

# Response of Sea Water Immersed GFRP Composite to Thermal Shock

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## Abstract

The work involves examining the effects of sea water immersion and temperature fluctuations, precisely that of up and down thermal shocks (lower to higher and vice-versa), on the glass fiber /epoxy laminated composites. These effects are studied in terms of sea water absorption, degradation in inter laminar shear strength (ILSS), alternations in the glass transition temperature ( $T_g$ ) as compared to the untreated samples and finally listing up of the mode of failure as established through scanning electron micrographs. The ingress of sea water is found to be anomalous, the rate of ingress picking up with time of immersion from an initial low value and then again slowing down with lapse of time. Shorter durations of exposure to up thermal shock exhibits an increasing trend in ILSS value while longer exposures do not affect the ILSS value much. The longest period of exposure to down-thermal shock causes a sharp decrease in the ILSS values. The  $T_g$  depression is more visible under up-thermal shock compared to that under down-thermal shock, the chief mode of failure being fiber pull out, fiber fragmentation and delamination.

**Keywords:** glass fiber/epoxy composite, inter laminar shear strength, thermal shock, glass transition temperature

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## INTRODUCTION

Glass fiber reinforced polymer (GFRP) composite materials have been widely used in the ship-building industry for decades now on account of the distinct advantages they offer over conventional materials like steel and aluminium in respect to their corrosion resistance, light weight, toughness, insulating properties, specific strength, etc. [1, 2]. Also composite pipes are increasingly on demand by offshore pipe and gas companies, where glass-fiber reinforced resin matrix composites are used to advantage over common steel pipes for the transport of liquids especially for water desalination plants. In fact, the cost of installation and maintenance of these composite pipes are reportedly lower than that of steel pipes [3]. Thus, glass/epoxy composites have been listed as specific materials along with several other materials for use in marine infrastructure. These materials, during their service life, are exposed to different aggressive environments such as temperature fluctuations, humidity, corrosive

environment, chemical exposures, etc. [4]. Therefore, the long term retention of structure related properties and stability under these unique service environmental exposures is of significant concern from a prolonged service life point of view of these materials.

Absorption of distilled water and sea water in glass/epoxy composites have been studied in great details [5]. This absorption is reported to be the prime cause of changes in the thermo-physical, mechanical and chemical characteristics of the epoxy matrix by plasticization and hydrolysis [6, 7]. It is also reported that the degree of damage and decrease in mechanical properties is dependent on the temperature of immersion whereas, swelling and plasticization may lead to relaxation of stresses generated during curing and compensate for any interfacial degradation due to moisture ingress at room temperature, high temperature immersion leads to an increase in moisture absorption and decrease in tensile strength and ductility [6]

and interfacial adhesion [8] of glass/epoxy composites.

Asbee *et al.* [9] report that a concentration driven osmotic process is responsible for moisture absorption in to the matrix of a composite though osmotic pressure is less of a problem in saline solutions than in ordinary water. Wood *et al.* [10] report that the salts present in sea water reduce the saturation moisture content in composites compared to distilled water. Mourad *et al.* [11] even observe that though large amounts of salts and trace elements are deposited on the surface of the specimens, X-ray spectra for specimen cross sections indicate little permeation of dissolved salt ions in sea water in to the matrix or fiber/matrix interface of the composite material after one year of hydrothermal exposure to sea water. However, fact remains that hydrothermal exposures promote thermo-oxidative degradation in the epoxy network and that weakening of the interfacial bond due to environmental exposure is the real cause of reduced shear strength of the composite treated hydrothermally [12].

Sea water immersion may result in fiber related mechanism for moisture transport in to the composite body. These mechanisms include moisture transport along the interface and/or continuous diffusion through the matrix. It is suggested [13] that surface of the glass fiber is actually etched by this transported moisture. Osmosis driven moisture at the fiber/matrix interface results in leaching of the alkali metal oxides from the E-glass thus, increasing the concentration of salt solutions and the concentration gradient so generated, causes further osmosis driven diffusion of moisture towards the interface. As mentioned elsewhere [14], these transported aqueous solutions may even hydrolyze the siloxane groups of the glass fiber and cause an enhanced rate of flaw growth.

Thermal shock and thermal fatigue are common factors in many applications of GFRP composites. Specially, if there is a sharp change in temperature due to high speed collision, electrical faults or even due to by-chance lightning and there exist defects in the composite during service and /or manufacturing, then the thermal stresses due to temperature fluctuations created, get

concentrated around these defects and failure can be catastrophic. In addition, a change of temperature is certain to bring in changes in relative rates of moisture absorption and relaxation processes in the matrix body. Moisture absorption at elevated temperatures may also cause cracking, blistering, chemical degradation and debonding, hydrolysis, oxidation and leaching of small molecules in the matrix/fiber, the processes being all irreversible [15]. It is therefore, only pertinent that some durability data of these materials with sea water ageing and concurrent thermal shocks are made available.

Glass transition temperature ( $T_g$ ) besides being dependent on the type of matrix chosen, is a function of the effects of the abusive environment to which the composite material is most likely to be exposed during its service life and needs a special mention pertaining to the long term life and durability of the composite material. The GFRP composite needs to be put to service at a temperature below the  $T_g$  where it is both glassy and stiff and can hold the fibers tightly with an well-defined appropriate fiber-matrix interface. Above the  $T_g$  the polymer matrix passes from a glassy state, in which it behaves essentially as an elastic solid and is relatively stiff and non-dissipative, to a rubbery state in which it behaves more like a highly viscous fluid with a very low stiffness, with a weak fiber-matrix bond resulting in a ill-defined interface [16]. It is on this context alone that the agents which lower the  $T_g$  of the matrix and thus the service temperature need to be identified and taken care of in particular.

There is severe lack of information concerning long term effects of sea water ageing of glass-epoxy composites. In fact, sea water ageing still remains an uncertain factor [17]. Durability data regarding the effects of sea water ageing combined with thermal shock are not abundant and need due concern. It is in this context that the present work aims at evaluating the response of sea water aged GFRP composite to up and down-thermal shocks.

## EXPERIMENTAL

Materials used for fabrication of composites include the following:

- (i) Epoxy Resin (Araldite LY-556 based on Bisphenol-A).
- (ii) Hardener (HY-951, an aliphatic primary amine, Ciba-Geigy).
- (iii) Glass Fiber (Woven E-Glass).

The main constituents in the E-Glass fiber are listed in Table 1. Typically the composition is in calcium aluminium borosilicate form as mentioned in literature [18].

**Table 1: Composition of E-Glass Fiber.**

Constituent	Weight Percent
SiO <sub>2</sub>	54
Al <sub>2</sub> O <sub>3</sub>	14
CaO + MgO	12
B <sub>2</sub> O <sub>3</sub>	10
Na <sub>2</sub> O + K <sub>2</sub> O	< 2
Impurities	Traces

An eighteen layered structure is fabricated by hand-laying method. 50:50 proportions for matrix and fiber is adopted. In hand lay-up method the woven E-glass fiber is put down to line a mould previously treated with release agent to prevent sticking and a gel coat to give a decorative or protective surface. The liquid epoxy resin (Araldite LY556) is mixed with curing agent/hardener (diamine HY951) and applied with a brush or roller taking care to work it into the glass fiber. The structure so formed is cured for 48 hours at room temperature. Short beam shear test samples (50 × 12 mm<sup>2</sup>) are cut out from the fabricated composite laminate, as per the ASTM D 2344-84(1984) standards. Any moisture that would have entered in to the specimen body during ambient curing is driven out by heating the specimens in an electric oven at 55<sup>o</sup>C to 60<sup>o</sup>C. The complete removal of moisture is ensured by alternate heating and weighing till a fixed weight is obtained.

The test specimens, in groups, are immersed in beakers containing sea water separately for 1, 2, 3 and 4 weeks. After the lapse of stipulated time of exposure these are wiped dry in tissue papers and weighed to determine sea water ingress.

The basic difference of the characteristics of sea water and distilled water lies in the

impregnation of sea water by certain salts. These salts have varied action on the composite, both the epoxy matrix and the fiber. These salts get absorbed in the body of the matrix to certain extent and get accumulated also on the surface of the composite. Data pertaining to Table 2 reveals the major salt components dissolved in the sea water as evident from literature [11]. The dissolution of the salt affects the moisture absorption by the composite material when it is treated by sea water.

**Table 2: Concentration of Salt Components in Sea Water [11].**

Element	Parts per million
Cl (Chloride)	21,700
Na (sodium)	19,497
SO <sub>4</sub> (sulfate)	2880
Mg (magnesium)	1838
K (potassium)	743
Ca (calcium)	602
HCO <sub>3</sub> (Bicarbonate)	200

The percentage of sea water ingress  $M(t)$ , as a function of time, is calculated according to the formula [19]:

$$M(t) = \frac{W_w - W_o}{W_o} \times 100 \quad (1)$$

Where  $W_w$  and  $W_o$  are weights of the wet and dry specimen, respectively.

An electric oven and a cryogenic chamber (deep freezer) are maintained as +50<sup>o</sup>C and –40<sup>o</sup>C, respectively. The sea water treated samples are put to up thermal (–40<sup>o</sup>C for 5, 10, 15, 20 minutes exposure in the cryogenic chamber then +50<sup>o</sup>C for 30 minutes exposure in the electric oven) shock and down thermal (+50<sup>o</sup>C for 5, 10, 15, 20 minutes exposure in the electric oven –40<sup>o</sup>C for 30 minutes exposure in the cryogenic chamber) shock, in groups, separately.

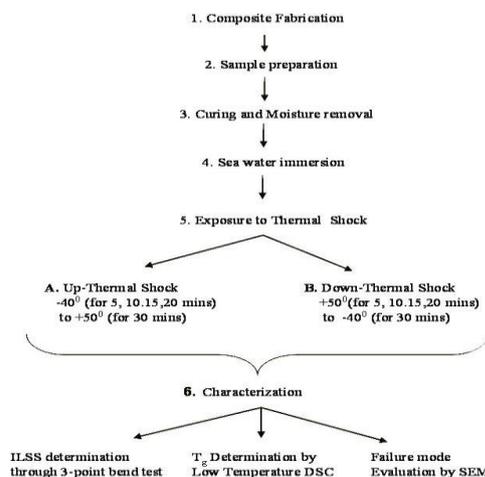
Inter laminar shear strength (ILSS) is determined using INSTRON-1195 from 3-point bend test data. The formula used for determining ILSS is given as [14, 20]:

$$ILSS = 0.75 \times 1000 (P_b / b.t) N / mm^2 \quad \text{or} \quad (MPa) \quad (2)$$

Where,  $P_b$  = Breaking Load (Load at rapture in KN),  $b$  = Width of the specimen and  $t$  = thickness of the specimen. Mettler–Toledo 821

with intra cooler using STAR software with alternate DSC (ADSC) module is used for DSC studies to determine the  $T_g$ . The temperature range adopted is  $30^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  and the first change of slope in the curve generated is scripted as the  $T_g$ . Scanning electron micrographs are examined to study the mode of failure in each case. To facilitate a comparison the characterization of as cured sample after moisture exposure is carried out separately.

The research methodology implemented has been presented in detail in Figure 1. Four samples are taken for the characterization (for determination of inter laminar shear strength) and average of these is taken as final result. Samples with extreme conditions of sea water (4 weeks) exposure and thermal shocks (for up-thermal shock;  $-40^{\circ}\text{C}$  for 20 minutes to  $+50^{\circ}\text{C}$  for 30 minutes and for down-thermal shock;  $+50^{\circ}\text{C}$  for 20 minutes to  $-40^{\circ}\text{C}$  for 30 minutes) are selected for the determination of glass transition temperature, the  $T_g$  and generation of scanning electron micrographs.



**Fig. 1:** Research Methodology Implemented.

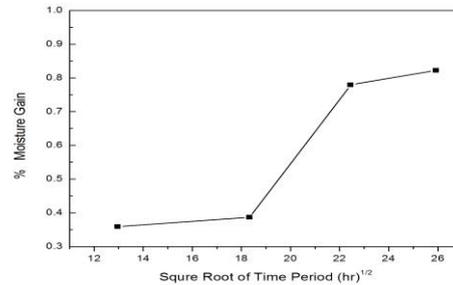
## RESULTS AND DISCUSSIONS

### Moisture Ingression

Data pertaining to moisture ingress as a result of sea water immersion are illustrated in Figure 2.

It is observed that moisture gain increase with time of exposure though the rate of absorption of moisture is anomalous. However, the graph is never flattened. This exhibits a continuing trend of moisture absorption. This trend is

indicative of supplementary mechanism of moisture intake establishing the fact that longer exposures help in greater degradation of the material which delays the saturation level assisting further moisture uptake.



**Fig. 2:** Percent of Moisture Gain for Sea Water Conditioning.

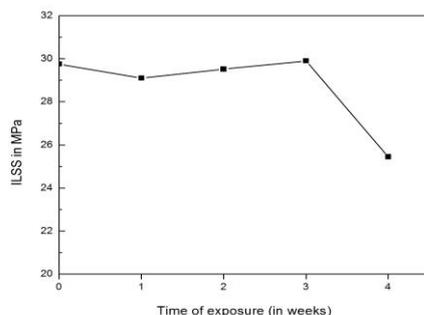
Experimental data reveals that even a comparatively higher period of sea water immersion results in lower moisture intake compared to hydrothermal/hygrothermal conditioning in distilled water [5]. Probably the bulky natures of salts present in sea water influence the osmotic process responsible for moisture intake. Whether the process of moisture absorption, diffusion and permeation is Fickian or non-Fickian depends on the relative rates at which the polymer structure and the moisture distribution in the composite body change. Initially, the polymer structure changes much faster than the moisture concentration; transport of moisture is concentration dependent and Fickian. Here, the rates of moisture diffusion are much slower than the relaxation processes. However, with the lapse of time, moisture absorption becomes anomalous and thus non-Fickian. This is attributed to the development of microcracks, delamination, debonding, etc. as a result of swelling of the matrix and/or a change in the diffusion behavior of the matrix by an alternation of the  $T_g$  as a consequence of moisture absorption. Similar observations, pertaining to Fickian/non-Fickian model of moisture absorption as a result of temperature fluctuations are proposed by Ellyin and Rohrbacher [6] who demonstrate that glass/epoxy laminates follow a Fickian model of moisture absorption at ambient temperatures while at an elevated temperature the rate of absorption continuously increase during immersion. It is reported by Ray B.C. [14] that sea water immersion may result in fiber related mechanism of moisture

absorption. The author proposes that the initial concentration dependent, osmotic pressure driven moisture, causes leaching of certain salts in glass fiber (alkaline metal oxides; siloxane groups). Thus a concentration gradient of salt solutions responsible for further diffusion of moisture towards the interface is generated and the rate of moisture intake is enhanced. This explains the intermediate enhanced rate of moisture ingress as presented in the present work.

Hamid *et al.* [11] investigated the penetration of trace elements from sea water beyond the surface of the glass/epoxy composite material using an energy dispersive X-Ray analysis. They report that there is no permeation of dissolved salt ions in sea water into the glass/epoxy composite. The relative decrease in the peak of sodium and magnesium after 1 year of exposing to sea water as evident from literature [11] may have led to dissolving and leaching of these elements from the glass fiber. This process may be responsible for the further diffusion of moisture in the composite body, termed to be fiber related mechanism. This is confirmed by Bradley *et al.*[10] who suggest that higher saturation levels of distilled water absorption as compared to sea water absorption may be a consequence of less readily absorbed salt and/or trace elements present in sea water in to the body of the glass/epoxy composite. This may also explain the retarded rate of sea water absorption in the present case during the final stages of immersion.

#### **ILSS of Sea water conditioned samples without thermal shock treatment**

Data pertaining to the above, as obtained from the 3 point bend test are shown in Figure 3.



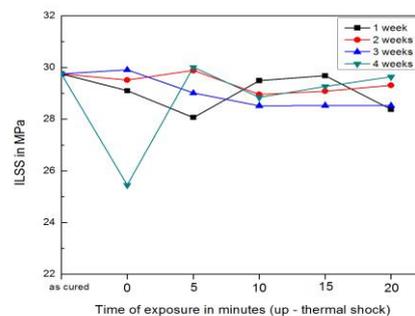
**Fig. 3** Variation of ILSS of Sea Water Treated Sample with Time (weeks) Without Thermal Shock.

The graph clearly shows that the ILSS values, after an initial decrease, do not change much from those for the as cured samples for an immersion period of up to 3 weeks. However, an immersion beyond 3 weeks causes a stiff decrease in the ILSS of the sample.

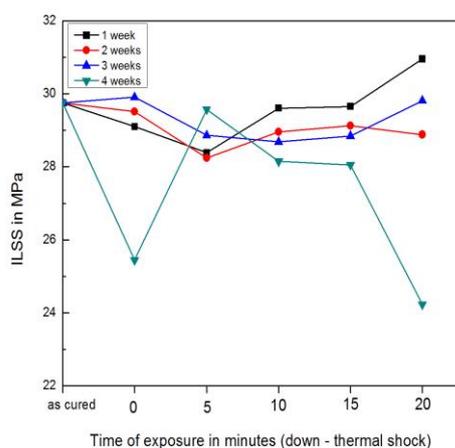
The initial decrease in the ILSS may be attributed to the general weakening of the matrix due to the formation of hydrogen bonds as a consequence of moisture ingress. The minimal variation of ILSS after the initial depression may be due to the nullification of the curing stress by the residual stress developed as a result of moisture absorption. The sudden drop in the ILSS value after the third week of immersion may be suggested to be a result of exchange of hydroxyl ions between the corresponding epoxy chains [21], decreasing the cross-linking density of the epoxy chains. Due to weakening/breaking of the organic bonds which may have caused the segmentation of the epoxy chains, a large extent of swelling stresses could have been generated which could have dominated the residual stresses and caused interfacial delamination leading to the formation of cracks at the glass/epoxy interfacial region leading to the decrease in the ILSS value. This is in line with the findings of Hamid *et al.*[11] who opine that moisture ingress, in addition to causing stress relaxation, swelling and mechanical adhesion, may also cause break down of chemical bonds between fiber and matrix at the interface.

#### **ILSS with Up and Down Thermal Shocks**

The ILSS values with the respective thermal shocks after sea water immersion are illustrated in Figures 4 and 5.



**Fig. 4:** Variation of ILSS of Sea Water Treated Sample with the Time of Exposure Under up Thermal Shock.



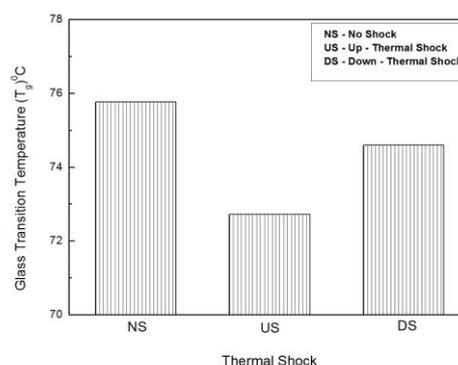
**Fig.5:** Variation of ILSS of Sea Water Treated Sample with the Time of Exposure under Down Thermal Shock.

For up-thermal shock the samples exposed to sea water treatment for the longest period, *i.e.* 4 weeks, show the greatest fluctuation in the ILSS (Figure 4). The ILSS of these samples is seen to increase initially for shorter durations of the shock as compared to the sample with no shock treatment. It is obvious that the longest exposure to sea water result in the maximum absorption of moisture as compared to other shorter exposures and during up-thermal shock moisture desorption is caused resulting in post curing strengthening [22] due to generation of residual stresses. Also the high moisture ingress coupled with low temperature exposures ( $-40^{\circ}\text{C}$ ) during the initial phase of up-thermal shock could have caused mechanical locking between fiber-polymer interfaces. As the polysiloxane layer could have got expanded the epoxy polymer could have got exposed to greater area of the fiber reinforcement via the siloxane layer increasing interfacial adhesion to certain extent there by increasing the ILSS [23]. After the initial stages of increased ILSS it is observed that the ILSS values actually vary over a range with increase in the treatment time and do not exhibit any specific trend. This is due to the various processes which must be taking place simultaneously during the treatment with opposing effects responsible for increase/decrease of the ILSS value. These opposing processes may include mechanical locking, differential contraction, post curing shrinkage stresses, increase in the cross-linking density, etc.

As evident from Figure 5, the four weeks sea water treated sample when exposed to down thermal shock, showed an increase in ILSS during the initial period followed by a nose diving trend during the later stages of the shock treatment. The initial increase in ILSS may be attributed to mechanical locking at the fiber/matrix interface [24]. The increase also could have been a result of  $-40^{\circ}\text{C}$  conditioning which could have caused differential contraction increasing the resistance to debonding and promoted a better adhesion of the interface. The decrease in ILSS during later periods could be related to the large misfit strain at the interface due to the varied expansion coefficients of the fiber and the matrix. Rapid fall of ILSS for maximum duration of down-thermal shock may be related to matrix and interfacial crackings [24]. The shock, lasting for greater lengths of time, could have caused maximum desorption of moisture and promoted crack initiation and growth, propagating the same to the interface, resulting in the nose diving of the ILSS value.

#### Variation of $T_g$ with Up and Down Thermal Shocks

Figure 6 illustrates the effect of up and down-thermal shocks on the  $T_g$  for the samples immersed in sea water for 4 weeks.



**Fig. 6:** Variation of Glass Transition Temperature of Sea Water Treated Sample with up and Down Thermal Shocks.

These effects are presented along with the  $T_g$  for the samples with no-thermal shock. It is an accepted fact that at and below the  $T_g$  about  $1/40^{\text{th}}$  of the total volume of the material counts for free volume [16] and that the  $T_g$  is lowered when free volume available increases. The recorded little variation in  $T_g$  with thermal shock as compared with the sample with no

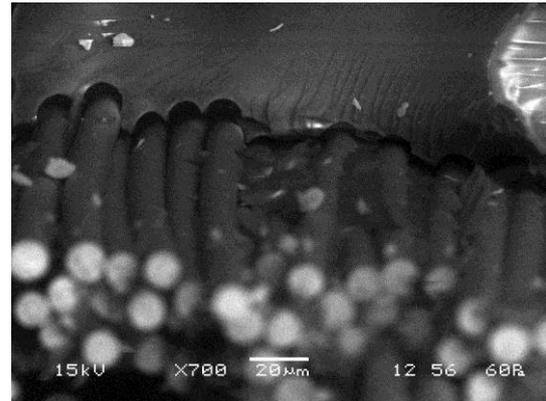
thermal shock may be due to small or no change in the free volume as a consequence of moisture absorption and subsequent exposure to the respective thermal shocks. It may also be possible that  $T_g$  did not get altered appreciably as there is plasticization of the matrix tending to lower the  $T_g$  and simultaneous formation of hydrogen double bonds which tend to elevate the  $T_g$  as a result of moisture absorption [25].

On minute observation one can find that the depression in  $T_g$  is greater in the case of up-thermal shock as compared to that during down-thermal shock. Obviously the free volume generation in case of up-thermal shock is greater than that in case of down-thermal shock. During down-thermal shock the initial phase of the shock (+50°C) must have generated swelling stress tending to increase the free volume which could have got countered by the cryogenic compressive stress during the last phase (-40°C) of the shock treatment. Thus the free volume generation is small accounting for relatively lower depressions of the  $T_g$ . On the other hand, up-thermal shock could have resulted in a chemical degradation of the matrix affecting the fiber-matrix interface adversely. This could have brought in an increase in the internal voids of the entangling polymer chain promoting chain expansion and micro crack formation in the polymer matrix [23–26]. Also, the swelling stresses during the last stages of the up-thermal shock (+50°C) could have resulted in generation of voids accounting for an increase in the free volume generation and thus a greater depression in the  $T_g$ .

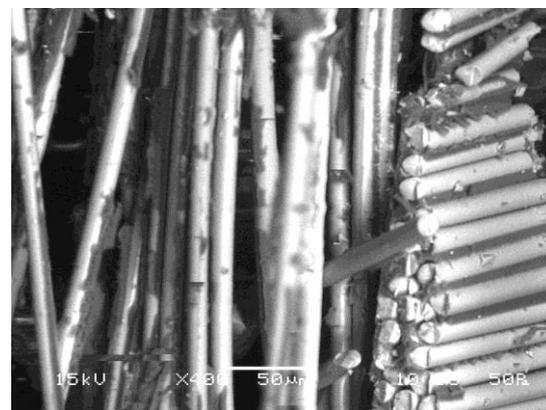
On the basis of the above, it can be established with authority that up-thermal shock during the life time of the composite under question is more detrimental compared to down thermal shock when the service temperature of the composite is under question.

#### Failure Modes

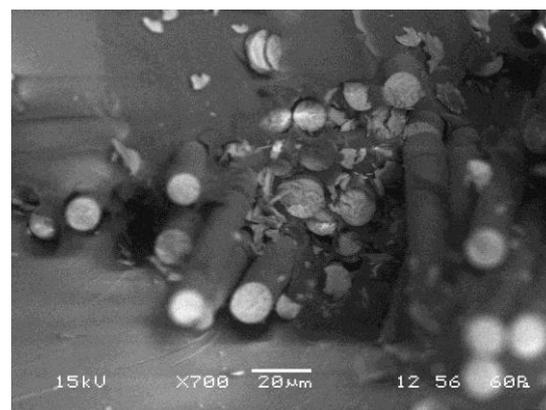
The failure modes have been examined and established with the aid of SEM Micrographs as presented in Figure 7 through Figure 9.



**Fig. 7:** Scanning Electron Micrograph of 4 Weeks Sea Water Treated Sample Without Thermal Shock.



**Fig. 8:** Scanning Electron Micrograph of 4 Weeks Sea Water Treated Sample After up Thermal Shock for Maximum Duration.



**Fig. 9:** Scanning Electron Micrograph of 4 Weeks Sea Water Treated Sample After down Thermal Shock for Maximum Duration.

The Micrographs clearly indicate that the mode of failure can be any combination of the following; viz, fiber/matrix delamination, debonding of the fiber matrix interface, fiber pull out, fiber fragmentation, etc. The prolonged exposure of glass fiber/epoxy

composite to sea water for 4 weeks might have promoted the segmentations of epoxy chain by breaking of organic bonds as shown in Figure 7. The swelling of epoxy resin due to desorption of saline water during the maximum duration of up-thermal shock could have caused for the loss of contact between fiber and matrix as illustrated in Figure 8. The generation of cryogenic compressive stresses during down-thermal shock could have increased the rigidity of the polymer as a consequence of which the fiber pull-out is observed during loading condition as in Figure 9.

## CONCLUSIONS

The study reveals that under the experimental conditions the ingress of moisture for the sea water immersed sample is anomalous, the ingress rates fluctuating over the entire period of immersion. It is observed that the ILSS value is adversely affected with the increase of immersion time. The observation which is most alarming is that the up-thermal shock is more injurious to the composite body compared to down-thermal shock when the service temperature of the composite is of greater concern.

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