Sea Water Ageing of GFRP Composites and the Dissolved salts

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Abstract. This paper houses the effect of sea water immersion on glass fibre reinforced polymer (GFRP) composites. The major sources of interest are study of sea water absorption, penetration of the dissolved salts, details of chemical and physical bonds at the interface, variations of mechanical properties and study of failure mechanisms as revealed through SEM fractographs. Eighteen ply GFRP composites are immersed in sea water for a period of one year in steps of two months durations. It is revealed that the moisture absorption transforms from a Fickian to non-Fickian behavior with lapse of time. The dissolved salt ‘K’ shows highest depth of penetration after one year of immersion while ‘Na’ shows a least depth of penetration, as revealed from the EDS spectra. It is also revealed that ‘Ca’ seems to have a sudden burst in the rate of penetration even surpassing that of ‘K’. This trend can be attributed to the combined effect of ionic mobility of the various dissolved salts and the probable interaction between ‘K’ and the –OH group of epoxy resin. This interaction between dissolved ‘K’ and the –OH group in the polymer could have arrested the further advancement of ‘K’ salts in the polymer, resulting in comparatively high rates of ‘Ca’ penetration. The mechanical properties such as inter laminar shear stress (ILSS), stress and strain at rupture, glass transition temperature (Tg) and elastic modulus show a decreasing trend with the increased duration of immersion. As revealed from the SEM fractographs pot-holing, fiber pull-out, matrix crack etc. are seen to be the major reason for failure of the immersed samples under load.

Keywords: GFRP composites, depth of penetration, ILSS, glass transition temperature (Tg), SEM fractographs

1. Introduction

Glass fibre reinforced polymer (GFRP) composites are recommended for use in marine infrastructures. These materials, due to their excellent corrosion resistance and light weight property have gathered tremendous attention in marine sectors for applications in ship building industry, water storage vessels, desalination plants, manufacture of leisure boats 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]. However, 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. Polymeric composites during immersion (fully or partly) in sea water may lead to mechanical property deterioration by plasticization and swelling of polymer [3]. Also, various salt components of the sea water may annihilate the moisture absorption rate compromising some properties of FRP systems subjected to sea water immersion [4].

The effect of moisture coupled with temperature on Glass/Epoxy composite in the presence of the dissolved salts in sea water has been reported by several workers [5-10]. Sea water absorption causes changes in the thermo-physical, mechanical and chemical characteristics of the matrix by the processes of both plasticization and hydrolysis. It is reported [11] that the effect of sea water on GFRP composites differs with matrix material and conditioning environment. In Glass/Epoxy composite, in particular, the mode of failure is altered from a brittle matrix and ductile fibre to ductile matrix and brittle fibre.

The ingressed moisture tend to result in plasticization and swelling of the matrix where as the dissolved salts penetrating to different depths in the composite body influence the moisture ingestion, thereby affecting the processes of deterioration of mechanical properties. On the other hand, these adverse effects are minimized by the dual mechanisms of stress relaxation and swelling [12]. Moisture absorption may also cause cracking, blistering, chemical degradation, debonding, hydrolysis, oxidation and leaching, the processes being irreversible [13]. Thus, some durability data with sea water aging for prolonged periods of immersion have to be obtained in order to precisely decide the utility of such composite material when immersed in sea water.

Keeping the above in mind, GFRP composite samples are immersed in sea water for a period of one year maximum in batches of two months each. The effect of moisture ingestion as influenced by the penetration of different dissolved salts is studied at length. Specifically, the effect of sea water immersion on the mechanical properties of GFRP composites such as ILSS, Stress and Strain at rupture, elastic modulus and Glass-transition temperature ($T_g$) are reported on the basis of the experimental data. Lastly, the mode of failure on load is determined and reported as obtained from the SEM fractographs.

2. **EXPERIMENTAL**

GFRP composites composed of woven E-Glass fibre and epoxy resin (Lapox L-12) are fabricated using conventional hand lay-up method. Diammine (Lapox K-6) is used as the hardener/curing agent. After 48 hr of room temperature curing, short beam shear specimens (50 mm length X 12 mm breadth) are prepared as per the ASTM D 2344-84 (2013) standards [14]. Complete removal of moisture is ensured by alternate heating (55-60°C) and weighing of as-cured composite specimens till a fixed weight is obtained. Some typical properties of epoxy resin as provided by ATUL limited (polymer division) are listed in Table 1.
Table 1: Typical Properties of Epoxy Resin (Lapox L-12)

| Properties                  |       |
|-----------------------------|-------|
| Tensile strength           | 55-70 MPa |
| Flexural Strength          | 120-140 MPa |
| Elastic Modulus            | 3.2 -3.6 GPa |
| Glass Transition Temperature \((T_g)\) | 110-130°C |
| (120°C as mid value)       |       |
| Co-efficient of Thermal Expansion | 64-68 K\(^{-1}\) |

The as-cured composite specimens are immersed in sea water at room temperature for 2, 4, 6, 8, 10 and 12 months. The percentage of moisture gain \(M(t)\) after each period of sea water immersion is determined from the weight gain of the specimen as a function of time [9] using the following formula.

\[
M_t = \frac{w_t - w_0}{w_0} \times 100
\]

where \(w_0\) and \(w_t\) are the weights of the dry and wet specimens at a time \(t\).

Data pertaining to Table 2 reveal the major salt components dissolved in the sea water as obtained from literature [11].

The immersed specimens are subjected to EDS (Energy Dispersive Spectroscopy) analysis to determine the depth of penetration of salt components of sea water into the composite body. Line EDS technique is adopted to determine the depth of penetration in micrometer range. This technique is performed across the specimen (which is cut after sea water treatment) from exposed end, till the reference salt components are absent in the EDS spectra. The length of this depth is measured according to the reference scale in the SEM micrograph.
Table 2: Concentrations of salt components in sea water

| Element          | Parts per million |
|------------------|-------------------|
| Cl (Chloride)    | 21,700            |
| Na (Sodium)      | 19,497            |
| SO₄ (Sulphate)   | 2880              |
| Mg (Magnesium)   | 1838              |
| K (Potassium)    | 743               |
| Ca (Calcium)     | 602               |
| HCO₃ (Bicarbonate)| 200               |

All the Samples (as-cured and sea water immersed) are then subjected to 3-point bend test by the help of INSTRON-1195 to record ILSS, stress at rupture, strain at rupture and the elastic modulus. Inter laminar shear strength values are calculated by using following formula [15].

\[
ILSS = 0.75 \times 1000 \times \frac{P_b}{bt} \text{ MPa}
\]  
(2)

Where \( P_b \) = breaking load (load at rupture in KN)  
\( b \) = width of the specimen  
\( t \) = thickness of the specimen.

Low temperature DSC technique is adopted to record the glass transition temperature (T<sub>g</sub>) of immersed samples. The T<sub>g</sub> measurements are performed on a Mettler-Toledo 821 with intra cooler using STAR software in DSC module. The experiments are performed in the temperature range of 30-150°C with scan rate 10° C/min. Scanning electron microscope (SEM; JEOL, JSM-6480 LV) fractographs are investigated to study the mode of failure in extreme cases of sea water conditioning at room temperature.

3. RESULTS AND DISCUSSION

3.1 Moisture gain

Figure 1 illustrates the variation of moisture gain with square root of sea water immersion periods. The percentage of moisture gain is increased with increase in immersion period. The rate of moisture absorption assumes a high value initially followed by a comparatively slower rate of variation up to a period of 8 months and then increases again. The initial increase in moisture gain is due to concentration driven moisture absorption. In this case, the absorption
behaviour is fickian. But, sea water ageing of FRP composites still remains an uncertain factor [1]. Ingression of pure water in to the epoxy polymer is quite more feasible than that of saline water due to presence of dissolved salts. A concentration driven osmotic pressure causing moisture ingress in to the polymeric composite body is less of a problem in saline solutions than in pure water. The bulky nature of various salt components of sea water, with their osmotic effect, influences the rate of moisture ingress with time. The flattened trend of moisture gain may be due to deposition of trace elements on the surface of composite body which intervene with the diffusion processes.

![Graph](image)

Figure 1. Variation of moisture gain with square root of immersion period

Gallert and Turley [1] opine that sea water immersion may result in fibre related mechanisms for transport of moisture in to the composite body. These mechanisms include transport of moisture along the interface and/or continuing diffusion through the matrix with accumulation of fibre. Asbee and Wyatt [12] report the etching of glass fibre surface with water. Prolonged immersion in water can degrade E-glass fibre due to leaching of alkali oxides (sodium and potassium oxides) by forming water skin. This may lead to formation of surface micro-cracks which can act as stress concentrators. It is reported [16] that the aggressiveness of leaching process is more prominent in case of de-ionized water than that of plane or sea water. Hence, after prolonged immersion in sea water (8 months), the leaching of glass fibre would have enhanced the rate of moisture absorption adopting a non-Fickian mechanism.
3.2 Effect of sea water ageing on mechanical properties

3.2.1 ILSS

The variation of ILSS with respect to period of immersion in sea water is illustrated in Figure 2. ILSS decreases with increased periods of sea water immersion. The continuous decrease of ILSS may be attributed to the exchange of hydroxyl groups among the neighboring epoxy chains as a consequence of moisture ingression [17]. This may lead to breaking of organic bonds in the polymer network resulting in segmentation of epoxy chain structure. In addition to this, prolonged sea water immersion is likely to cause mechanical property deterioration concomitant to plasticization and swelling leading to interfacial debonding assisting further moisture uptake. The present findings are well in agreement with the work of Wei [18]. As reported by Wei, the bending strength as well as the tensile strength of glass fibre/epoxy composite continuously decreases with increased immersion period in sea water.

![Figure 2](image_url)

**Figure 2.** Variation of ILSS with periods of immersion

Figure 3 illustrates the variation of ILSS with percentage of moisture gain. The variation of ILSS with percentage of moisture gain exhibits a non-equilibrium zig-zag trend up to 8 months of immersion. This may be due to a complex deformation behavior as a consequence of local swelling in the matrix and/or matrix/fibre interface when the absorbed moisture forces apart the polymer micro-molecules causing an expansion of the glass fibre reinforced composites. Probably, the initial time periods of immersion are not sufficient to bring about an average response to the external stimulation.
In general, composite samples show a decreasing trend in ILSS with increased moisture content. There is a 10% reduction in ILSS after 6 months of immersion followed by 23% reduction after 1 year of immersion. This increasing trend can be attributed to the leaching of the glass fibres as a result of a prolonged exposure to sea water ageing [16].

3.2.2 Stress and Strain at Rupture

The combined variations of stress and strain at rupture with different periods of immersion in sea water are illustrated in Figure 4. Both stress and strain at rupture decrease with increased periods of immersion in sea water. Up to 4 months of immersion, the variations of stress and strain at rupture values show a zig-zag trend. The initial decrease after 2 months of immersion may be attributed to the non-homogeneous distribution of water in the composites. During this period, the water distribution in the glass/epoxy composite would not have reached equilibrium. This is likely to create localized stresses which act as regions of defect leading to lower strength. The inconsistent deviation in the strength property is likely to be due to certain localized defects.
Stress at rupture reduces to 21% of that for as-cured sample after 6 months of sea water immersion and 16% after 1 year showing somewhat recovery in the stress at rupture values. Similarly, the strain at rupture values decrease 12% after 6 months and 20% after 1 year revealing a continued decreasing trend within the limits of experimentation. It has to be clearly understood that any recovery in stress at rupture values adds to the strength properties where as the decrease in strain at rupture values may indicate the stiffening of the matrix. This varied trend can be attributed to several competing phenomena occurring simultaneously. The prolonged sea water immersion causes damages in the composite material due to plasticization and swelling [9] which affect the stress and strain values at failure and the tolerance capacity of the composite is severely affected.

3.2.3 Modulus

Figure 5 shows the variation of elastic modulus with respect to the period of sea water immersion. The modulus decreases for the first 2 months of immersion then increases slightly and again decreases reaching the minimum value after 6/8 months of immersion, being decreased by 25%. The extent of reduction in the elastic modulus is then compensated, the final reduction being made up from an initial value of 25% to 5% after the lapse of 1 year.

The initial reduction in modulus is due to plasticization of the matrix and the ability of the matrix molecules to move against each other [11]. However, the increase of the modulus in the later stages may be attributed mostly to swelling which improves mechanical adhesion between fibre and matrix. These two reversing trends result in decrease of the modulus by 5% only, making it up from 25% to 5% after 1 year.
To sum up the increasing/decreasing trend of modulus may be attributed to a combined effect to the following competing phenomena:

(i) Initial non-homogeneous water distribution creating localized defect
(ii) Relaxation of residual stress
(iii) Plasticization resulting in lower modulus and high strain to failure
(iv) Swelling leading to increase in modulus and lowering of strain to failure

Figure 5. Variation of modulus with periods of sea water immersion

3.2.4 Glass Transition Temperature \((T_g)\)

The DSC curves of sea water immersed samples are illustrated in Figure 6. The onset values of \(T_g\) are indicated in the graph. Figure 7 represents the variation of \(T_g\) with the duration of immersion.
Figure 6. DSC curves of sea water immersed composite samples

Figure 7. Variation of $T_g$ with period of sea water immersion

$T_g$ values of sea water immersed samples are lower compared to that for as-cured samples, lowest $T_g$ being recorded for the samples after 2 months of sea water immersion. $T_g$ of polymeric materials depends on the extent of cross-linking density [19]. Due to imperfect curing/cross-linking of the polymer, some voids could have been created in the polymer. These voids, referred to as free volume, occupy $1/40^{th}$ of total polymer volume at/below glass transition temperature.
transition temperature [20]. Thus, the reason for early lowering of glass transition temperature is due to the increase of internal voids/free volumes in the epoxy polymer. This could have happened due to less confinement of epoxy network in a particular volume.

Probably, the bulky nature of various salts present in sea water with their osmotic effect [1] promotes the epoxy chain extension by breaking the polymeric network. This leads to the creation of free volumes in epoxy resin. This phenomenon is prominent for lower period of immersion (2 months). Hence, lowest $T_g$ is recorded for this sample. For higher periods of immersion, however, increased salt penetration could have restricted the above phenomenon by accommodating the free volumes of epoxy polymer giving rise to increase in $T_g$.

3.2.5 Depth of penetration of dissolved salts

Figure 8 and Figure 9 illustrate some EDS spectra indicating depth of penetration of various salt components of sea water. Figure 10 represents the variation of depth of penetration of various salt components with period of sea water immersion.

Following observations are evident from the results.
(i) Various salt components penetrate in to the composite body to different depths.
(ii) ‘K’ shows highest depth of penetration after 1 year of sea water immersion.
(iii) Depth of penetration is found to increase continuously for ‘K’.
(iv) ‘Ca’ shows instant increase in penetration after 6 months of sea water immersion and then decreases slightly.
(v) ‘Na’ shows least depth of penetration.
Figure 8. EDS Spectra indicating depth of penetration of salt components after 2 months of immersion period
Figure 9. EDS Spectra indicating depth of penetration of salt components after 12 months of immersion period
‘K’ shows higher depths of penetration due to higher ionic mobility compared to the other salt components. After 6 months, ‘K’ would have interacted with –OH group of epoxy chains (due to having higher reactivity), got arrested, the paired bond inhibiting further penetration of ‘K’ and encouraging ‘Ca’ penetration through a free ionic movement. Hence, sudden increase in ‘Ca’ penetration rate is visible.

Another interesting observation is that despite higher ionic mobility compared to ‘Ca’, ‘Na’ penetrates into the composite body to a lower extent compared to ‘Ca’. This may be attributed to the greater affinity of Na⁺ ion for this Cl⁻ ion compared to that of Ca²⁺ ion with Cl⁻ ion. Hence the greater extents of Na-Cl bond pair encounter greater resistance while attempting to penetrate into the composite body compared to lesser amount of Ca-Cl bond pair.

It is worthwhile to evaluate GFRP composites pertaining to the event of salt penetration. It is obvious that the penetrated salt bodily obstruct moisture ingestion by their likely presence in inter laminar space, voids, whiskers and even in micro cracks. While the salts must be obstructing the movement of H₂O molecules along the fibre/matrix interfacial areas followed by diffusion from the interface into the resin, the direct diffusion of H₂O molecules into the matrix may not be affected. This is established through experimentation of the authors when GFRP composite samples are immersed in plain distilled water [21]. In the case of plain water the moisture uptake after the lapse of a period of 4 months is seem to be 1.64 %, whereas in the present case moisture ingestion even after a period of 1 year is only 1.48 %. Further the high amounts of ‘Na’ (19,497 ppm) would get a chance of reacting with the negligible amount of ‘Na’ (0-1 wt %) increasing the molar ratio of ‘Na’ in the glass fibre and enhancing the process of a bond formation, thereby increasing the strength/stiffness. On the other hand, both ‘Ca’ (602 ppm) and ‘K’ (743 ppm) in the sea water may not get a chance for bond formation with the E-glass fibre. Also, the salt penetrations could have resulted in swelling of the matrix bringing about an intimate contact between the matrix and fibre, improving the fibre-matrix adhesion. Simultaneously, the E-glass fibre may get degraded due
to leaching of alkali oxides as a consequence of prolonged periods of immersion. The detrimental effects of moisture ingress could have been countered to certain extent by the bond formation on account of penetration of ‘Na’ in to the composite body and the fibre-matrix adhesion brought about by the swelling of the matrix as a consequence of salt penetration. On the other hand the competing phenomena of plasticisation and leaching of the fibre due to prolonged immersion could have added to the deterioration of the mechanical performance of the GFRP composite.

3.2.6 Mode of Failures

The SEM fractographs (Figure 11) of the sea water immersed samples revealed some chief mode failures. The mode of failures can be any combinations of the following: pot holing, fibre pull-out, matrix crazing, matrix cracking, cusp formation in polymer, fibre breaking, river line mark in polymer showing debonding etc.

![SEM fractographs](image)

Figure 11. SEM fractographs of sea water immersed samples (a) 2 months (b) 4 months (c) 6 months (d) 8 months (e) 10 months (f) 12 months

4 CONCLUSIONS

The following conclusions can be drawn from this work:

(i) Sea water ingress in to the composite body increases with period of immersion, despite the fact that the presence of penetrated salts bodily obstruct moisture ingress.

(ii) Mechanical properties such as ILSS, stress and strain at rupture, elastic modulus exhibit a general trend of deterioration with the increase of immersion period.

(iii) Different salts penetrate to different depths in the composite body, ‘K’ showing the highest depth of penetration and ‘Na’ the lowest depth of penetration after a period of 1 year.
(iv) The Tg values of the sea water immersed samples decreased in general, as a consequence of moisture ingestion.

(v) As revealed by SEM fractographs, the mode of failures include pot holing, fibre pull-out, matrix crazing, matrix cracking, cusp formation in polymer, fibre breaking, river line mark in polymer showing de-bonding etc.

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