

Effect of Hydrothermal immersion and Hygrothermal Conditioning on Mechanical Properties of GRE Composite

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Abstract: Glass fibre reinforced epoxy (GRE) composite meet several degrading agents like moisture and temperature while its use in real time applications in civil infrastructures. Keeping this in mind, the short beam shear (SBS) specimens of GRE composite were exposed to such laboratory created stringent environment as a combination of moisture and elevated temperature for several periods. The environments are as: immersion in distilled water coupled with 65°C as hydrothermal conditioning and an ambience containing 95% relative humidity at 60°C as hygrothermal conditioning. Moisture treated SBS specimens were subjected to 3-point bend test to reveal inter laminar shear strength (ILSS), stress/strain at rupture and modulus values with periods of exposures. The concerned sample suffered 23% of degradation in ILSS values after 120 days of hydrothermal immersion and 25% after 90 days of hygrothermal conditioning. Samples at some optimum exposing conditions of both the exposures are thermally characterized by adopting differential scanning calorimetry (DSC) test. Glass transition temperature (T_g) of such representing samples were determined from the DSC thermograms. About 8 % reduction in T_g values was observed for the GRE composite sample, expectedly, due to moisture induced matrix plasticization and swelling. The fractographs as obtained through scanning electron microscope (SEM) revealed some causes of failures indicating the prime modes of failure of the treated GRE samples with optimum duration of both the exposures.

Key Words: GFRP Composite, Hygrothermal Conditioning, Inter Laminar shear strength (ILSS), Glass Transition Temperature (T_g), SEM Fractographs

1. Introduction

Glass Fibre reinforced epoxy (GRE) composites, in recent days, are considered as the most suitable alternatives for application in civil infrastructures [1], aerospace structures [2] and many more [3]. In such applications, metallic counterparts, expectedly, degrade due to corrosion and crack formation property with respect to any kind of mechanical hurdles [4]. Owing to some specific properties [5] like high strength to weight ratio, corrosion free, ease of fabrication and installation, higher fatigue performance, cost effectiveness, GRE composite system creates a special attention among materials



expert community and of course be a material of choice for the applications under question. These materials need rigorous investigations pertaining to their exposure to various stringent environments.

GRE composites while its use in different civil structural applications can meet several environmental severities, out of which moisture is the prime agent combined with concurrent ambience like temperature [6]. Thus, an environment combined with moisture and temperature (elevated/ambient/sub-ambient) is the key point to be considered as one important conditioning exposure of such material.

Moisture is the chief detrimental factor for GRE composite being affected by some matrix dominating property likes Plasticization [7], swelling [8] and hydrolysis of polymer [9]. Though, a little amount of moisture is very helpful for this material in a way of creating better contact area between fibre and polymer layer via siloxane coating agent [10], still its attack to the concerned material with a huge amount can deteriorate considerably by delamination, fibre (glass) leaching, strength degradation and strain misfit between fibre and matrix as a result of unequal moisture induced expansion [11, 12].

In addition, temperature is one of the driving factors for moisture absorption in to the GRE composite body. Higher temperature can accentuate the rate of moisture absorption process, generally in a moisture laden ambience [13]. Moisture absorption at elevated temperatures may also cause cracking, blistering, chemical degradation and debonding, hydrolysis, oxidation and leaching of small molecules in the matrix/fibre, the processes being all irreversible [10, 14]. Loos and Springer [15] found that the maximum moisture content is a strong function of the relative humidity of the exposure environment while the diffusivity is a strong function of the temperature. An ambience laden with moisture is expectedly most degrading for the GRE composite, as unlike the hydrothermal exposure where the sample is actually immersed in water, here the interface between the composite and the ambience continuously changes giving a scope for higher rates of interactions causing greater uptake of moisture and accelerating the associated damage-intending processes [16]. On this aspect, epoxy resin with higher mechanical properties is very prone to moisture attack under the influence of higher temperature. Hence, epoxy resin, on this issue, need to be investigated for its better implementation as polymer matrix in FRP composite system.

Unlike some polymers like vinyl ester, poly-propylene, polyester, epoxy with double oxirane group (from Bisphenol type) is prone to polymerization process with a very limited curing interval and gains excellent strength and mechanical property [17]. Its brittle property demands for its use as matrix incorporation with some reinforcing agent like glass fibre, carbon fibre, Kevlar fibre and also some ceramic particles to enhance the toughness as required for different engineering applications. Glass fibre, on the way towards of it, can be a suitable choice on the basis of its low cost with some mechanical properties to be compromised with respect to carbon fibre [18-19]. Also, Glass fibre is not usually affected by moisture unless until the leaching induced damage will not affect the glass fibre subject to prolonged huge moisture attack [20]. Hence a safety zone below a certain amount of moisture pick up is to be claimed for the GRE composite system with compromised level of mechanical degradation to avoid the leaching induced damage of glass fibre.

The present investigation is an attempt of investigating the physical and mechanical response of E-glass fibre/epoxy composite exposed to prolonged continuous hydrothermal immersion and hygrothermal conditioning (moisture laden with some higher temperature) for various lengths of time. The mechanism of the moisture ingression and the damages caused specially the mechanism of failure under such exposures are examined at length on the basis of the results of the experiments conducted. The present paper can reveal the material for its suitable applications for civil structural applications subject to prolonged exposure to moisture of different stringent moist environment.

2. Materials and methods

The glass fibre reinforced epoxy (GRE) composite was fabricated by adopting the conventional hand lay-up method [6] considering epoxy resin (LAPOX L-12) as polymer matrix and woven E-glass fibre as reinforcing agent. Specific characteristic properties of the components are mentioned in our research paper [9]. Epoxy resin was mixed with Diamine (LAPOX K-6) as hardener/curing agent in the ratio of 10:1 by weight prior to its application on glass fibre. After 48 hours of curing, at ambient condition, short beam shear (SBS) specimens were prepared by the help of diamond cutter keeping the sample size as per the ASTM D 2344-84(1984) standards for 3-point bending test (Figure 1). One batch of such samples was immersed in distilled water at 65° C in an electric oven up to 120 days (referred as hydrothermal conditioning). Samples after completion of each 20 days of hydrothermal immersion were kept out of this concerned exposing condition to record the percentage of moisture gain data and for further characterizations. Another batch of GRE composite samples was exposed to a moisture laden environment i.e. hygrothermal environment (95% Relative humidity at 60°C) in a humidity cabinet for 90 days. After each 15 days of such conditioning period, group of samples were removed from the Hygrothermal chamber and moisture gain data for corresponding periods are claimed. The periods (in days) of exposure to hygrothermal and hydrothermal conditioning are different owing to the fact that moisture ingress rate in case of hygrothermal exposure is higher than that in the case of hydrothermal exposure [6, 21].

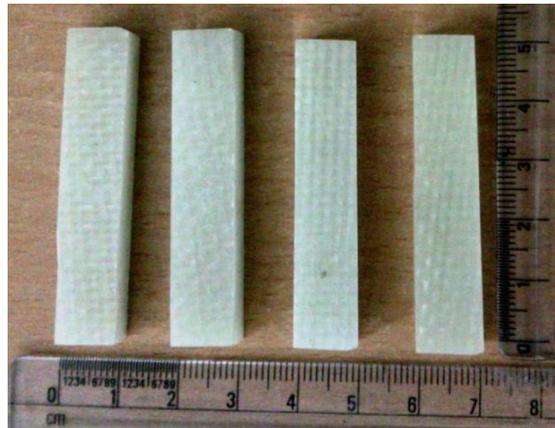


Figure 1. Short beam shear specimens of GRE composite

The percentage of moisture gain data of GRE composite samples subject to both type of conditioning environments were determined by the help of the weight gain data as a function of time of exposure, as [9]

$$M(t) = \frac{w_t - w_o}{w_o} \times 100 \quad (1)$$

where, ‘ w_t ’ is weight of the sample after concerned exposure (hydrothermal immersion and hygrothermal conditioning) and ‘ w_o ’ is initial weight (fix weight) of the samples before conditioning.

All such conditioned group of samples for concerned periods (20, 40, 60, 80, 100 and 120 days for hydrothermal immersion/ 15, 30, 45, 60, 75 and 90 days for hygrothermal conditioning) were subjected to 3-point bend test in INSTRON-1195 as one universal testing machine. The test revealed the data like load at rupture, stress at rupture, strain at rupture and modulus, all being recorded to monitor the mechanical properties.

Inter laminar shear strength (ILSS) data of the moisture treated samples were calculated by the formula [4-6]:

$$ILSS = 0.75 \frac{P_b}{bt} \quad (2)$$

where, P_b = breaking load (load at rupture in KN), b = width of the specimen in mm and t = thickness of the specimen in mm.

Samples after optimum duration of both the conditioning environments (hydrothermal immersion and hygrothermal conditioning) were allowed for glass transition temperature (T_g) measurement by differential scanning calorimetry (DSC) test by the help of Mettler Toledo-821 (ADSC) module compiled with STAR software. The DSC scanning was performed for the range 30-150° C at 10° C/min. The first change in slope in DSC thermogram reveals the glass transition temperature (T_g). For maximum period of both the conditionings, the fractured specimens after 3-point bend test were viewed by scanning electron microscope (SEM; JEOL; JSM-6480 LV and ZEISS, EVO 60) to reveal the mode of failures.

3. Result and Discussion

3.1 Moisture gain

Similar trend of moisture gain variation with respect to time of conditioning of hydrothermal immersion and hygrothermal exposure was observed. The percentage of moisture gain, as revealed in Figure 2, is increased with increase in conditioning time of both the exposures (hydrothermal and hygrothermal). Initially the slope assumes a higher value, flattens somewhat and then again increases. The maximum percentage of moisture gain by glass/epoxy composite after 120 days of hydrothermal immersion was found to be 1.642 and that after 90 days of hygrothermal conditioning to be 1.682.

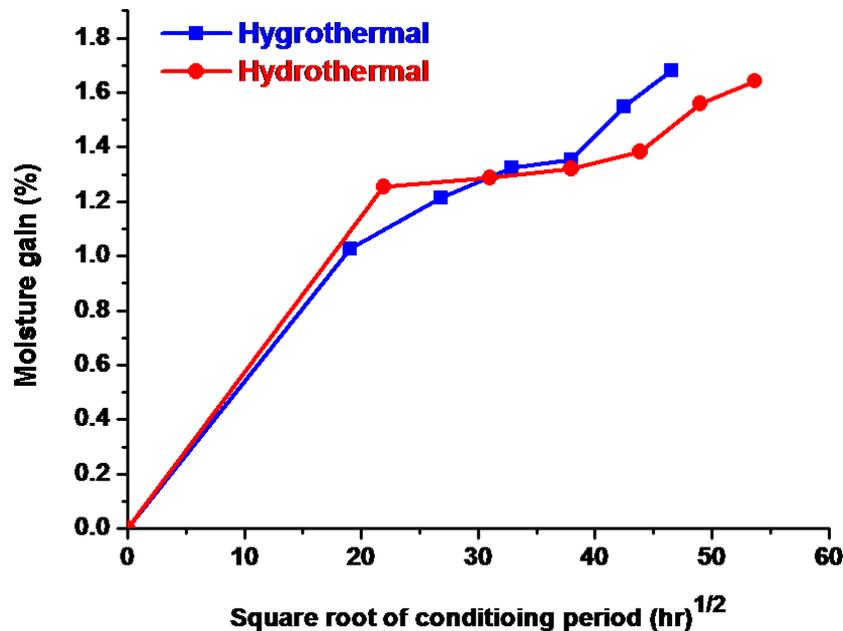


Figure 2. Percentage of Moisture gain of moisture conditioned GRE composite samples

Many investigators [22] have tried to explain the transport of moisture through the process of diffusion in resins and resin-glass composites. The initial continuing uptake trend in moisture gain is due to the difference in concentration of moisture between the composite body and the ambience. The reported rate of moisture absorption is also due to the enhanced rate of moisture pick up by the epoxy polymer; since epoxy resin is prone to moisture absorption due to the presence of –OH groups which can attract polar water molecules by hydrogen bonding [6]. Initially, the moisture absorption is concentration

dependent and obeys Fick's 2nd Law i.e. the absorption of moisture is a direct function of the time of exposure. The process of moisture ingress can be explained due to the action of some driving force (higher exposing temperature; 65°C for hydrothermal immersion and 60°C for hygrothermal conditioning) associated with absorption, diffusion and permeation; all these phenomena being gradient driven [23].

The present reported result pertaining to moisture gain of GRE composite is true for an exposure to plane/distilled water or to an atmosphere laden with moisture i.e. under hygrothermal as well as hydrothermal exposures. The environment associated with hygrothermal conditioning is laden with moisture, and here the moisture lies in the form of molecular dimension where the group of water molecules being linked by hydrogen bonds to the polymer. Hence, the permeation of moisture in to the composite body is easier in hygrothermal process and the ingress is said to be more, as revealed in the plot of moisture gain (Figure 2). The higher extents of moisture ingress in the case of hygrothermally treated samples may be due to the dynamic interface between the ambience and the composite body.

The rate of moisture intake, after the moisture ingress reaches a threshold value obeying the Fick's Law [24], decreases and then again increases, as a consequence of exposure to longer periods. This is non-Fickian where the linearity of the plot between moisture gain and square root of time of exposure is disturbed. Finally, for the higher conditioning periods after attaining saturation in moisture content, the composite material behaves differently with added moisture ingress. The glass transition temperature (T_g) changes promoting plasticization and swelling causing reduction of modulus. The deteriorating process exhibited huge moisture ingress at later stages of hygrothermal conditioning/hydrothermal immersion.

Therefore, the huge increase in moisture ingress at the later stages of both conditioning environments indicating Non-Fickian nature of diffusion process could ameliorate the cause of deterioration in the composite material and this depends upon the relative rates at which polymer structure and property changes. In this case, the concentration gradient rate decreases with the ingress of more and more moisture. Here, the moisture absorption is anomalous, can't be explained by Fick's Law and is thus Non-Fickian. This is attributed to the creation of some defects like micro-cracks, delamination, debonding between fibre and polymeric matrix as a result of swelling of the matrix and also to a variation of absorption behaviour by alternation in T_g values (as revealed in DSC results).

3.2 Inter laminar shear strength (ILSS)

ILSS of the GRE composite samples continuously decrease with increase in duration of both hygrothermal and hydrothermal exposures (Figure 3) and also with increased moisture ingress (inserted figure of Figure 3).

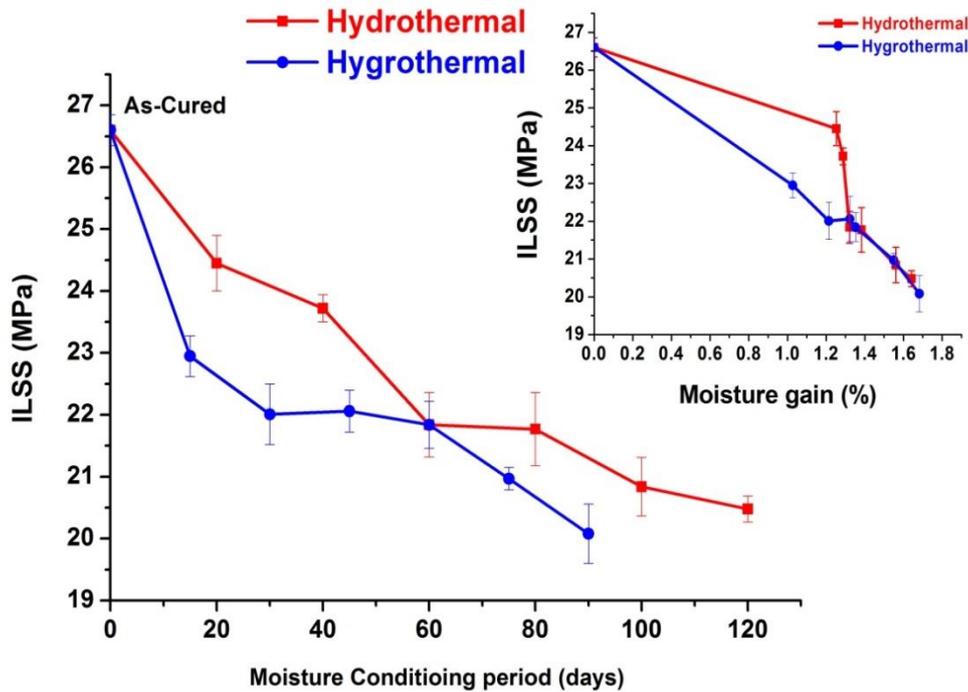


Figure 3. Variation of ILSS of GRE composite with moisture conditioning period (Inserted figure: Variation of ILSS with moisture gain percentage)

Hygrothermal conditioning causes 17% reduction in ILSS after 45 days of exposure and 25% after 90 days of same treatment. The continuous decrease in ILSS with increasing hygrothermal ageing duration establishes the fact that, prolonged moisture conditioning coupled with higher temperature causes greater mechanical degradation pertaining to creation of cracks, voids in the epoxy polymer of the composite assisting further moisture uptake and delaying the saturation level of moisture uptake [11, 25]. This result is also reflected in Figure 3 indicating decrease of ILSS values up to about 23% after 120 days of immersion in distilled water. The plot pertaining to the inserted figure of Figure 3 shows the decrease of ILSS with increased moisture gain during hygrothermal and hydrothermal treatments.

It may be inferred that, the continuous decrease in ILSS is due to the plasticization of the polymer matrix by continuous moisture absorption promoting break down of chemical bonds between polymer and fibre and/or secondary forces of attraction at the interfaces. In the present work, time and temperature have significant synergetic effect on inter laminar shear property of the composite body. With increasing time of exposure the laminar strength decreases up to a significant extent. Similar results were reported by Shivkumar *et al.* [26]; the ILSS of Glass/epoxy composite decreased with increasing time and temperature of hygrothermal atmosphere belonging 85% R.H. Also, the results reported by Kim *et al.* [13] are in agreement with the present trend; the tensile strength of E-glass fibre/vinyl ester composite decreased with increasing hydrothermal immersion period and with increasing temperature compared to as-cured sample.

3.3 Stress/strain at Rupture

As evident from Figure 4 and Figure 5, the composite samples require lesser amount of stress values for rupturing with increased hydrothermal as well as hygrothermal conditioning periods. Subsequently the strain at rupture values also assumes lower proportions for both the exposing environments. Stress at

rapture for 90 days hydrothermal conditioning decreases to 21% of that for the as-cures sample and that for 120 days of hydrothermal immersion to be same amount (21%).

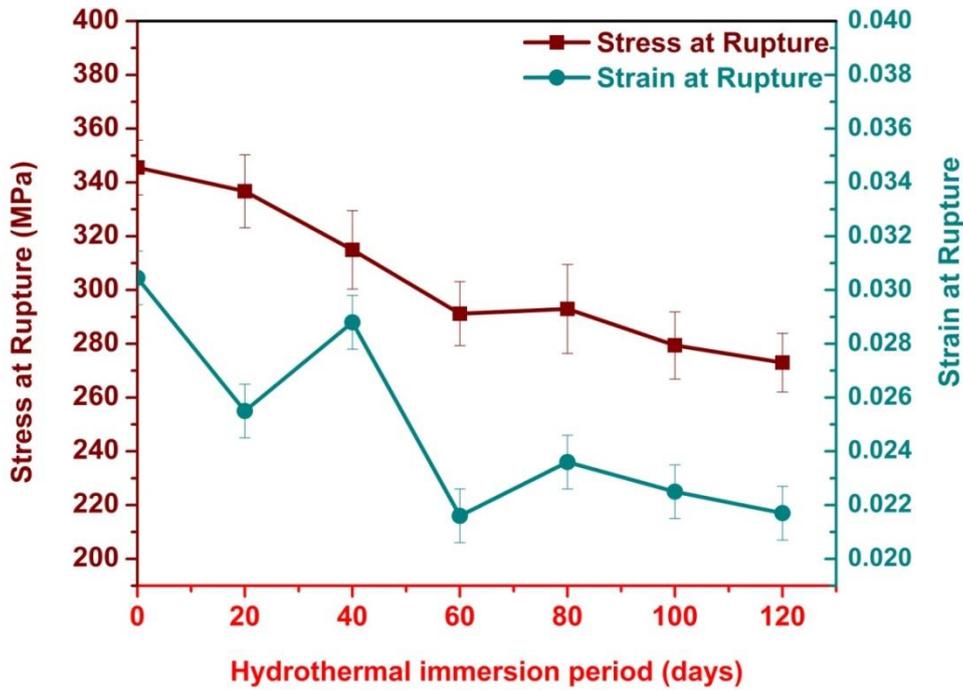


Figure 4. Variation of stress at rupture and strain at rupture values with hydrothermal immersion period

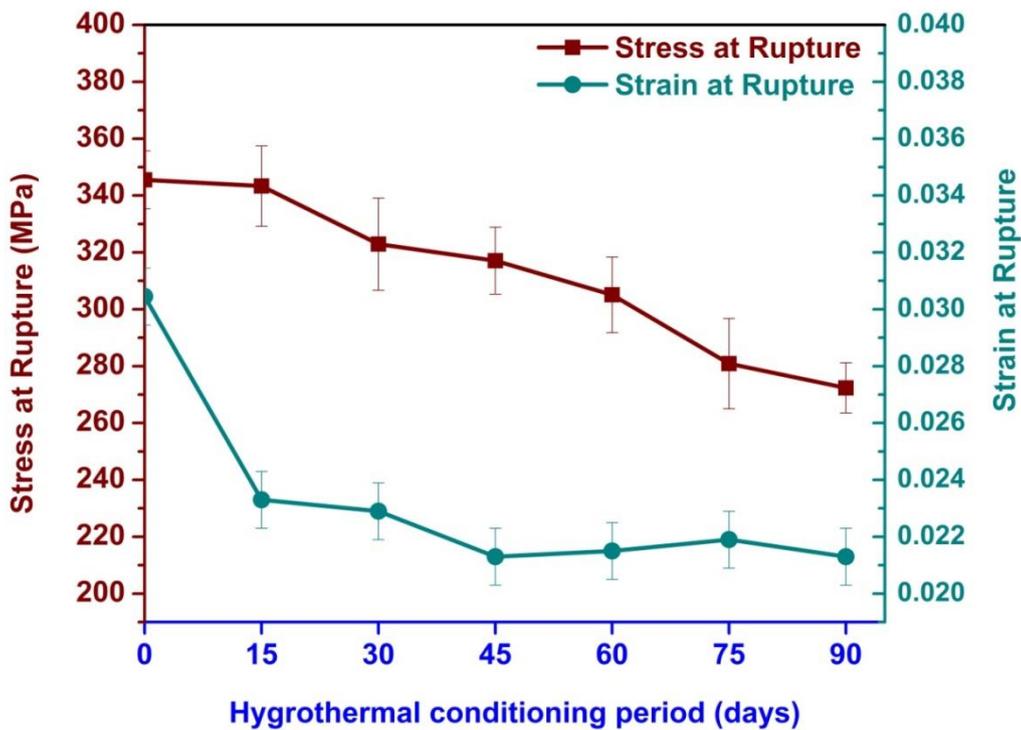


Figure 5. Variation of stress at rupture and strain at rupture values with hydrothermal conditioning period

As described in this paper, the continuous decrease in ILSS reveal the deterioration of the composite body, which thus can stand lesser amounts of stress values after prolonged hydrothermal immersion/hydrothermal conditioning. As a consequence strain at rupture values decrease severely, affecting the tolerance limit of the composite. The difference in the values of stress requirement for rupture and subsequent strain at rupture are quite less even a higher duration difference between both the conditioning environments. Thus, the deterioration of GRE composite is found more prominent due to hydrothermal conditioning of duration lower than the maximum duration of hydrothermal immersion.

The thermal expansion mismatch between fibre and polymer is responsible for the generation of the residual stress in the overall composite structure [6]. After prolonged hydrothermal/hydrothermal exposure, this residual stress in the composite body would not allow the composite to accommodate the applied external stress in the way of prohibiting such level of straining as being observed for as-cured specimen.

3.4 Modulus

Data pertaining to Figure 6 reveal the variations in Modulus of the GRE composite samples with respect to durations of hydrothermal immersion and hydrothermal conditioning. Around 6 % decrease in modulus is observed after 90 days of hydrothermal conditioning and about 9% after immersion in distilled water.

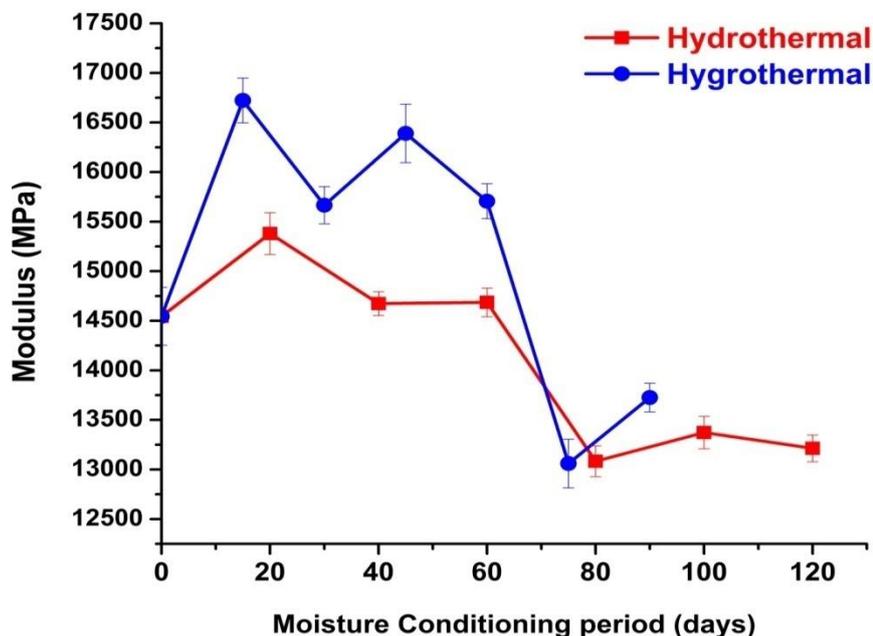


Figure 6. Variation of Modulus with periods of hydrothermal immersion and hydrothermal conditioning periods

Modulus values decreased irrespective of an initial increment with increasing conditioning period of both the exposures. The initial increase in modulus may be due to creation of better contact area between fibre and matrix due to weakening of hilly structure of Silane coupling agent of E-glass fibre.

This may happen due to initial small quantities of moisture absorption, which in turn may effectively decrease the attachment of Siloxane layer from glass fibre [10].

The result pertaining to decreasing trend in modulus is in agreement with the corresponding ILSS results of hygrothermally and hydrothermally treated GRE composite samples. The polymeric matrix during the concerned treatments is affected by plasticization and reduces the modulus and glass transition temperature. Modulus of layered FRP composites is analogous to the perfect fibre/matrix interfacial adhesion and of course rigidity of polymer structure, which in turn demand the better elastic limit during mechanical loading. The stress and strain variations indicating decreasing stress and straining amount with respect to increasing exposure period authenticates the modulus result by establishing a decreasing trend in elastic limit after prolonged hygrothermal and hydrothermal treatments.

3.5 Glass transition temperature (T_g)

Figure 7 and Figure 8 show the DSC curves for hygrothermally and hydrothermally treated composite samples, respectively. The samples with extreme conditions of both hygrothermal and hydrothermal treatments are chosen on the basis of time of exposure (15, 60 and 90 days for hygrothermal conditioning while 20, 80 and 120 days for hydrothermal immersion). The onset values of the glass transition temperature (T_g) as recorded from the DSC curves of the above representative samples are graphically illustrated in inserted figures of Figure 7 and Figure 8.

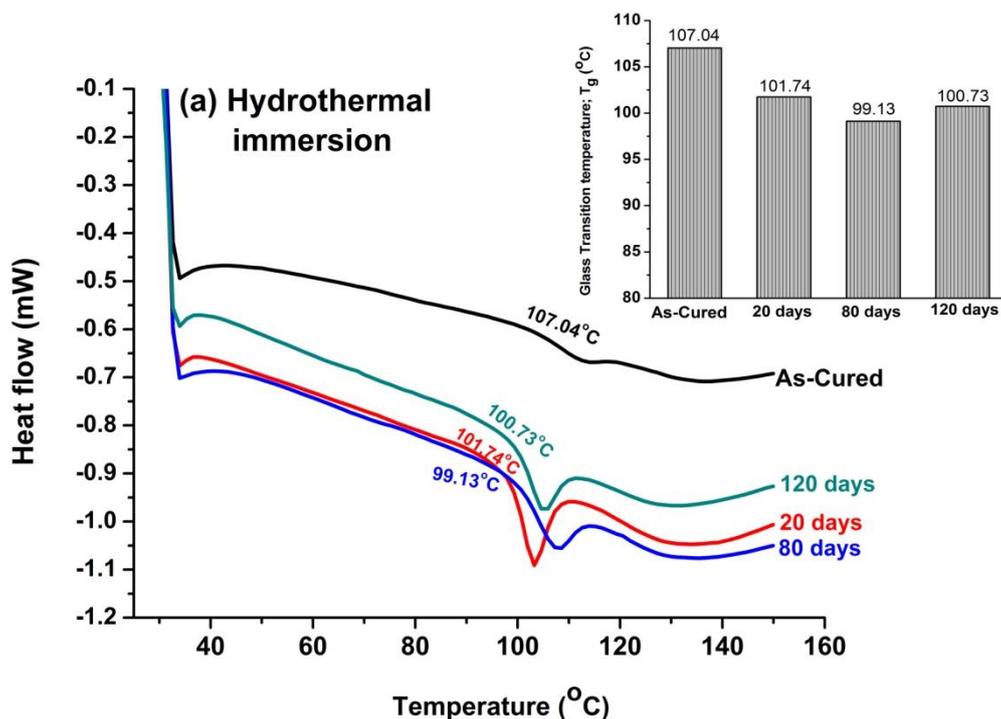


Figure 7. DSC thermograms of hydrothermally immersed GRE composite
 (Inserted figure: T_g variation of GRE composite with respect to time of hydrothermal immersion)

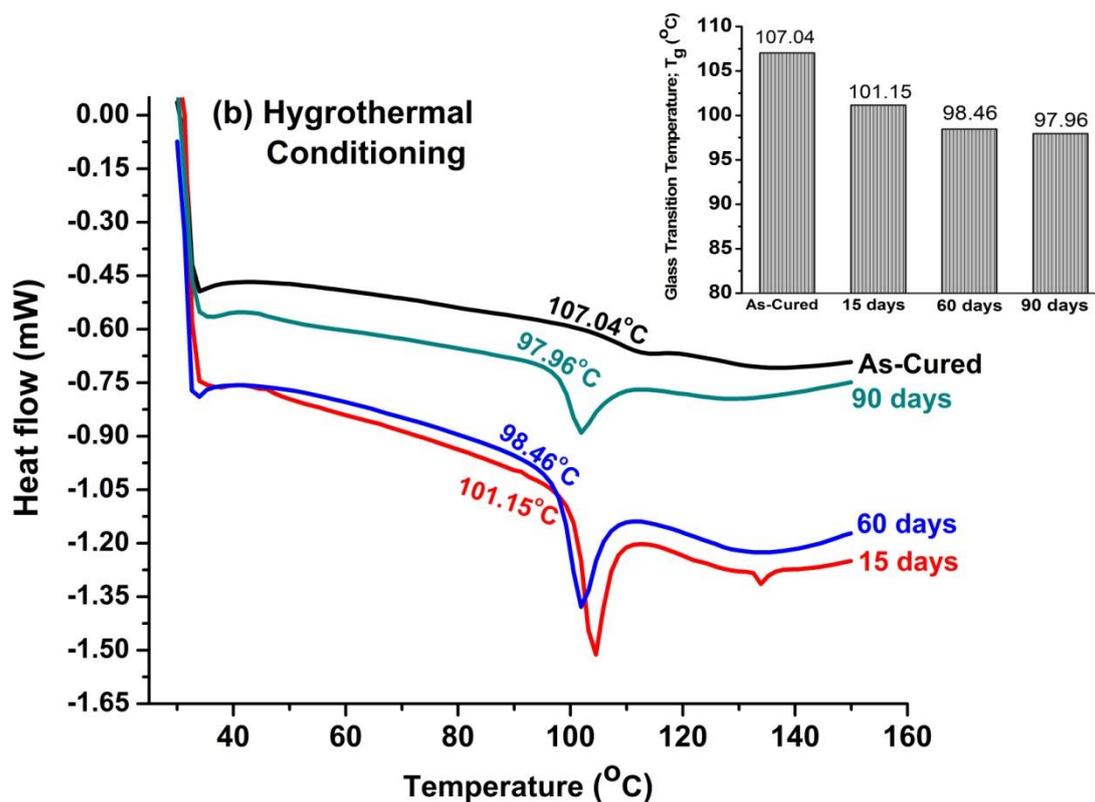


Figure 8. DSC thermograms of hygrothermally conditioned GRE composite
(Inserted figure: T_g variation of GRE composite with respect to time of hygrothermal conditioning)

The T_g values decreased with increasing period of hygrothermal and hydrothermal exposures. About 8% reduction in T_g is observed after 90 days of hygrothermal conditioning. About 6% reduction in T_g is observed after 120 days of hydrothermal immersion of the composite specimens. T_g of polymeric materials depends on the extent of cross-linking density [27]. Due to imperfect curing/cross-linking of the polymer, some voids could have been created in the polymer. These voids, referred as free volume, approximately occupy 1/40th of total polymer volume at/below glass transition temperature [6]. The T_g deterioration is affected when the extent of free volume/voids increase. Hence, it may be inferred that, on prolonged hygrothermal/hydrothermal treatment, polymer matrix could be affected by plasticization leading to chain scission/breaking by the action of hygro-elastic swelling stress. This may lead to increase in internal voids/free volumes in the polymer structure giving rise to early glass transition process. The greater percentage of T_g reduction for GRE composite subject to maximum duration of hygrothermal treatment could be due to more damaging effects concomitant with severe plasticization, swelling of epoxy polymer as a result of huge amount of hygro-elastic swelling stress. Hence, thermal stability of the material is more hampered after hygrothermal treatment of less duration compared to maximum duration of hydrothermal immersion.

3.6 SEM fractographs

As evident from Figure 9 and Figure 10, the SEM Micrographs for hydrothermally immersed and hygrothermally conditioned fractured specimens show some prime modes of failures like fibre breakage, fibre pull out, fibre-matrix debonding.

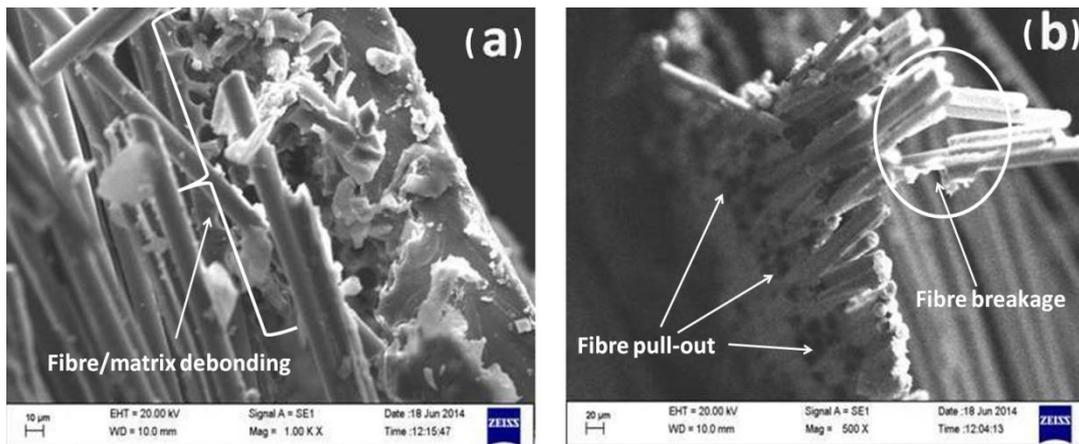


Figure 9. SEM fractographs of hydrothermally immersed GRE composite samples
(a) 20 days (b) 120 days

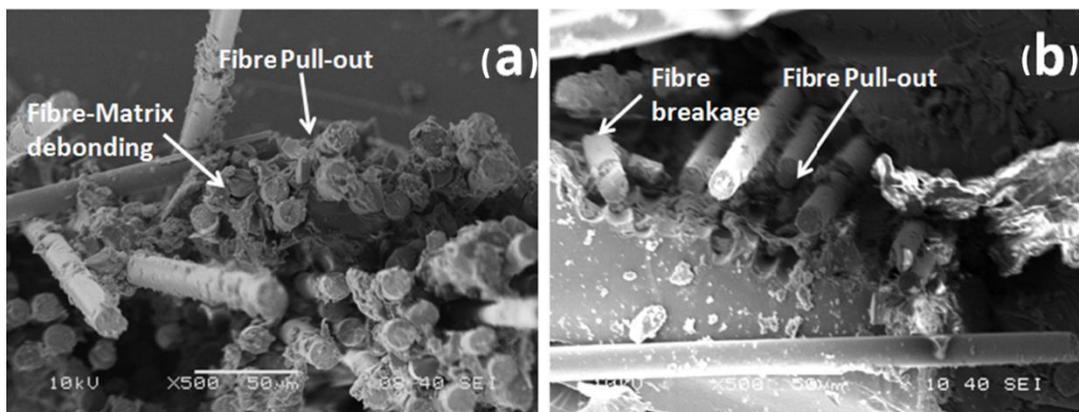


Figure 10. SEM fractographs of hydrothermally conditioned GRE composite samples
(a) 15 days (b) 90 days

The causes of failure are found anyone of the modes or any combinations. The degrading phenomenon might have caused the irreversible damages in the composite body and the prolonged moisture treatment coupled with elevated temperature could have affected the polymer matrix to a great extent. Hence, fibre pull-out coupled with fibre breakage, matrix holes are created due to debonding of fibre from matrix material. Especially, fibre breakage is visible for the GRE composite samples after maximum duration of both the conditioning environment (hydrothermal and hygrothermal). Thus, the damage of GRE composite is quite comparable for both the conditioning exposures irrespective of variation of periods of exposures for both the cases.

4. Conclusion

The findings as established through the present experimentation indicate the following concluding remarks:

- (i) Moisture ingress, whether due to hygrothermal or hydrothermal exposures is detrimental for the well being of the GRE composite.
- (ii) Hygrothermal exposure is more effective towards deterioration of the properties of the composite.
- (iii) Whether the exposure is hygrothermal or hydrothermal, time of exposure also plays an important role towards the mechanical stability of GRE composite.
- (iv) Property degradation of GRE composite is comparable with respect to the both the exposures, irrespective of higher time of exposure for hygrothermal conditioning.

- (v) Design stress of the GRE composite can thus, be made less than 25% of ILSS value of the as-cured sample so that the component can be safely used under hygrothermal and hydrothermal ambience.

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