/epoxy specimens in artificial seawater, fibres were not broken as the same as those in the case of pristine specimens, showing fibres pullout and matrix debonding, indicating the damage to the fibre-matrix interface as shown in Fig. 8 b, c, and d. After the specimens were aged under seawater, the carbon/epoxy specimens showed a brittle fracture. The fibres surfaces had become smooth for the aged carbon/epoxy specimens, and there were no residual flakes presented in the aged specimens, resulting in weak fibre-matrix adhesion. The severe degradation of the fibre-matrix adhesion resulted in decrease of mechanical properties of the aged carbon/epoxy specimens.

Conclusion

In the present work, moisture absorption and its impact on mechanical properties of the carbon/epoxy composite laminates were experimentally investigated. Carbon/epoxy laminates were aged in artificial seawater for 12 months under ambient, sub-zero, and humid conditions. Tensile, flexural and impact tests were performed once in three months. From the obtained results the following deductions can be drawn.

(1) The gravimetric measurements have shown that the moisture absorption behaviour of carbon/epoxy lami-

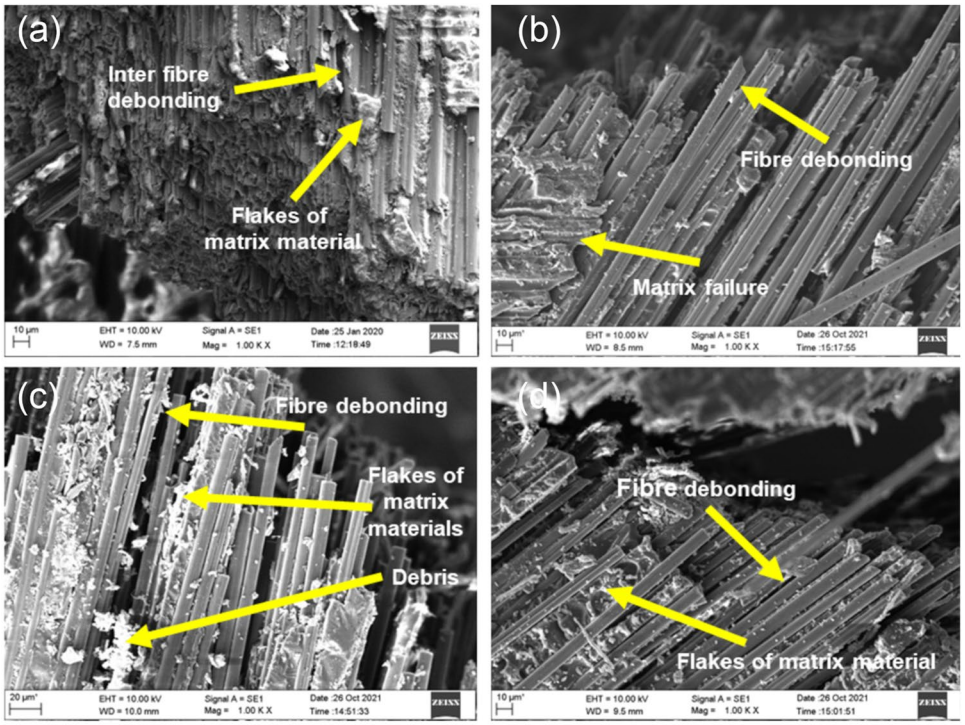


Fig. 8 SEM micrographs of the failure surface of carbon/epoxy composite specimens at: **a** pristine, **b** ambient, **c** sub-zero and **d** humid conditions

nates mainly depends on environmental conditions and the duration of ageing. The moisture absorption for carbon/epoxy composite laminates followed non-fickian distribution. The matrix-dominated characteristics have been reduced because of the ageing process and moisture absorption. A higher percentage of moisture content and higher diffusion coefficients were observed in the carbon/epoxy specimens immersed in ambient conditions compared with the other two conditions.

(2) The tensile, flexural and impact properties mainly depended on ageing period. Tensile properties were degraded more at ambient condition. The moisture induced into the material weakened the fibre-matrix adhesion resulting in the decrement of tensile properties. In contrast, the flexural properties were degraded more in the carbon/epoxy specimens aged under sub-zero condition, and impact properties were degraded more in humid conditions. The absorbed moisture caused plasticization, which weakened the impact properties.

(3) The thermogravimetric study showed that the carbon/epoxy composites were thermally stable up to 400 °C in a nitrogen atmosphere. The epoxy matrix started to degrade at around 400 °C, and epoxy was completely degraded at around 500 °C. From the results, it can be concluded that the thermal stability of the epoxy matrix material improved after incorporating carbon fibres.

(4) SEM fracture analysis showed that fibres pullout and fibre-matrix interface debonding were the significant destructions observed for pristine and aged carbon/epoxy specimens. The SEM micrographs also showed that after hygrothermal ageing, the carbon/epoxy composites experienced degradation in the fibre-matrix interface, resulting in decline of mechanical properties.

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Data Availability The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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