Effect of Post-thermal shock on Prolonged Sea Water aged GFRP Composite

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Abstract: The present investigation is an attempt of evaluating the suitability of glass fibre reinforced polymer composites to thermal shock treatments of various lengths of time subject to pre-immersion in sea water for 1 year. Mechanical properties like inter laminar shear strength (ILSS), stress at rupture, strain at rupture and modulus values are recorded by adopting 3-point bend test method. Mechanical properties show a general decreasing trend at higher durations of up and down-thermal shock exposure irrespective of showing initial non-equilibrium zig-zag trend. Glass Transition temperature ($T_g$) with respect to optimum durations of thermal shock treatment show considerable variation for the sample with minimum sea water immersion period. SEM fractographs of the thermally shocked specimens revealed the mode of failures like fibre pull out, fibre/matrix debonding, cusp formation indicating polymer crazing, matrix cracking, fibre breaking etc.

Key Words: GFRP composite, Thermal Shock, Inter laminar shear strength, Glass Transition Temperature ($T_g$), fibre pull-out

1. Introduction

Glass fibre reinforced polymer (GFRP) composites have gained tremendous attention in various marine applications like offshore pipes, ship structures, water storage vessels etc. [1]. The cost of installation and maintenance of these composite structures are reportedly lower than that of some conventional materials like steel and aluminium [2]. Out of these specific uses, the marine ship structures composed of GFRP composite laminates are subjected to immersion in sea water for years together necessitating accumulation of experimental data in this respect. Chakraverty et al. [3] have reported the response of E-glass fibre/epoxy layered composites to one year immersion in sea water at room temperature. Inter laminar shear strength (ILSS) of such immersed composites decreased up to 23% of that for as-cured one and glass transition temperature after initial decrease increased up to some extent. Polymeric composites during immersion (fully or partly) in sea water may lead to mechanical property deterioration by plasticization and swelling of polymer [4]. Also, various salt components of the sea water may annihilate the moisture absorption rate compromising some properties of the material subjected to sea water immersion [5]. On the basis of the above, the long
term retention of structure related properties and stability under the sea water immersion condition is of significant concern from a prolonged service life point of view of these materials.

These components are supposed to meet fluctuating thermal conditions (thermal shock) during their use; specially, if there is a sharp change in temperature due to high speed collision or during weather change, change of temperature from one particular sea location to other during immersion period or simply due to a lightening in a rainy day. In such cases, thermal stresses due to temperature fluctuations concentrated around the defect tips across fibre/matrix interface would be catastrophic [6]. Added to it, temperature fluctuations from elevated to sub-ambient temperatures or vice-versa may influence the moisture desorption kinetics as well as the relaxation process in the matrix body [7]. Sometimes, huge thermal stresses due to higher thermal gradient may create irreversible mechanical degradation in the composite body. It is therefore, only pertinent that some durability data of GFRP composites with prolonged sea water immersion and concurrent thermal shocks be made available. The present study aims at evaluating the performance of the GFRP composite immersed in sea water for different lengths of periods when exposed to up and down thermal shocks for different durations.

2. Materials and methods

Conventional hand lay-up method [6] is adopted for the fabrication of GFRP composite comprising woven E-glass fibre and Epoxy resin (Lapox L-12). Diamine (Lapox K-6) is used as hardener/curing agent. The composite, after 48 hours of room temperature curing, was allowed for cutting in a diamond cutter for preparation of short beam shear (SBS) specimens (50 mm length X 12 mm breadth) as per the ASTM D 2344-84 (2013) standard [8]. The specimens are then heated in an electric oven up to 55-60°C of temperature and weighed; this process being repeated to ensure the complete removal of moisture during fabrication. Typical properties of Epoxy resin as provided by ATUL polymer division are cited from our previous article [3].

All the immersed composite specimens are allowed for thermal shock treatments. An electric oven and a cryogenic chamber (deep freezer) are maintained at +50°C and -40°C, respectively. The sea water immersed samples are allowed for up-thermal shock treatment (-40°C for 1, 2, 3, 4 and 5 hours in the cryogenic chamber, then suddenly put in an electric oven set at +50°C for 2 hours of fixed duration) and Down-thermal shock treatment (+50°C for 1, 2, 3, 4 and 5 hours in the electric oven, then suddenly put in cryogenic chamber set at -40°C for 2 hours of fixed duration).

The post-thermally shocked samples after 1 year of sea water immersion are allowed for 3-point bend test in INSTRON-1195 to determine inter laminar shear strength (ILSS). Stress at rupture, strain at rupture and modulus values of all treated composite samples are also recorded from the same test. ILSS is determined by using the following formula [9]

\[
ILSS = \frac{0.75 \times 1000 P_b}{b t} \text{ N/mm}^2 \text{ or (MPa)}
\]

\[
(1)
\]

where,

\[ P_b = \text{breaking load (load at rupture in kN)} \]
\[ b = \text{width of the specimen} \]
\[ t = \text{thickness of the specimen} \]

Glass transition temperature (Tg) of the treated samples are recorded by adopting low temperature DSC test. The Tg measurement is performed on Mettler-Toledo 821 with intra-cooler using STAR software in DSC module. The scanning range is maintained as 30-150°C with the rate of 10°C/min. The fractographs of the samples treated for optimum durations of sea water immersion and thermal shock treatments are investigated by scanning electron microscope (SEM, JEOL, JSM-6480 LV) and the failure modes are divulged for corresponding treated samples.
3. Result and Discussion

3.1: Mechanical Properties

Fig. 1 represents the variation of ILSS with duration of up and down-thermal shocks to sea water immersed samples. ILSS values of all sea water immersed samples with up and down-thermal shocks show minor variations with an initial non-equilibrium zig-zag trend which may be due to non-equilibrium moisture desorption kinetics during the initial periods of thermal shock exposure.

Sea water immersion at room temperature for 1 year is insufficient to bring about an average response by the composite body, as a consequence of which locally confined swelling in the matrix or matrix/fibre interface causes complex deformation due to local in-homogeneity leading to non-equilibrium zig-zag variations in ILSS. The response to sea water immersion, therefore, may be due to a non-uniform localised swelling, which can disturb the mechanical behaviour under load. In addition to this, different locations of the composite body response to the ILSS values differently. This may cause a zig-zag effect in the response.

On immersion of GFRP composites for a prolonged period of 1 year in sea water, its mechanical properties deteriorated as evidenced by the drop of ILSS values up to 23% [3]. Both up and down thermal shocks are found not to have caused any further deterioration in the mechanical behaviour (Figure 1). In other words, thermal shocks (up and down) have not created any remarkable excitements (matrix hardening due to -40°C and fine whisker forming by moisture desorption process due to +50°C [7]) as evidenced from no change in the ILSS values of the immersed samples. This signifies that the laminar strength degradation due to prolonged sea water immersion is irreversible and is not altered even after thermal shock treatments.

Fig. 2 and Fig. 3 illustrate the variations of stress at rupture and strain at rupture with varying time period of both types of thermal shock treatments. Both stress at rupture and strain at rupture values, despite of showing initial non-equilibrium zig-zag trend, decrease for the samples with maximum period of sea water immersion (1 year) at higher durations of up-thermal/down-thermal shock treatments. Up-thermal and down-thermal shock of higher durations cause decrease in stress at rupture values in general. Larger thermal gradient during higher durations of both up and down-thermal shocks are responsible for not allowing the accommodation of residual stresses generated due to thermal expansion mismatch between the matrix and the fibre [10]. This phenomenon becomes more prominent for the samples immersed in sea water for prolonged periods (10 and 12 months). This signifies the less requirement of stress at rupture for the GFRP composite samples with higher duration of sea water immersion.
immersion followed by up/down-thermal shock for higher during +50°C and cryogenic matrix hardening during -40°C exposure. This competing phenomenon is expected to be more prominent for the samples with higher sea water immersion period. For this case, samples with higher moisture absorption could have responded the moisture desorption and cryogenic matrix hardening in a very prominent manner to show the strain misfit between fibre and epoxy polymer. This may give rise to a permanent mechanical deterioration by which stress requirement at rupture was found to be decreased compared to the value as observed during initial duration of both up and down-thermal shock treatments with a non-equilibrium zig-zag trend.

Fig. 2: Variation of stress at rupture for sea water immersed samples with time of exposure of (a) up-thermal shock (b) Down-thermal shock

Fig. 3: Variation of strain at rupture for sea water immersed samples with time of exposure of (a) up-thermal shock (b) Down-thermal shock

Strain at rupture values show a general decreasing trend with higher periods of thermal shock exposure (Fig. 3). As explained earlier, higher durations of thermal shock treatments with larger thermal gradient are likely to result in thermal expansion mismatch creating strain misfit between fibre and matrix. This could have reduced the required strain at rupture values of the composite specimens subjected to mechanical loading. The GFRP composite samples after one year of sea water immersion show minor decreasing trend in strain at rupture with increasing durations of up/down-thermal shock treatments. This is because of the occurrence of irreversible mechanical damages in the composite samples due to prolonged sea water immersion. The permanent damage due to prolonged sea water immersion is not
likely to allow any recovery of the strain property of the treated samples during the thermal shock exposures. The rate of decrease of strain at rupture is not very prominent for the samples with higher sea water immersion period. For this case, the mechanical deterioration occurred after sea water immersion is not responsible for any scope to compensate such decrease of strain at rupture during any of the thermal shock conditioning. This can indicate the less impact of thermal shock treatments to the strain property of GFRP composite sample with higher sea water immersion.

The variations of modulus values of the sea water immersed samples with varying periods of up and down-thermal shocks are presented in Fig. 4. Modulus values of all the samples increase at higher durations of up-thermal shock treatment. However, minor changes in the modulus values are observed with higher durations of down-thermal shock. The non-equilibrium zig-zag variations in modulus are likely to be the effects of localised swelling in the matrix (in some restricted areas only) due to non-homogeneous moisture desorption kinetics during initial durations of thermal shock treatments, the initial periods not being sufficient to bring about an average response of the composites to the external excitements by showing variation in modulus values.

The increasing trend in modulus values during higher durations of up-thermal shock puts the signature of moisture induced swelling, which finally results in a lowering of the strain at failure. This result is well in agreement with the variation of strain at rupture values of the immersed samples with up-thermal shock treatment. In the present case, the increased durations of exposure to -40°C under the up-thermal shock treatment, enhance the moisture to ice transformation. This process of transformation to ice dominates the moisture desorption process due to +50°C of duration 2 hours only. Thus, swelling of the matrix is caused, which in turn results in increase of modulus values [5]. For the samples immersed in sea water for maximum period (1 year), moisture distribution is quite homogeneous leading to the resultant overall swelling in the matrix. This may cause continuous increase in modulus with increasing durations of up-thermal shock treatment.

Modulus values are observed to vary within minor ranges during higher durations of down-thermal shock treatment. In the present case, increasing durations of +50°C cause the formation of fine whiskers/ inter-connected pores. These processes are likely to neutralize the effect of freezing of moisture due to exposure to sub-ambient temperature of -40°C for 2 hours only. This may lead to minor resultant swelling in the matrix. Thus, minor variations in modulus values are observed for the immersed samples with increasing durations of down-thermal shock treatment.

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Fig. 4: Variation of modulus for sea water immersed samples with time of exposure of
(a) up-thermal shock (b) Down-thermal shock
3.2: Glass Transition Temperature ($T_g$)

The $T_g$ values as obtained from the DSC thermograms are plotted for different thermal shock treatments and illustrated in Fig. 5. Fig. 6 represents the DSC thermograms of the immersed samples after the exposures to up-thermal and down-thermal shock treatments for optimum durations. The $T_g$ variation plot indicates the minimal ranges of variation for all immersed samples (except for 2 months of immersed one) subject to post thermal shock treatments including both up and down-thermal shocks.

The samples subjected to 2 months of sea water immersion show remarkable variations in $T_g$ values with respect to up and down-thermal shock treatments. The thermal stress due to minimum/maximum thermal gradient cause a combined effect pertaining to fine whisker formation due to desorption of moisture during $+50^\circ C$ and cryogenic hardening during $-40^\circ C$ [7]. These two competitive phenomena influence the extent of free space constituting voids or free volumes in the polymer matrix [6]. In the present case, the particular sample, with less absorbed moisture, respond to the above competitive phenomena in such a way that the cryogenic hardening dominates over the fine whisker formation. Thus, the free volume decreases with increase of mechanical locking [11]. Hence, the $T_g$ for the sample show higher values after the thermal shock treatments for shorter duration of sea water immersion.

The immersed samples with immersion period greater than 2 months, however, show minor changes in $T_g$ values with negligible fluctuations. Under such conditions the higher extents of moisture gain would result in more/less balancing of the effect due to the two competitive phenomena (whisker formation and matrix hardening) which is responsible for minimal variations of $T_g$ values.

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**Fig. 5:** Variation in $T_g$ values with optimum durations of up and down-thermal shock treatments for sea water immersed samples.
Fig. 6: DSC thermograms of sea water immersed composite samples subject to thermal shock treatments

3.3: SEM Fractographs

The fractographs as revealed in Fig. 7 and Fig. 8 represent the failure modes associated with the fractured composite specimens subject to sea water immersion of extreme periods (2 and 12 months) and optimum (minimum and maximum) durations of up-thermal and down-thermal shock treatments. The fractographic images revealed some chief mode of failures like fibre pull out, fibre/matrix debonding, cusp formation indicating polymer crazing, matrix cracking, fibre breaking etc.
Fractographs, in some cases clearly show fibre imprints as a result of debonding of fibre from the matrix. The debonded matrix body sometimes show some crazing mark (cusp) signifying the stress concentrations for prior failure under load. Fibre breaking and matrix cracking are mostly visible in case of the immersed samples subjected to maximum durations of up-thermal and down-thermal shocks. During fibre pull-out, fibre breaking or matrix cracking can be observed depending on the load sustaining capacity of both the components.

Fig. 7: SEM fractographs for 2 months sea water immersed samples
(a) up-thermal shock [-40°C (1 hour) to +50°C (2 hours)] (b) up-thermal shock [-40°C (5 hours) to +50°C (2 hours)] (c) down-thermal shock [+50°C (1 hour) to -40°C (2 hours)] (d) down-thermal shock [+50°C (5 hours) to -40°C (2 hours)]

Fig. 8: SEM fractographs for 1 year sea water immersed samples
(a) up-thermal shock [-40°C (1 hour) to +50°C (2 hours)] (b) up-thermal shock [-40°C (5 hours) to +50°C (2 hours)] (c) down-thermal shock [+50°C (1 hour) to -40°C (2 hours)] (d) down-thermal shock [+50°C (5 hours) to -40°C (2 hours)]
4. Conclusions

Some following conclusions as drawn from the present findings are mentioned below.

(i) Thermal shock treatments to the sea water immersed samples cause initial zig-zag trend in mechanical property variation with a general lowering trend for the higher durations.

(ii) $T_g$ values for the thermally shocked samples show small variations. However, for the samples immersed for 2 months, $T_g$ values are increased for both up and down-thermal shocks.

(iii) SEM fractographs of the thermally shocked GFRP specimens revealed the mode of failures like fibre pull out, fibre/matrix debonding, cusp formation indicating polymer crazing, matrix cracking, fibre breaking etc.

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