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Research Article

Effect of Hydrothermal Ageing on Glass Fibre Reinforced Plastic (GFRP) Composite Laminates exposed to Water and Salt Water

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Abstract

Glass fibre reinforced plastic (GFRP) composites are being used in a large number of diverse applications ranging from aerospace to sports equipment. The reinforcement materials are highly hygroscopic; the matrix material provides protection to the reinforcement. When the edges of composite materials parts made of are exposed to environment, water molecules passes along the reinforcement. This leads damage to the interfacial bonding and affects the performance of the composite laminate. It is necessary to perform mechanical and environmental characterization to enhance their application spectrum. There is an imminent need to investigate the mechanical behavior of these materials when subjected to different environmental conditions at different exposure schedules. The aim of the present work is an attempt to provide the investigation procedure to assess influence of moisture absorption on strength degradation coupled with temperature and estimated the life cycle time of polymer composite components. From the results and mathematical analysis, it was clear that the tensile behavior and flexural modulus of the conditioned specimens were significantly reduced due to the environmental impact.

Keywords: *Glass fibre reinforced polymer; Environmental conditions; Resin transfer molding; Tensile and Flexural modulus.*

1. Introduction

Polymer matrix composites (PMCs) are increasingly being used in a wide range of applications where long-term service in different environmental conditions. In recent years GFRP/Polyester resin was received considerable attention as alternatives to steel and aluminum due to their high strength-to-weight ratio, competent mechanical properties and ease of handle. Especially in structural materials in the construction, gas and liquid tanks, pipes, offshore platforms, marine, aircraft applications, automotive, recreational equipments and aerospace industries. To study the effects of moisture on retention of mechanical properties of glass fiber reinforced composites during long-term environmental exposure is very crucial which are used for industrial applications.

Glass fibre reinforced polymer composites (GFRP) show relatively low degradation in various corrosive environments in the unstressed state, however, they are very susceptible to stress corrosion, especially in dilute mineral acid environment. There are many studies about the effect of environment conditions and exposure times on GFRP composites and other composites. Here, a few important relative studies focused to supporting the present work. Chin et al. characterized the chemical and physical changes in the polymeric matrix resigns by exposing to different environments like ultraviolet radiation, moisture, temperature, and high pH. They identified the factors that are degrading the matrix resin under varied environmental conditions and mechanical stresses. Straub *et al.* (1997) conducted a series of experiments by the microbond method to determine the effect of testing rate and temperature on the fiber/matrix interfacial shear strength. Results showed that the interfacial shear strength was found to decrease with the increasing testing rate and the effect was more pronounced below the glass transition temperature.

Thwe and Liao (2003 a, b) studied the behavior of composites and hybrid composites of short bamboo and glass fibers in a polypropylene matrix under hygrothermal aging and under tensile–tensile cyclic load. Results suggested that bamboo fiber reinforced polypropylene composite has better fatigue resistance than bamboo-glass fiber reinforced polypropylene hybrid composite at all the tested load levels. Han and Nairn (2003) and Imielinska (2006) also studied the effects hygrothermal ageing of polyimide matrix composites of variable moisture conditions on the fracture toughness of concrete/FRP bonded system are studied by means of the peel and shear fracture toughness determined from the conditioned test specimens. The degradation of the reinforcements played

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an important role in strength reduction of fibre-reinforced composite as they are the major load-carrying constituents and also the moisture conditions n resulted in strength degradation. Karbhari and Zhang (2003) investigated the durability of 2 and 4 layered specimens of E-Glass/Vinylester fabricated from uniaxial, biaxial, and triaxial, non-woven immersed in deionized water at two levels of temperature and a potassium based pH. It was shown that the coefficients of apparent diffusion and levels of moisture gain are the highest for the deionized water immersed samples at higher temperature, and these results in the highest levels of tensile strength and modulus degradation.

Mula *et al.* (2006) evaluated the mechanical behavior of polymer composites under the influence of extreme and complex conditions. They observed the variations in mechanical properties during aging process. Tests were carried out on carbon fiber reinforced polymer (CFRP) bonded to concrete. The test results indicated that the presence of water during the CFRP application, the bond quality has decreased and most of the resulting failures were seen in adhesive failures along the primer/concrete interface (Wan *et al.* (2006). Nishizaki and Kishima (2007) focused on different environmental conditions on GFRP and tested using tensile test. The test results showed that the tensile strength was affected at different levels of environmental conditions for various exposure periods. Mouzakis *et al.* (2008) studied on the different types of FRP laminates produced using the wet lay-up technique and exposed to different environments. The results showed a significant loss of strength and ultimate strain for glass FRP, especially in environments with high pH values, while carbon and hybrid glass-carbon laminates showed very little loss of mechanical properties.

Agarwal *et al.* (2010) characterized the tensile behavior of GFRP composites exposed to brine, acid and base solution, Ganga water, freezing conditions, and kerosene oil at different exposed times. The conclusions were made as tensile strength of the GFRP plates affected with different exposure times. Ramya Krishna *et al.* (2010) carried out studies on RT-cured glass/epoxy composite specimens, subjected to different post-cure schedules at 50, 60, 70, and 85°C and durations and immersed until saturation in distilled water at 50°C. The effects of different post-cure schedules, on the moisture diffusion characteristics of the composite were studied. Results showed that the saturation moisture levels decreased with increased post curing, a trend attributed to increased matrix cross-linking, as the increase in glass transition temperature values with extent of post cure.

Rao *et al.* (2012) investigated strength degradation of glass fibre reinforced plastics (GFRP) laminates under different environmental impact. The results obtained as the tensile strength and flexural modulus were reduced significantly, of the GFRP laminates specimens subjected to water soaking and varying temperature. Felipe et al. (2012) studied and analyzed about glass fiber reinforced plastic sheet under the environmental deterioration on its surface, when placed in a chamber built and also the observed the mechanical behavior when subjected to uniaxial tension. Aniskevich *et al.* (2012) reported on short-term exposure to severe freeze–thaw cycling in the temperature range from –30°C to 20°C of polyester-based glass fiber reinforced plastic both dry and wet. The effect of freeze–thaw cycling of flat specimens cut from I-beam pultruded profile was estimated by use of three-point-bending tests and dilatometric investigation in the temperature range from 20°C to 125°C. It was found that freeze–thaw cycling results in an increase of flexural modulus and decrease of ultimate strength, and strain. Felipe *et al.* (2012) studied and analyzed about glass fiber reinforced plastic sheet under the environmental deterioration on its surface, when placed in a chamber built and also the observed the mechanical behavior when subjected to uniaxial tension.

The main objective of this work is to investigate the effects of hydrothermal aging under different environmental conditions on performance and durability of glass fibre reinforced polymer. Also life prediction analysis has been carried out by mathematical modeling. In this investigation study the tensile and flexural behavior of glass fibre reinforced polymer composite material due to water absorption and temperature effect under different environmental conditions. Finally compared predicted values with experimental values. The number of specimens are prepared and exposed to accelerated hydrothermal environmental conditions and series of experiments are conducted, the results are interpreted to know the behavior of materials. Also the relation between stress verses strain and load verses deflection curves are drawn to evaluate tensile and flexural modulus of material.

2. Experimental Methodology

2.1 Production of laminates using Resin transfer molding

The materials used for GFRP laminates are polyester resin with density 1.35 g/cm^3 and glass fibre mats of woven fabric glass fibre with density 450 g/cm^3. The laminates were produced by mixing 60% of polyester resin and 40% of glass fibre using Resin transfer moulding (RTM) machine which has a closed mould process and consists of resin injection equipment. The resin injection equipment has a hollow cylinder fitted with pressure gauge, valve and pressure pump and mould plates as shown Fig. 1.The parameters considered in RTM for producing the laminates were (i) injection pressure range of 30-40 psi (ii) curing temperature – room temperature.

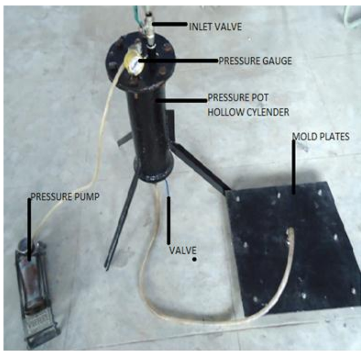

Fig. 1 Resin transfer molding machine

The glass fibre mats were placed in-between the mould plates and clamps. The resin was mixed with 2% of accelerator (cobalt nathylene) and 2% of catalyst (methyl ethyl keypricperoxide) then poured into the cylinder through the valve.The valve was closed immediately then air pumped into hollow cylinder such that pressure should reach 40 psi. The bottom valve of the cylinder was slowly released so that pressurized chemical resin enters in to the mould and it has to spread equally in to all directions. The laminates were kept for 4 to 5 hours idle time in the mould to get required shape. After curing the laminate, the mould was unsealed and separated the lower and upper mould parts. The laminate was removed from the mould then sliced into test samples as shown Fig. 2.

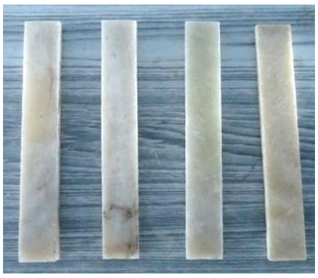

Fig. 2 Specimens of GFRP laminate with dimensions of 250 mm×30 mm×8 mm

2.2 Testing of the Laminates

The laminates were tested under different environmental conditions at constant temperature in both water and salt water bath tubs. In total 120 specimens were exposed to both water bath and salt bath tubs over period of 60 days at 60ºC constant temperature. Initially 20 samples were taken from the bath in 10 days interval then tensile and three point bending tests were conducted on universal testing machine.

2.2.1 Tensile testing

The mechanical properties of GFRP samples were measured using tensile tests as per ASTM-D638 standard. Tensile tests were performed at a nominal cross-head speed of 1mm/min and at room temperature on conventional universal testing machine attached with data acquisition systems and repeated thrice for each set to check the reproducibility. Failure from grip or slippage during testing was not observed. All the GFRP tensile samples were made parallel to the loading direction (longitudinal direction) only, so that glass fibres participate in deformation during tensile testing. The load-stroke behavior obtained during testing was converted into engineering stress – strain and calculated the tensile strength and elastic modulus. The tensile modulus was calculated using the below formulae

$$E_T = \frac{STRESS}{STRAIN} \qquad (1a)$$

Where stress was taken corresponding to strain percentage of 0.8,1 and 1.2 from stress strain relation and average it.

2.2.2 Three point bending test

Three point bending tests were performed at a nominal cross-head speed of 1mm/min and at room temperature on conventional universal testing machine attached with data acquisition systems and repeated thrice for each set to check the reproducibility similar to tensile tests. The same test samples as per ASTM-D638 standard were used for these tests also. The loading direction was in transverse direction for all three point bending tests of GFRP samples. The load-stroke behavior obtained from the bending test. It was converted into load verses deflection relation and calculated the flexural modulus. The flexural modulus was calculated using equation 1b.

$$E_f = \frac{L^3 m}{4bd^3} \qquad (1b)$$

Where E_f = Flexural modulus; L = Support span (Specimen gauge length) in mm; *b* = Width of specimen in mm; *d* = Depth or thickness of specimen in mm and *m* = the gradient of the initial straight-line portion of the load deflection curve in N/mm.

2.3 Performance Prediction Analysis

An indirect indication of service life is obtained simply by comparison of the performance of materials under given test conditions, the one which shows the smaller change being deemed to perform better. To make a direct estimate of service life of materials, it is necessary to apply some form of extrapolation technique to their experimental data. The life estimation of GFRP composites in these environmental conditions were analyzed by employing exponential regression analysis life prediction mathematical models. The life predication equation was derived on the basis of experimental data in terms of the degradation coefficient (decay constant), soaking time, minimum strength and exponential coefficient for different environmental conditions. Exponential linear regression provides powerful technique for fitting the best relationship between dependent and independent variables based on this technique life estimation of composite materials was being established as follows.

$$Y(X) = Y_0 + A_1 exp - (X - X_0)/t_1 \ldots\ldots\ldots (2)$$

Where Y(X) is dependent parameter; X is exposure time in terms of days; Y_0 is minimum strength property after long exposure of time; t_1 is the degradation coefficient or decay constant

3. Results and Discussion

3.1 Tensile and three point bending behavior of GFRP at different environmental conditions

The GFRP composite laminates which are exposed to normal water with different time intervals engineering stress-strain behaviours are shown in Fig. 3 and Fig. 4 shows the engineering stress-strain behaviours of GFRP

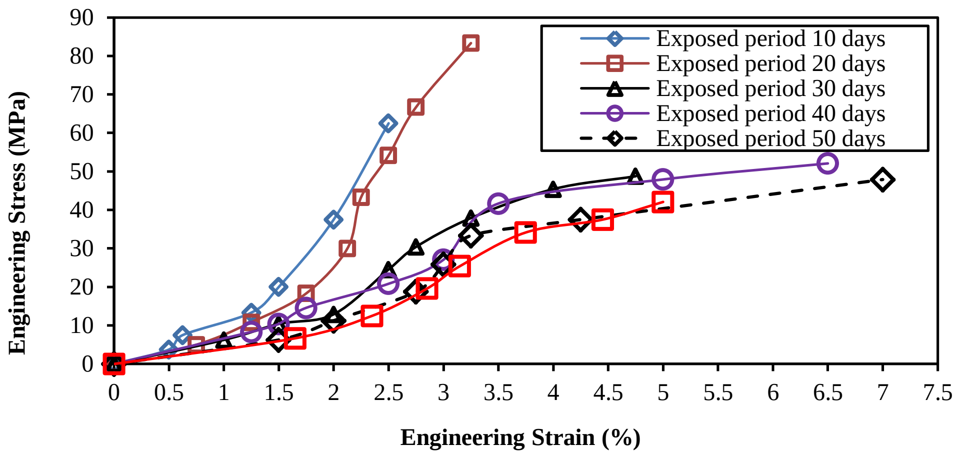

Fig. 3 Tensile behavior of GFRP specimens exposed to water at 60^0C temperature at different time intervals

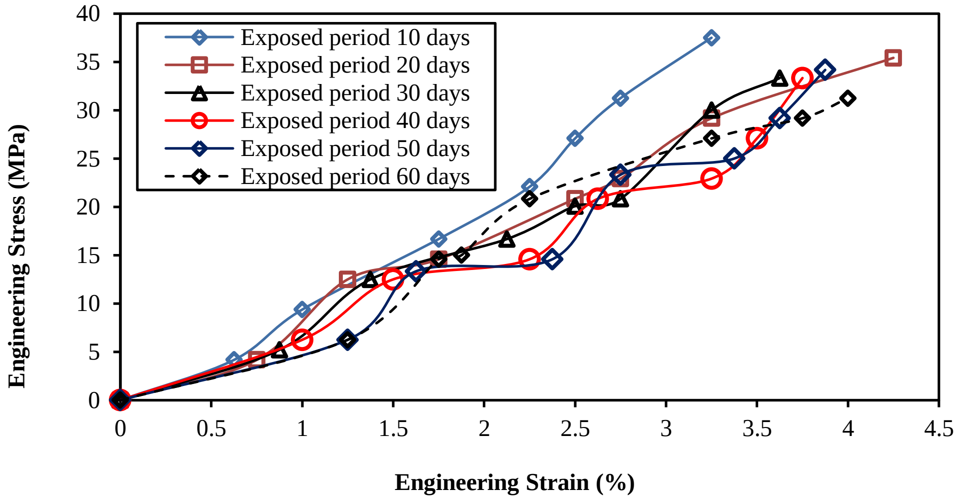

Fig. 4 Tensile behavior of GFRP specimens exposed to salt water at 60^0C temperature at different time intervals

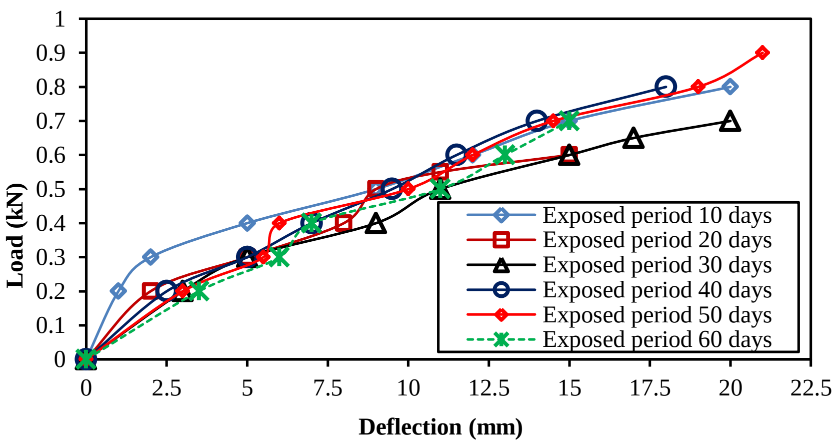

Fig. 5 Three point bending behavior of GFRP specimens exposed to water at 60^0C temperature at different time intervals

composite laminates exposed in the salt water with different time intervals over a period of 60 days. Similarly loads vs. deflection plots are drawn to study the three point bending behaviour as shown in Fig. 5 and 6. From Fig. 3 and 4 tensile modulus of the GFRP specimens are calculated within the elastic limits choosing the three points in a straight line portion corresponding to strain. For example, tensile modulus of specimen which is exposed to salt water for 10days is calculated at end of10 days,

$$E = \frac{\left(\frac{7}{0.8} + \frac{9.375}{1.0} + \frac{13.5}{1.2}\right)}{3 \times 100} = 0.97 \text{ GPa}$$

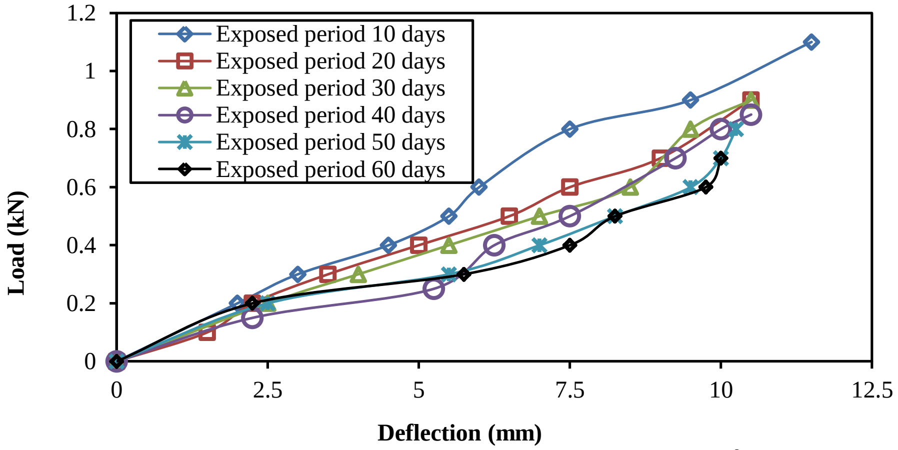

Fig. 6 Three point bending behavior of GFRP specimens exposed to salt water at 60^{0}C temperature at different time intervals

Table1 Tensile and flexural modulus of GFRP composite laminates (a) Exposed to water at constant temperature 60°C

Exposure time (days)	Tensile modulus (GPa)			Flexural modulus (GPa)		
	Predicted	Experimental	Error	Predicted	Experimental	Error
0	0.970	0.970	0	11.553	11.553	0
10	1.118	1.12	0.89	5.780	5.786	-0.11
20	0.829	0.825	0.48	5.238	5.199	0.74
30	0.707	0.701	0.85	4.776	4.852	-1.56
40	0.654	0.680	-3.77	4.382	4.332	1.15
50	0.632	0.623	1.44	4.047	4.043	0.08
60	0.622	0.615	1.20	3.762	3.773	-0.29
70	0.618	-	-	3.519	-	-
80	0.617	-	-	3.312	-	-
90	0.616	-	-	3.135	-	-
100	0.615	-	-	2.986	-	-
110	0.615	-	-	2.858	-	-
120	0.615	-	-	2.749	-	-
130	0.615	-	-	2.656	-	-
140	0.615	-	-	2.577	-	-
150	0.615	-	-	2.510	-	-

(b) Exposed to salt water at constant temperature 60°C

Exposure time (days)	Tensile modulus (GPa)			Flexural modulus (GPa)		
	Predicted	Experimental	Error	Predicted	Experimental	Error
0	0.970	0.970	0	11.553	11.553	0
10	0.974	0.979	-0.45	5.646	5.698	-0.91
20	0.843	0.825	2.20	5.143	5.028	2.28
30	0.730	0.750	-2.57	4.690	4.752	-1.32
40	0.634	0.642	-1.17	4.283	4.232	1.20
50	0.552	0.528	1.27	3.917	4.032	-2.85
60	0.482	0.492	-2.08	3.588	3.524	1.82
70	0.421	-	-	3.293	-	-
80	0.370	-	-	3.027	-	-
90	0.326	-	-	2.789	-	-
100	0.288	-	-	2.575	-	-
110	0.256	-	-	2.382	-	-
120	0.228	-	-	2.209	-	-
130	0.205	-	-	2.205	-	-
140	0.185	-	-	1.914	--	-
150	0.164	-	-	1.788	-	-

In the similar manner tensile modulus is calculated for all the specimens. All the results are tabulated in the Table 1 a&b from both normal and salt water.

Flexural modulus of elasticity is calculated using the data which is represented in Fig. 5 and 6. For specimens exposed to water and salt at constant temperature 60^{0}C with deferent exposure time intervals. The flexural modulus of the sample which is exposed to salt water is calculated by using the equation 1 as

$$E_f = \frac{L^3 m}{4bd^3}$$

$$m = \frac{\Delta Y}{\Delta X} = \frac{0.08}{1.75} = 0.45$$

$$\text{Flexural modulus } (E_f) = \frac{220^3 \times 0.045 \times 10^3}{4 \times 30 \times 8^3} = 7.798 \text{ GPa}$$

Likewise all the samples flexural modulus is calculated and summarized all the results and tabulated in the Table 1 a & b.

3.2 Prediction values of tensile and flexural modulus

The predicted values of tensile and flexural modulus for GFRP composites are calculated using the mathematical exponential linear regression which provides for fitting the best relationship between dependent and independent variables. This technique helps to estimate the life of composite materials. Using the mathematical equation 2 tensile and flexural modulus are calculated for all GFRP samples exposed to water and salt water at 60^0C is established by experimental data. Few illustrations are shown in below calculations.

Tensile modulus of sample exposed to water at 60^0C temperature is

$$Y\ (x_i) = 0.6154 + 1.1791 exp - (x_i)/11.7411..........(3)$$

Flexural modulus of sample exposed to water at 60^0C temperature

$$Y\ (x_i)\ = 2.12343 + 4.2930 exp - \ (x_i)/62.28153.......(4)$$

Tensile modulus of sample exposed to salt water at 60^0C temperature is

$$Y\ (x_i) = 0.0646 + 1.0635 exp - (x_i)/64.069........(5)$$

Flexural modulus of sample exposed to salt water at 60^0C temperature

$$Y\ (x_i) = 0.67539 + 5.5318 xp - (x_i)/\ 93.5493.......(6)$$

From the calculation results of the predicted values of tensile and flexural modulus values are compared with experimental values as shown Table1a & b.

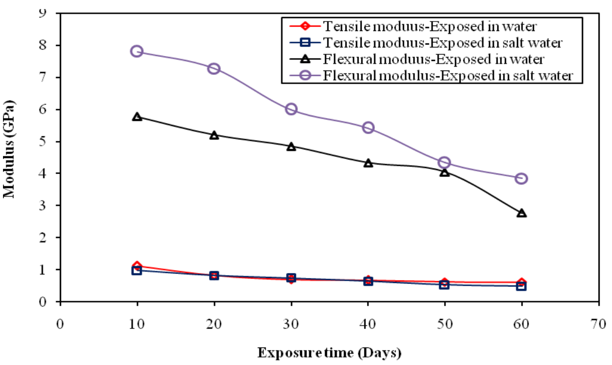

Fig. 7 Modulus v/s Exposure time

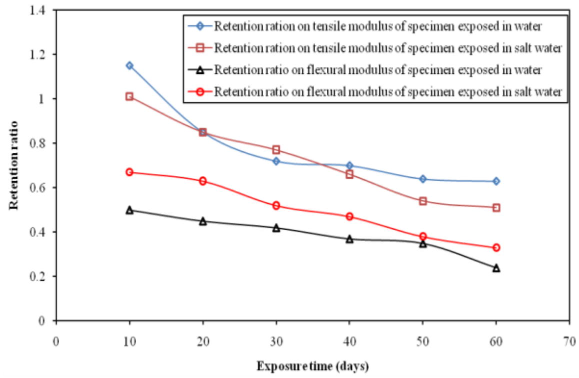

Fig. 8 Retention ratio v/s Exposure time

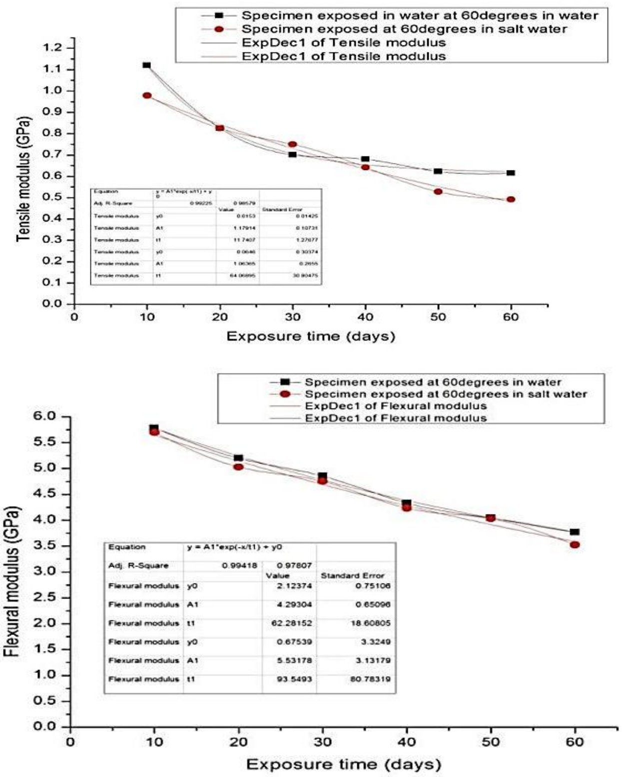

Fig. 9 Mathematical modeling of GFRP laminates exposed to different environmental conditions

The experimental results revealed mechanical properties of the GFRP (E-Glass/Polyester) samples subjected to aging at 60^0C constant temperature in water and salt water as shown in Table 1. From the experimental results, initially tensile strength appear to be increased as soaking (exposure) time is increasing this is because of cross linking reaction in polyester resin is still in progress up to 2 weeks of laminate preparation. The damage degradation water molecular sleep age is dominated by cross linkage speed. Hence there is nominal increment in the mechanical properties is appear. After that rapid reduction in mechanical properties is observed and gradual decrease is observed over the exposure time as shown in Fig. 7. Figure 7 shows flexural modulus has a sharp reduction for the specimen exposed to water as compared to specimens exposed to salt water because of more moisture interference in fibre matrix in the water than salt water. The samples subjected to aging at the constant temperature water bath (60ºC) showed a hyperbolic decrement in the tensile strength and the flexural modulus. On the whole it is observed that tensile and flexural modulus decreased to some extent with the presence of moisture and temperature.

There is significant reduction in modulus because of loosing bonding strength of the polyester resin at temperature. It is clear that the tensile and flexural modulus rapidly decreases due to hydrothermal aging because moisture generally affects any property which is dominated by the matrix and/or interface. However the flexural strength being a fibre dominated property the strength reduction occurs only if the fibres themselves are affected by hydrothermal environmental conditions. The retention ratio (ratio of strength of exposed specimen to unexposed specimen) has been calculated for tensile and flexural modulus as shown Fig. 8 and it is clear that gradual reduction over exposure time of 60 days.

The regression analysis is performed for each of the time steps and this yields a set of exponential linear relationships between the tensile, flexural modulus and exposure time at different conditions as shown Fig. 9. The relationships so obtained are shown in equations 3, 4, 5 and 6 can be used to determine the tensile and flexural modulus of the composite specimen for different time steps at constant temperature 60^{o}C. For predictions of response due to immersion in water and salt water at 60^{o}C, the values of tensile, flexural modulus at each time step are obtained by substituting the exposure time in days in the equations 3, 4, 5, and 6, the values are listed in Table1. The obtained predicted values are compared to experimental data and they are similar also calculated the percentage error. Based on this analysis it has to be noted that as temperature increases the predicted values are increases that indicate rate of degradation increase. The life estimation of composite materials has been possible by prediction models.

4. Conclusions

The investigation showed a remarkable reduction in mechanical strength (tensile and flexural modulus) of GFRP composite laminates which are subjected to different environmental conditions over exposed time. The flexural and tensile strength values of the specimens are decreases over exposure period of 60 days in water and salt water at constant temperature. As per the results tensile modulus initially slightly increases and gradual decrease over long period and expected to maintain considerable minimum strength over service but flexural modulus gradual decreases over long period exposure and maintain the minimum strength over service.

The following conclusions are drawn from test results and mathematical modeling.

1. The Composite material moisture absorption is more. The presence of moisture or water particles in the matrix, fibre-matrix interface and also attack on the glass fibres are all the reason for reduction of properties due to environmental impact.
2. The tensile and flexural modulus reduction is more in hygrothermal aging because of temperature is a key factor for accelerated aging in the processes of water diffusion and chemical degradation.
3. It is worth noticing that aging at elevated temperatures strength degradation is more in salt water exposure compared to normal water.
4. It is worth noticing that aging at elevated temperatures will also cause color change in samples.
5. It is clear that retention ratio gradual decreases under tensile and bending loading with different environmental conditions.
6. On the basis of the analysis the minimum strength material has been estimated.

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