

Effect of graphene nano-platelets coating on carbon fibers on the hygrothermal ageing driven degradation of carbon-fiber epoxy laminates

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Abstract

While spray coating of graphene nano-platelets (GNPs) on-to long carbon fibers (CF) is a viable strategy to enhance the strength of carbon fiber reinforced plastics (CFRP), the degradation of these laminates under hot and humid conditions remains unexamined. Here, Pristine and 0.4% GNP coated CF (0.4GNP) laminates are manufactured using vacuum assisted resin transfer molding (VARTM) technique and subjected to hygrothermal ageing in de-ionized water at 75°C for 30 days. Mechanical and structural characterization are performed after 15 and 30 days of hygrothermal ageing once the specimens were dried long enough to attain a saturation in mass. 0.4GNP laminate offered higher water resistance than Pristine laminate as 0.4 wt% non-functionalized GNP coated CFs were more hydrophobic than Pristine CF as quantified through contact angle-based measurements. Additionally, a thick carbonaceous hydrophobic interphase is formed between the CF and epoxy for 0.4GNP laminate which hinders water transport in composite. The thicker interphase also enhances the tensile strength and interlaminar shear-strength (ILSS) of 0.4GNP laminate in the unaged condition through enhanced CF – epoxy mechanical locking and epoxy strengthening in the vicinity of CF. However, both tensile strength and ILSS decreased with hygrothermal ageing time and the enhancement in strength achieved through GNP addition is completely lost after 15 days of hygrothermal ageing. Under tensile loading, the stress-strain plots showed a step-wise decrement in stress due to a ply-by-ply failure triggered by failure of the weakened inter-ply epoxy regions. In case of ILSS specimens the number of delaminations triggered increased considerably with hygrothermal ageing.

Keywords: Carbon fiber, Graphene nanoplatelets, Hygrothermal ageing, Strength, ILSS

1. Introduction

Carbon fiber reinforced plastics/laminates (CFRPs) are fast replacing traditional structural materials owing to their light weight as well as tailorable properties. The tailorability of CFRPs is facilitated by the option of altering the orientation of carbon fibers (CF), sequencing of the CF fabrics and controlling the volume fraction of CFs[1]. However, the bonding between the CFs and the epoxy matrix, often becomes the reason for concern because these regions are more prone to failure initiation. Hence, a lot of studies focus on the interface region between the CF and epoxy such that there is a continuation of properties between the matrix and the fiber and the 'interface' can act as an 'interphase'[2-6].

An efficient interphase region should not only bond the CF and epoxy well but also allow good stress transfer between the epoxy matrix and the CF[7]. Thus, surface treatment of CF and use of micro/nano fillers have become common place to enhance the interphase properties. Surface treatment of CF is often done with the help of acids like nitric acid, hydrochloric acid, sulphuric acid or combination of acids, plasma treatment or even ozone treatment [8,9]. Some examples of nano fillers or secondary reinforcement are : functional graphene sheets (FGS) [10,11], carbon nanotubes (CNT) [12,13], graphene nano-platelets (GNPs) [13,14] or nanospheres such as nanosilica [13] or nanoalumina [15]. The presence of such well-dispersed nano-particles in the matrix in small proportions (usually less than 2 wt %) is able to efficiently increase damage resistance and tolerance by providing mechanical locking and deflect propagating crack and hence mechanical properties are enhanced with insignificant addition to the weight and dimensions of the composite [11]. Of these nano-fillers graphene based nano-fillers such as GNPs are easily produced from abundantly available graphite through exfoliation of graphite. GNPs are shown to enhance the mechanical properties by strengthening the interphase region and they also provide mechanical locking of the epoxy at the CF/matrix interface thus restricting significant epoxy movements [2,3,16-18]. In the present study we shall restrict our attention to the use of non-functionalized GNPs as nano fillers and evaluating the performance of composites made using them when subjected to a harsh, hot and humid environment.

The two main components of a laminate, the CF and the epoxy matrix, respond differently to hot and humid conditions. While CF is relatively inert to water molecules [19], the epoxy matrix succumbs to significant degradation in both structural and mechanical properties

accompanied by dimensional changes caused by swelling due to water molecules [20–24]. Considerable plasticization starts building up in the epoxy matrix which is accompanied by hydrolysis reactions. The products of the hydrolysis reaction which are usually organic acids and alcohols act as catalyst for further reaction [20,21]. The changes in the epoxy both due to the structural changes and swelling weaken the CF/matrix interface/interphase. The incompatibility between the expansion of CF and epoxy leads to generation of internal stress and also formation of defects [25]. The chemical reactions in the epoxy and the defect generation in the laminate make space for water molecules to come in and thus facilitate further reaction. Overall, there is considerable degradation in strength of the composites and it becomes extremely challenging for design engineers to predict a safe working loading condition [26,27].

Although, GNP reinforced CF based laminates offer significant enhancement in initial strength, it becomes very important to understand how the strength changes and how much of the strength enhancement is retained after long durations of hygrothermal ageing. However, hygrothermal ageing of GNP reinforced laminate has received very little attention. A very recent study by Jarrett and Korkees [28] was dedicated to the addition of 2% amine functionalized GNP(NH₂-GNP) by shear mixing the NH₂-GNP into the epoxy prior to laminate manufacturing. The authors hygrothermally aged the specimens in distilled water at 25°C, 40°C and 75°C for nearly 27 days. With addition of NH₂-GNP, the diffusion coefficient decreased by ~ 43% and the amount of water taken in decreased by ~ 7% for ageing done at 70°C. Another recent study by Manjunatha and Sharma [29] studied the effect of 0-5% loading of GNP (by weight of epoxy) on the hygrothermal ageing of laminates. Prior to laminate making, Manjunatha and Sharma [29] dispersed the GNPs into the epoxy utilizing ultrasonication and twin-screw extrusion technique. In this case the specimens were hygrothermally aged at 50°C and 60°C till a saturation in mass was obtained. They have also reported an enhancement in water resistance measuring the diffusion coefficient and mass at saturation with GNP loading. They have also reported an enhancement in the hydrophobicity of epoxy with GNP mixing using contact angle based measurements prior to laminate manufacturing. Tsung-Han Hsieh et al. [30] and Chin-Lung Chiang et al. [31] also studied the effect of GNP dispersion in epoxy prior to laminate manufacturing on the mechanical properties and the evolution of mechanical properties during hygrothermal ageing. The laminates were prepared using GNP dispersed carbon hybrid/MEK/epoxy prepreg utilizing the compression molding technique. GNP dispersion in epoxy (in the range of 0.25-0.5 wt. %

of epoxy) not only enhanced the initial mechanical properties but also showed better interlamellar shear stress behavior after hygrothermal ageing in a moist environment for 14 days[31]. However, these studies refrained from altering the CF with GNPs prior to hygrothermal ageing. For manufacturing the hygrothermal ageing resistant epoxy components researchers have aimed at incorporating fillers such as Talc and nano-fillers such as graphene nano-fillers into a cycloaliphatic epoxy in varying proportions [32,33]. Although introduction of talc improves water resistance, it does not prevent degradation of mechanical properties of epoxy[32]. However, addition of GNP provides modest retention in stiffness and glass transition temperature of epoxy nano-composites with hygrothermal ageing[33]. Starkova et al. [34] have identified graphene based material as a potential filler for developing long term hygrothermal ageing resistant composites. Graphene oxide based nanocomposites (up to 1.72 % by wt. of polymer) provides enhanced resistance to hydrothermal ageing and results in enhanced storage modulus (~ 60%), larger activation energies for glass transition (~40%), better temperature and water- shift functions. Above studies are restricted to epoxy nano-composites with no reinforcement of carbon fiber but they identify the potential of graphene based fillers to manufacture hygrothermal ageing laminates.

Unlike prior studies, we have attempted to coat the carbon fiber instead of epoxy infusion, with the aim to enhance the hydrophobic properties of the laminate. The first step in this direction was to evaluate the change in the hydrophilic/hydrophobic nature of the CF with increasing percentage of GNP loading on to the CF fabric utilizing a contact angle measurement based technique. After choosing the most optimum condition of hydrophobic behavior + efficient distribution of GNPs, laminates were manufactured using vacuum assisted resin transfer molding (VARTM) technique; first laminate with pristine CFs and the second with 0.4 wt % of GNP coated CFs. Both the laminates were subjected to hygrothermal ageing by immersing in DI water maintained at 75°C for a period of 30 days. It is observed that the 0.4GNP laminate offered the highest resistance to water absorption during hygrothermal ageing; both in terms of a decrease in diffusion coefficient with GNP addition and mass of water taken in by the specimen at any instant of time. The degradation in tensile and interlaminar shear strength due to aging and the reasons for the same are discussed in detail.

2. Materials and methods

2.1. Material preparation

The carbon fiber (CF) used in the present study is a polyacrylonitrile (PAN) based unidirectional (UD) long carbon fiber procured from Hindoostan Composites Solutions, India. The carbon fiber has 3000 filaments per tow with an average filament diameter of 7 μm . The as received CF has a sizing layer which is a polymeric coating often used to improve handling. The UDCF tows are held together with a nylon weave thread that runs perpendicular to the CF axis. The non-functionalized graphene nano-platelets (GNPs) was procured from Ad-Nano Technologies Private Limited, India. The GNPs are not functionalized and have 2-4 layers presenting a surface area of $\sim 380\text{m}^2/\text{g}$ and a purity of $>99\%$. The structure of the non-functionalized GNP used in the present study was characterized with the help of transmission electron microscope (TEM), Fourier-transform infrared spectroscopy (FTIR) and Raman Spectroscopy. The details of the experimental techniques used for the TEM, FTIR and RAMAN spectroscopy is available in S1. The TEM images identify the shape of GNP to be flake like with a hexagonal diffraction pattern. The FTIR results (Figure 1(e)) reveal the lack of proper development of functional groups on the non-functionalized GNP as compared to a carboxyl functionalized GNP or an amine functionalized GNP. The carboxyl functionalized GNP or an amine functionalized GNP are used as reference in the present study. The Raman spectra identified 3 characteristic peaks, I_D (1347 cm^{-1} , disorder or defects in graphitic structure), I_G (1573 cm^{-1} , sp^2 carbon network or graphitic structure) and I_{2D} (2708 cm^{-1} , overtone of the D-band). The ratio I_D / I_G indicates the degree of disorder and a value of ~ 0.23 indicates a very low degree of disorder or high structural integrity[35].

The epoxy-hardener system used in the present study is a low viscosity laminating grade epoxy supplied by Fine Finish Organics Pvt. Ltd, India. As per the suppliers specifications, 100 parts by weight of the Bisphenol A diglycidyl ether (DGEBA) based epoxy (EPOFINE® - 5052) is cured using 38 parts by weight of an amine based hardener FINEHARD™ - 5052. Weight measurements were performed using a digital weighing balance having a least count of 0.0002 grams. It is very important to maintain stoichiometric ratios of epoxy and hardener as excess of either of the components could affect the water absorption kinetics.

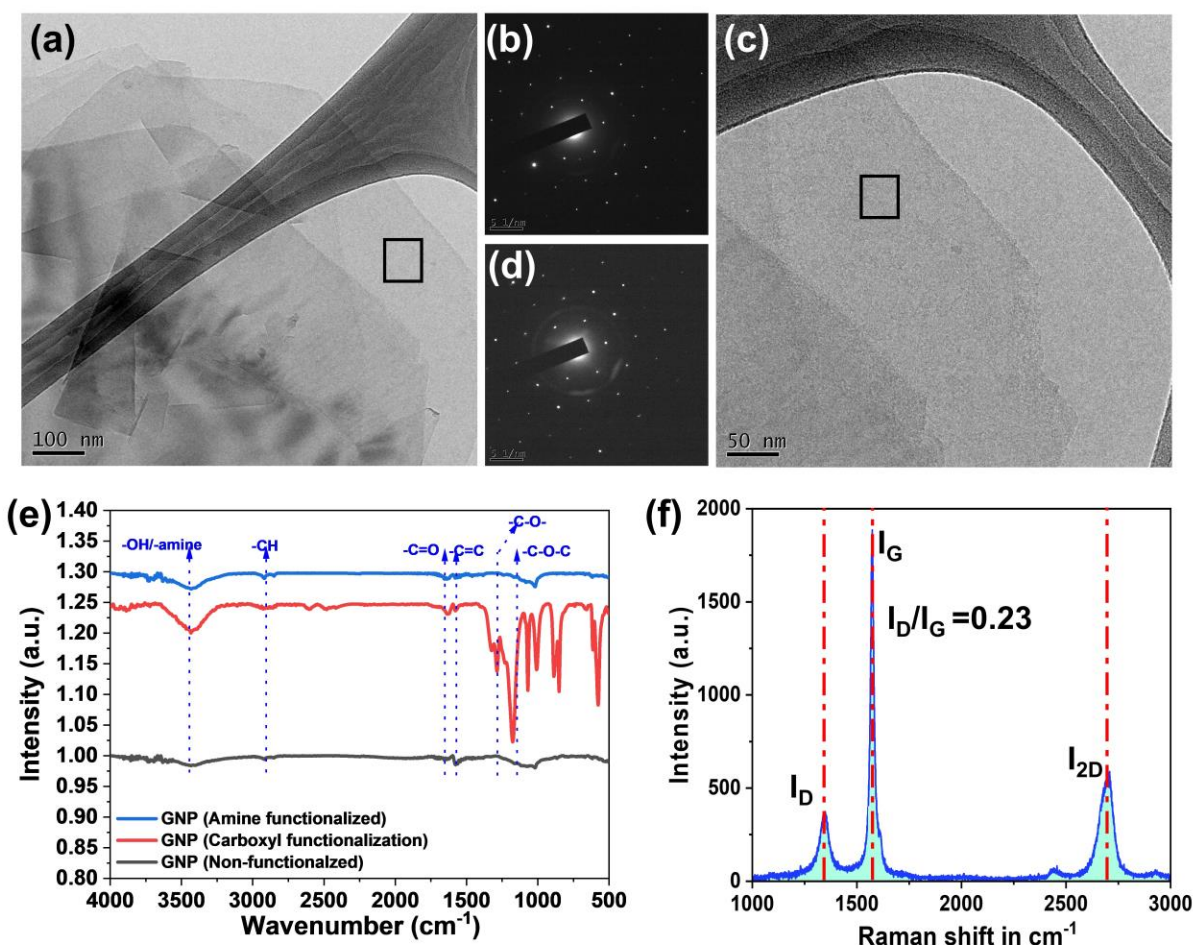


Figure 1 (a) and (c) present the TEM micrograph of the graphene nano-platelets. (b) and (d) presents the diffraction pattern of regions marked by rectangles on TEM micrographs in (a) and (c) respectively. (e) presents the FRIT spectra of non-functionalized GNP, carboxyl functionalized GNP and amine functionalized GNP (f) presents the Raman spectra of non-functionalized GNP.

2.2. Surface treatment of carbon fibers

The as received CF has a sizing layer which is a polymeric coating often used to improve the processing and handling of CF prior to and during laminate manufacturing. GNPs were coated on to the CF using the spray coating technique where the GNPs were initially dispersed in ethanol followed by probe sonication in an ice bath for 15 minutes and ultra-sonication in an ice bath for 15 minutes. The two step sonication process in an ice bath is essential to achieve a good dispersion of GNPs that would result in a more uniform coating. The coating was done using an air spray brush which was actuated by an air pump. The spray coating of GNP was carried out using a Pilot Power AB-15 airbrush system manufactured by

Manik Radiators Pvt. Ltd. India, which is equipped with a high performance single-piston Airbrush air compressor. The spray pressure was maintained at 2.5 kg/cm². The spraying distance was ~ 10 cm from the CF fabric. Both sides of the CF fabric were coated with equal quantity of GNPs. A total of 8 layers of CF fabric were coated to the same condition and were used as the reinforcement material for one laminate.

The loading of GNPs on to the carbon fiber was varied between 0 to 1 weight percent (wt%) of the weight of the CF used and the incremental step was 0.2 wt%. The CF with 0 wt% or no GNP addition would be referred to as 'Pristine CF' while other CF shall be referred to as 'XGNP CF' where X is the percentage value of GNP loading on to the CF. For example, CF where 0.4 wt% of GNP is loaded, shall be referred to as 0.4GNP CF. A schematic of the spray coating process is presented in **Figure 2(a)**.

2.3. Laminate manufacturing

Figure 2(b) presents the schematics of the laminate manufacturing process using the vacuum assisted resin transfer molding (VARTM) technique. 8 layers of CF fabric that were coated to the similar loading of GNPs were stacked up on the laminate manufacturing platform with all the UDCF aligned in a similar sense before the vacuum bagging was done. Prior to infusion, the epoxy-hardener mix was prepared to proportions as mentioned above followed by thorough stirring for proper mixing and vacuum degassing to remove any trapped air. Following the infusion, the vacuum in the vacuum bagging was maintained for 24 hours. The laminate was cured in two steps; 24 hours at room temperature inside the vacuum bagging followed by 2 hours at 100°C in an oven. The size of each laminate was 30 cm × 30 cm. The thickness of the laminate was similar ~ 1.66-1.71. The laminates manufactured from different GNP loading shall be referred to as 'XGNP', where 'X' is the wt% of GNP loading on the carbon fiber obtained through spray coating.

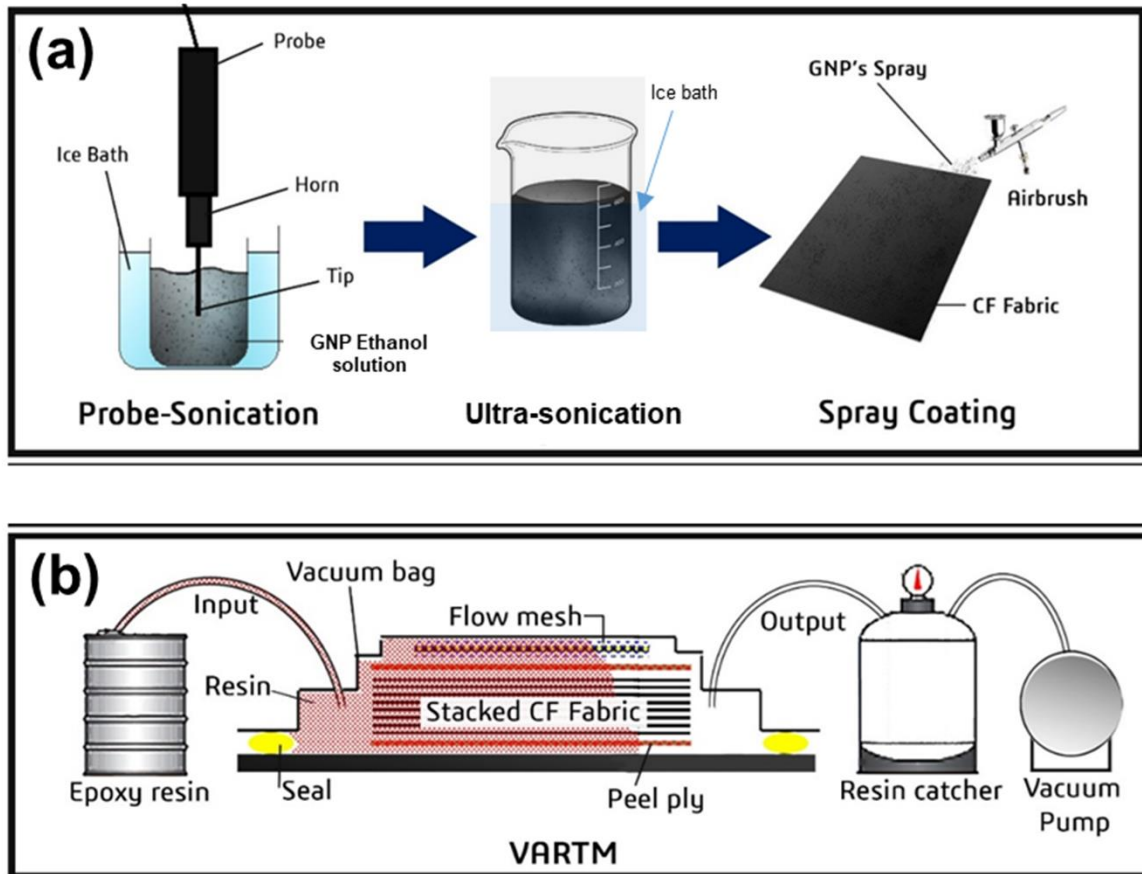


Figure 2 (a) Schematic of the spray coating process (b) Schematic of the VARTM process

2.4. Hygrothermal ageing

14 specimens having dimension $120 \text{ mm} \times 10 \text{ mm} \times t$ and 20 specimens having dimensions $15 \text{ mm} \times 2 \text{ mm} \times t$, where 't' is the laminate thickness, were cut from each of the manufactured laminates for the hygrothermal ageing. A schematic of the hygrothermal ageing process is shown in *Figure 3*. Hygrothermal ageing was performed for a period of 30 days by immersing all the specimens in a bath of deionized water maintained at 75°C . To record the increase in mass of the composite due to water absorption, specimens were removed from the bath and the weight was recorded using a digital weighing balance having a least count of 0.2 mg. Prior to weight measurement, the specimens were thoroughly and carefully wiped with a tissue paper to remove any surface water. After completion of the period of hygrothermal ageing, the specimens were dried at room temperature till the weight of the specimen saturated and there was no change in the weight of the specimens over a period of 72 hours.

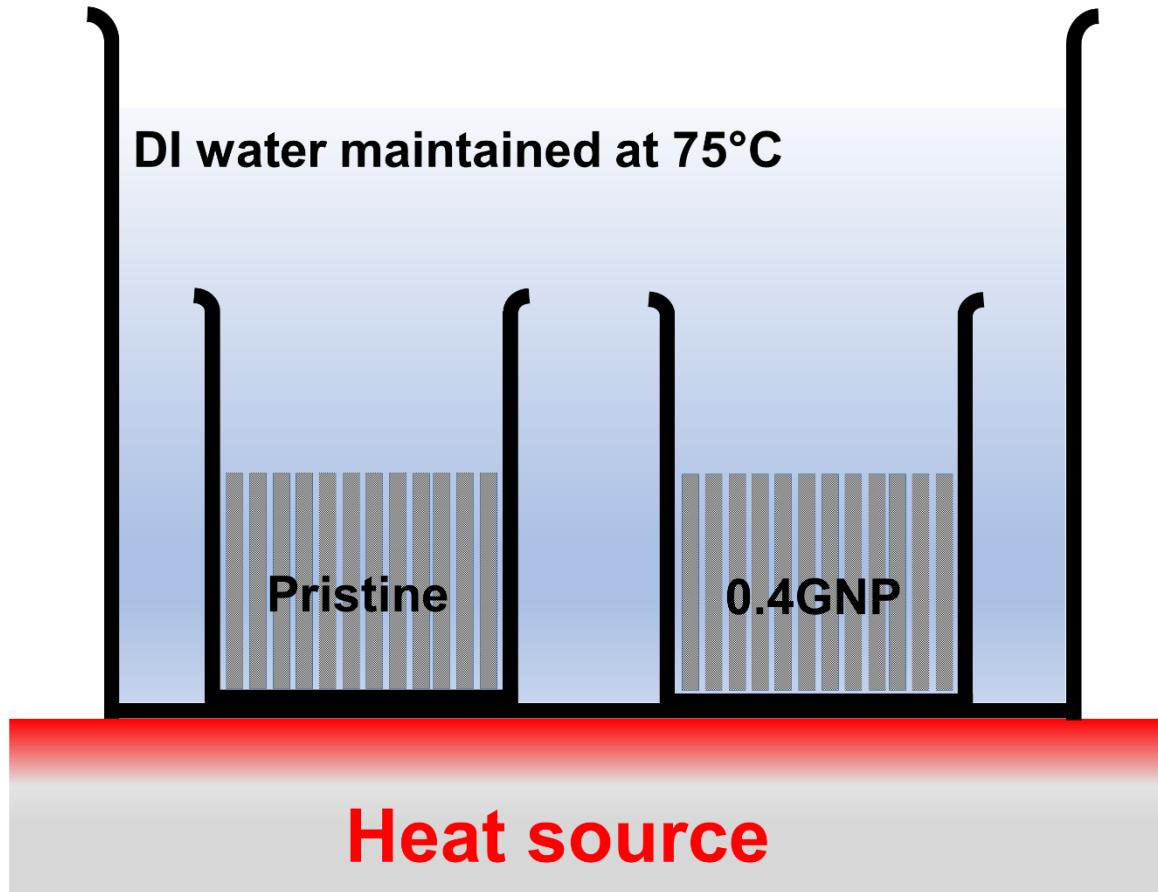


Figure 3 Hygrothermal ageing setup

The change in mass during the hygrothermal ageing process was calculated using the following formula [36].

Equation 1

$$M_t(\%) = \frac{W(t) - W_0}{W_0}$$

Here, M_t is the percentage change in mass at time 't'. $W(t)$ is the weight of the specimen at time 't' and W_0 is the initial weight of the specimen. An average of reading taken from at least 4 specimens was used for determine the change in mass.

Submersing the specimens completely in temperature-maintained water baths limits the study pertaining to effect of relative humidity (RH) on the hygrothermal ageing driven degradations. However, it does accelerate the hygrothermal ageing process and allows us to study long duration field ageing effects over a shorter duration of time.

2.5. Gel content measurement

The gel content is measured through refluxing utilizing the standard solvent extraction technique. The extracted specimens were weighed multiple times using a digital weighing balance having a least count of 0.0002 g and completely wrapped inside a filter paper and then placed into the refluxing chamber. THF (Tetrahydrofuran) was used as the solvent and the specimens were refluxed at 65°C for a period of 72 hours followed by drying until mass saturation was attained. In the extraction step, the gel-fraction does not dissolve in to the solvent and remains inside the filter paper, while the non-cross-linked or loosely cross-linked fraction would dissolve and migrate in to the solvent. Experimental based studies by Cardoso et al. [37] have suggested the crosslink density of polymers may be proportional to the values of the gel content based on the reactive portion of the stocks, which is, exclusive of plasticizers. The gel content is estimated using the following equation [36].

Equation 2

$$\text{Gel content (\%)} = \frac{W_{sat}}{W_{initial}} \times 100$$

W_{sat} - Saturation weight of the dried specimen

$W_{initial}$ - Initial mass of the specimen

A minimum of three specimens were tested per condition to determine the crosslink density.

2.6. Mechanical testing

To track the change in the mechanical properties of pristine CF laminates and GNP coated CF laminates for both unaged condition and as hygrothermal ageing progresses, tensile and inter-lamellar shear stress (ILSS) were performed. Mechanical testing was performed for the unaged condition, 15 days hygrothermally aged condition and 30 days hygrothermally aged condition.

2.6.1. Tensile test

The tensile test was performed on flat tensile specimens having a cross-section of 10 mm × t mm and a gauge length of 60 mm. Here, 't' is the laminate thickness. The grips were tabbed with tabs made out of with glass fiber reinforces laminates. The tabs prevented stress accumulation at the point of the gripping region and the start of the gauge region thus removing any experimental art effects. The specimen dimension used for the tensile test is shown in **Figure 4**.

The tensile tests were performed on 250 kN capacity servo hydraulically actuated universal testing machine (UTM) equipped with an extensometer. The tests were performed under displacement control mode at a constant cross-head velocity of 0.5 mm/min. The test protocols were in accordance with ASTM D3039.

2.6.2. Interlaminar shear strength (ILSS)

The ILSS was calculated through short beam shear (SBS) specimens where specimens had a width of 2 mm and thickness equal to the laminate thickness. The span length was maintained at 6 mm. The ILSS tests were performed on a pneumatically + electrically actuated 1 kN load capacity Instron UTM. The crosshead velocity was maintained at 1 mm/minute. A stereo zone camera was used to record the initiation and propagation of a crack during the ILSS test. The specimen dimension used for the ILSS test is shown in **Figure 4**. The test protocols were in accordance with ASTM D2344.

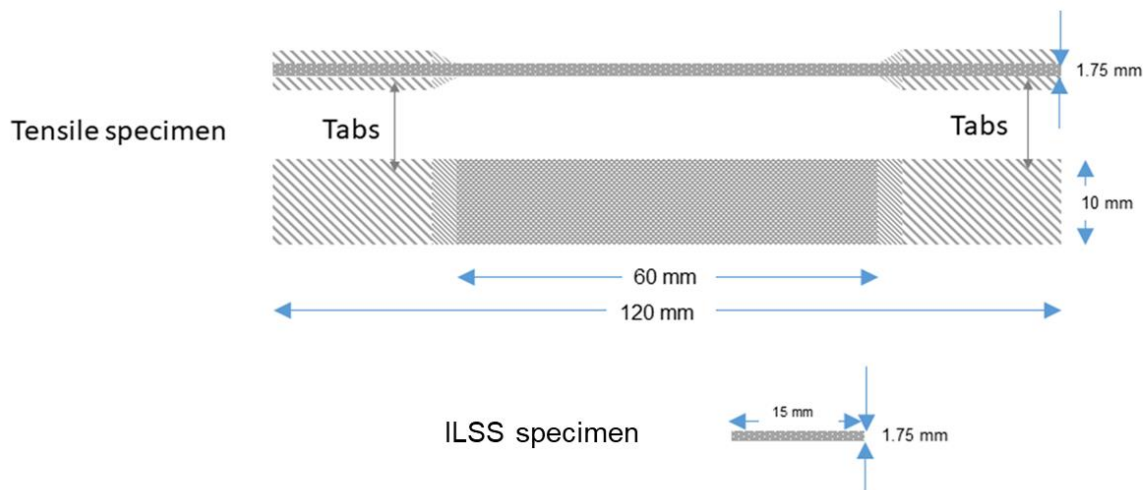


Figure 4 Specimen dimension (a) tensile test (b) Specimens for ILSS test

2.6.3. Dynamic mechanical analysis (DMA)

DMA tests were performed on both unaged and hygrothermally aged specimens in a temperature sweep mode at a constant frequency of 1 Hz in the 3-point bend configuration. The span length was maintained at 12 mm while the specimen dimension was 2 mm x t mm and 15 mm, where 't' is the laminate thickness. The test protocols were in accordance with ASTM D7028.

2.6.4. Scanning electron microscopy (SEM)

The fracture surface of the tensile tested specimens was examined using a Hitachi S3400, W filament SEM. The specimens were coated with carbon black to prevent charging of specimens during SEM.

2.6.5. Determination of CF-Epoxy interphase region

To determine the thickness of the interphase region of the as prepared laminate and the hygrothermally aged and dried laminates, Energy-Dispersive X-ray Spectroscopy (EDS) was carried out along the cross-section of the laminates. The carbon content was measured using a line map which spanned over a CF, CF-Epoxy interface and into the epoxy region. An AURIGA ZEISS dual beam FIB (Focused Ion Beam)-SEM equipped with an EDX facility was used for the measurement. The interphase region was determined using a combination of SEM imaging and the variation of carbon concentration over the length of the line map.

3. Results and discussion

3.1. Criterion for laminate manufacturing

In this study, to develop a water resistant laminate, we have tried to devise a method to make the CF more hydrophobic while also enhancing the strength of the laminate through secondary reinforcement. For this we have selected GNPs as the secondary reinforcement as it has been observed previously that GNPs demonstrate hydrophobic behavior even when present as a thin film on a hydrophilic surface[38,39]. To detect the change in the hydrophobicity with GNP addition, the contact angle for pristine CF, 0.2 GNP CF, 0.4 GNP CF, 0.6 GNP CF, 0.8 GNP CF and 1 GNP CF has been measured using DataPhysics Instruments Contact angle measurement set-up. CF fabrics were spray coated on both sides to different amount of GNP loading (0 to 1 wt%) and mounted carefully on a glass slide. Care was taken to have the CF fabric surface perfectly flat and not to disturb the integrity of the CFs. DI water (~10 μ l in volume) was dispensed on to the CF fabric surface and the contact angle was measured after the shape of the droplet was stable. The droplet size was large enough to spread even on an entire tow of CF. A minimum of four such measurements were performed for each CF coated condition.

Figure 5(a) shows the change in the contact angle with increasing weight % of GNP coating on to the CF fabric while **Figure 5(b-g)** shows the representative images of a stable DI water droplet on CF fabric for pristine CF and increasing GNP wt %. It is observed that the Pristine CF was the most hydrophilic. This could be due to the chemical inertness of CF and hydrophilic nature of polymer sizing layer that is present on the CF. With increasing GNP

coating on to the CFs, the CF surface becomes hydrophobic and the contact angle increases up to 0.4 wt % of GNP coating. Following which the contact angle decreases up to 1 GNP CF.

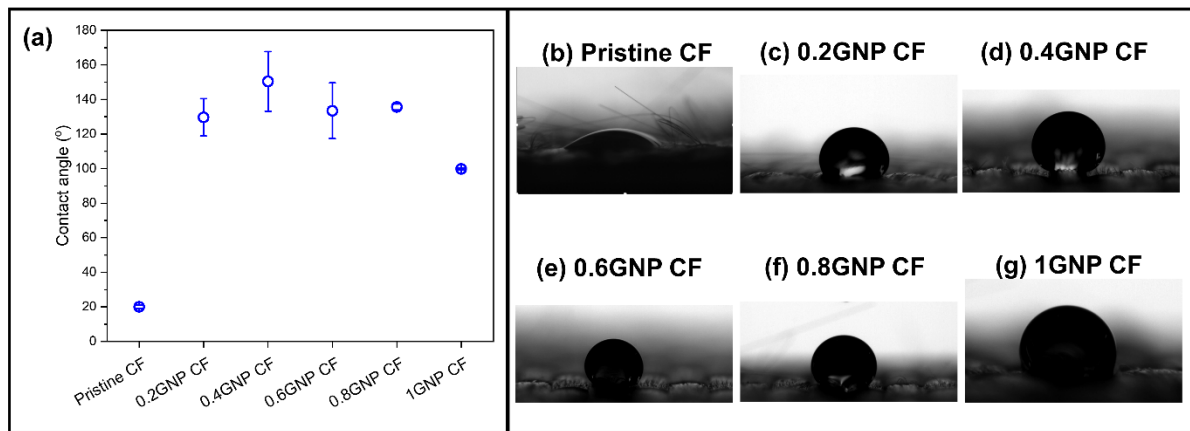


Figure 5 (a) Change in contact angle with increasing weight % of GNP coating on to the CF fabric (b-g) representative image of a stable droplet of DI water on CF fabric for pristine CF, 0.2 GNP CF, 0.4 GNP CF, 0.6 GNP CF, 0.8 GNP CF and 1 GNP CF respectively

Figure 6(a-e) presents the SEM micrographs of CF with 0.2 GNP CF, 0.4 GNP CF, 0.6 GNP CF, 0.8 GNP CF and 1 GNP CF respectively. It is observed that GNP coating is very uniform up to 0.4 wt % of GNP addition. 0.6 GNP, 0.8 GNP and 1 GNP CF images show formation of agglomerates of GNPs. Agglomerate formation becomes more intense with GNP addition beyond 0.6 GNP. An ample and uniform distribution of hydrophobic GNPs on to the CF fabric results in 0.4 GNP CF being the most hydrophobic. Formation of agglomerates is detrimental to the mechanical properties and could ease the process of defect nucleation. Hence, laminate manufactured using 0.4 GNP CF is expected to be the best in terms of water resistance and also mechanical properties. Basing on the results 2 laminates were manufactured: pristine CF laminate (control specimen) and the 0.4 GNP laminate.

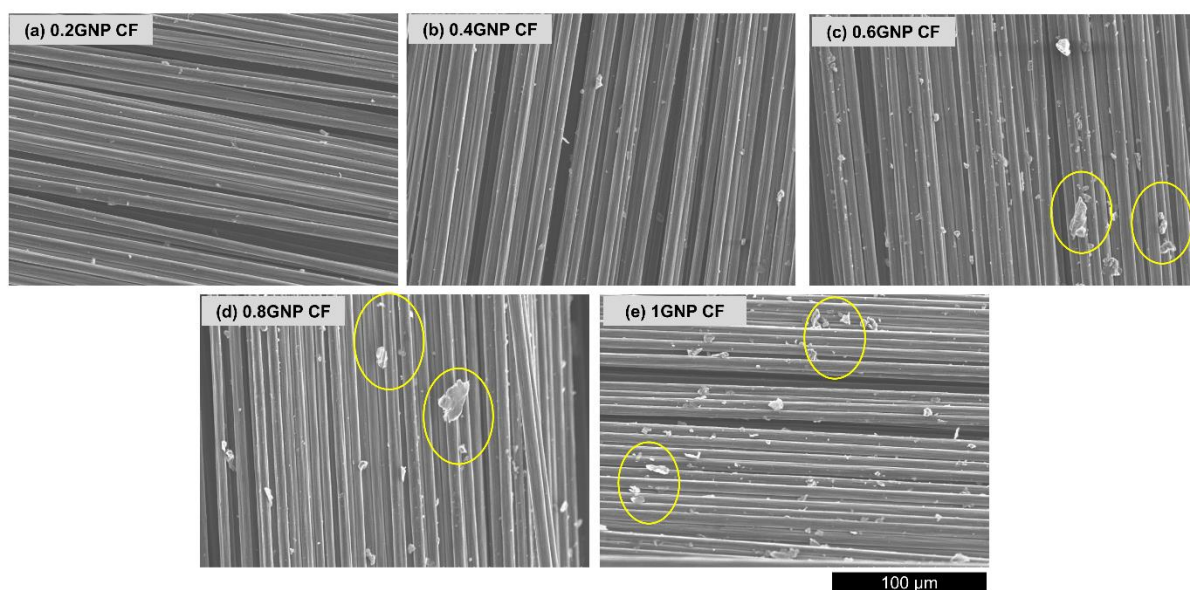


Figure 6 SEM micrographs of CF with a coated with (a) 0.2 GNP CF (b) 0.4 GNP CF (c) 0.4 GNP CF (d) 0.8 GNP CF (e) 1 GNP CF. The circled regions on the SEM images show the formation of GNP agglomerates after spray coating.

3.2. Hygrothermal ageing

Figure 7(a) shows the percentage change in mass for pristine and 0.4 GNP laminate with hygrothermal ageing time. It is observed that over the first three days, the rate of increase in mass (which corresponds to the rate of water intake) is the highest and subsequently the rate of water intake decreases progressively with hygrothermal ageing time but without attaining a saturation. **Figure 7(b)** plots the percentage change in mass against the square root of time and a saturation in the mass of water taken in not observed. This behavior deviates from a typical Fickian diffusion model where the water intake is expected to saturate. This indicates that water intake is a combination of diffusion and degradation. The degradation or reactions caused by water molecules residing in the laminate makes space for the intake of more water molecules, thus preventing saturation [20,21]. The degradation of epoxy due to reactions are detailed elsewhere [20,21]. From **Figure 7(a)** it is clear that at any given point of time 0.4GNP specimens absorbed the lowest amount of water and hence presented the best water-resistant behavior. This is in accordance with the hypothesis presented in Section 3.1 where it was shown that 0.4 GNP CF were the most hydrophobic and also presented a uniform deposition of GNP on to the CF fabrics.

Figure 7(c) presents the % loss of water with time during the drying/desorption of the specimens in ambient condition for specimens hygrothermally aged up to 30 days, while

Figure 7(d) presents the % loss of water with square root of time during the drying/desorption. From **Figure 7(b,d)** it is clear that the nature of curve for water absorption and desorption process is different. For the desorption cycle at the end of 30 days of hygrothermal ageing, the % change in mass with $\sqrt{\text{time}}$ shows a linear region followed by a saturation region which is typical for a Fickian process (**Figure 7(d)**), unlike the absorption cycle where saturation region is not observed post the linear region (**Figure 7(b)**). In the desorption cycle as the water molecules come out of the laminate at ambient lab temperature (25°C), the process is predominantly driven by diffusion.

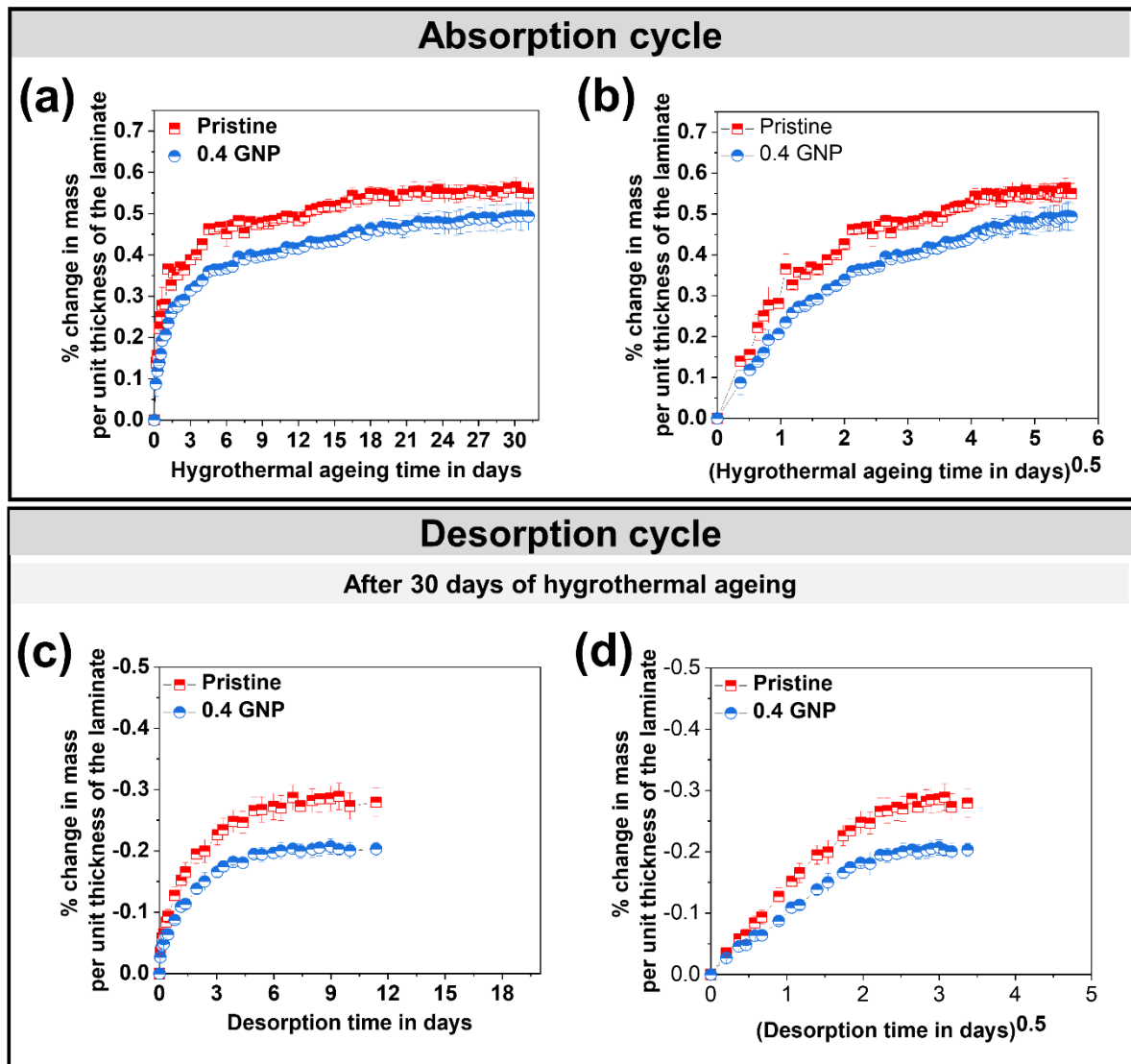


Figure 7 (a) Presents the % increase in mass per unit thickness of pristine and 0.4GNP laminate with days of hygrothermal ageing. (b) Presents the % increase in mass per unit thickness of pristine and 0.4GNP laminate with square root of days of hygrothermal ageing. (c) Presents the % decrease in mass per unit thickness of pristine and 0.4GNP laminate with

days of drying/desorption after 30 days of hygrothermal ageing respectively. (d) presents the % decrease in mass per unit thickness of pristine and 0.4GNP laminate with square root of days of desorption/drying after 30 days of hygrothermal ageing respectively.

From **Figure 7(d)**, it is observed that only a fraction of the absorbed water could diffuse out during the drying cycle and a saturation was reached after only 4 days of drying/desorption. This implies that a portion of the water was easy to remove during the drying cycle and a certain portion of the water was retained in the laminate even after long duration of drying (even drying for more than 30 days). It is shown previously that for hygrothermally ageing at elevated temperature a fraction of water molecule form complex hydrogen bonding with the polar groups of epoxy and becomes immobile and hence, are retained in the epoxy matrix of the laminate even after long periods of desorption/drying[24,40]. **Figure 8** presents the mass and the mass percentage of absorbed water that is retained in the laminate after completion of the desorption/drying cycle. The desorption /drying cycle is considered to be complete when no change in the mass of the specimen is recorded over an observation period of 72 hours during the drying cycle. The percentage mass of retained water after drying was higher in case of 0.4GNP laminate. From **Figure 7(d)** it is observed that at any given instant of time during the desorption cycle, pristine laminate got rid of a higher percentage of absorbed water which indicates that similar to water absorption GNP's offer hindrance to water molecules diffusing out of the 0.4GNP laminate.

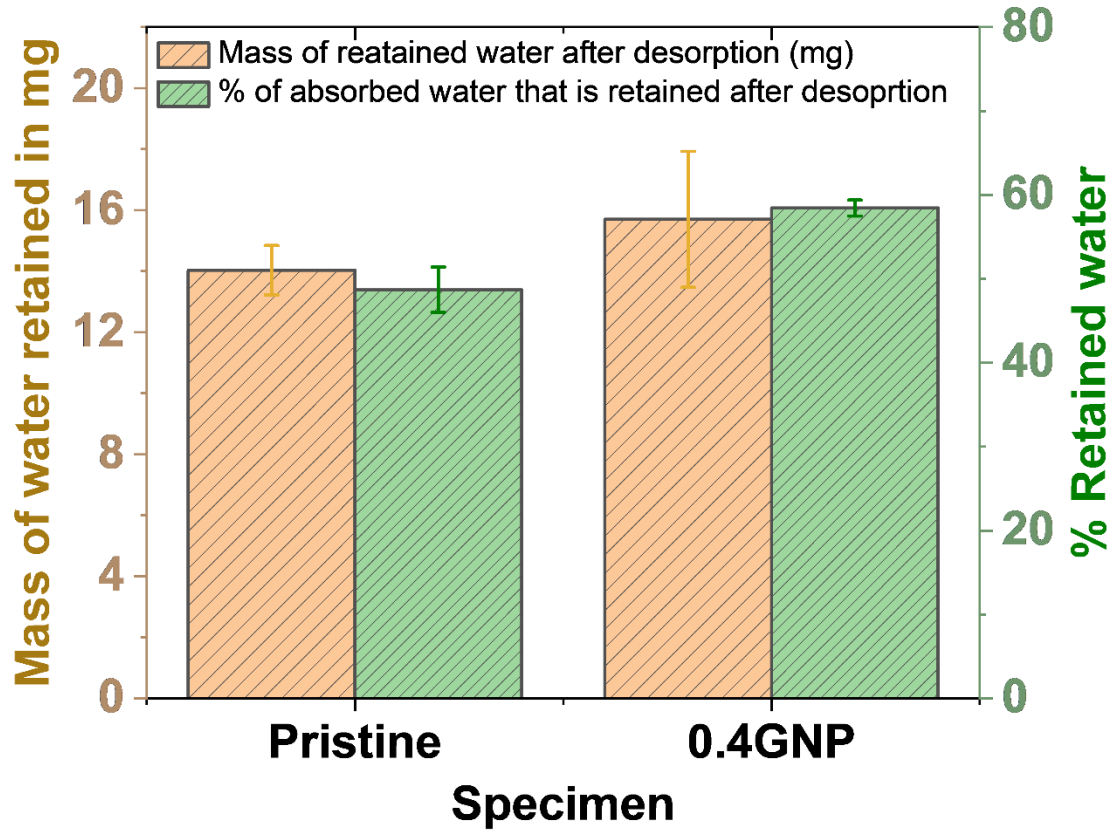


Figure 8 Mass of retained water and % mass of retained water (w.r.t. absorbed water) for different specimens subjected to hygrothermal ageing for 30 days and after complete drying

The diffusion coefficient was measured using the specimen's change in mass with $(\text{time})^{0.5}$ data during the hygrothermal ageing cycle for both pristine and 0.4GNP laminate. During the hygrothermal ageing cycle, both diffusion and degradation affect water intake. Hence, the diffusion coefficient is also measured using the desorption/drying data after 30 days of hygrothermal ageing. Here, the water transport is expected to be dominated by diffusion. As the thickness of the laminate is much smaller than the other dimensions of the laminate, the diffusion process can be assumed to be single dimensional. The diffusion coefficient can be calculated using the slope of the graph in **Figure 9(a)** and Equation 3 for short durations of hygrothermal ageing and **Figure 9(b)** and Equation 3 for short durations of desorption/drying cycle.

Equation 3

$$D = \frac{\pi}{16} \left(\frac{l^2}{M_{\text{infinity}}} \right) (\text{Slope})^2$$

Where

$M_{infinity}$ is the mass of water intake at saturation

D is the diffusion coefficient, t is time and l is laminate thickness.

‘Slope’ here refers to the slope of the %change in mass plotted against the square root of time both during the absorption and desorption cycle as shown in **Figure 9(a,b)**.

However, for calculating the diffusion coefficient using Equation 2, a proper estimation of the specimen saturation mass ($M_{infinity}$) is necessary and the lack of saturation during the absorption cycle would lead to an error in the estimation of $M_{infinity}$. The water absorption curve tends towards saturation but does not attain saturation. However, in case of epoxy based laminates, a lack of saturation in mass during hygrothermal ageing is expected and is well known from literature [20,21,41–43] because water triggered reactions with the polar groups present inside the epoxy matrix would make space for intake of more water molecules preventing saturation. Hence, $M_{infinity}$ for the water absorption cycle (hygrothermal ageing cycle) has been recorded as the point where the % change in mass plotted against the square root of time deviates from linearity and the curve becomes progressively non-linear accompanied by an appreciable decrease in the rate of water absorption. This is shown in **Figure 9(a)**. For the desorption cycle since a proper saturation in specimen mass with drying time is observed, $M_{infinity}$ is taken as the final saturated mass as shown in **Figure 9(b)**.

From **Figure 9(c)** it is observed that the diffusion coefficient during the hygrothermal ageing cycle (where the water molecules enter the laminate and diffusion is accompanied by degradation) decreases marginally (~3%) with addition of GNPs. While in the desorption cycle, where diffusion is dominant, the diffusion coefficient of 0.4GNP laminate is much lower than the pristine laminate and we observe a ~ 21 % reduction in diffusion coefficient with GNP addition. This indicates that making the CF more hydrophobic through addition of more hydrophobic GNP, increases the water transport resistance.

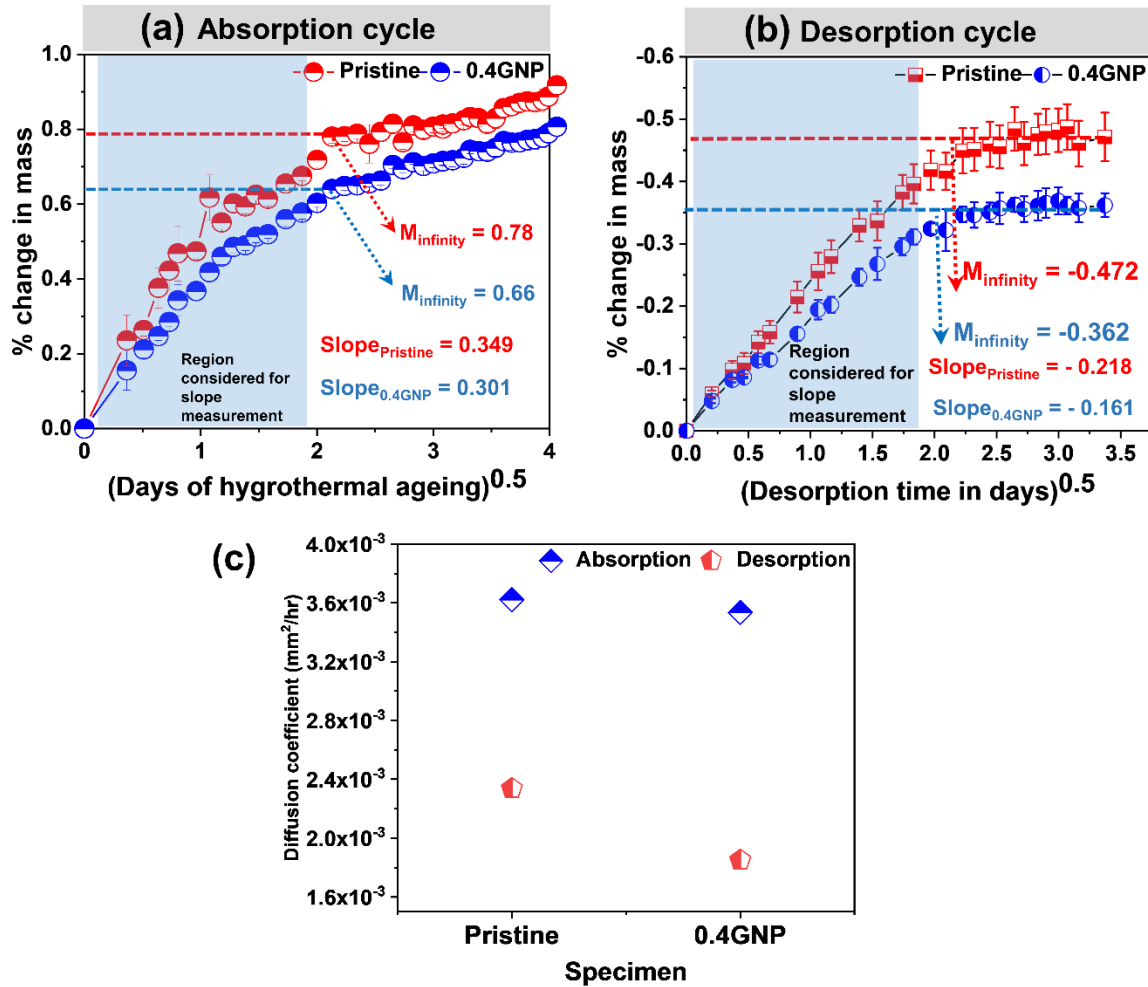


Figure 9 (a) Representative plot used for calculation of diffusion coefficient during the water intake cycle (b) Representative plot used for calculation of diffusion coefficient during the drying cycle (c) Diffusion coefficient measured for pristine and 0.4 GNP laminates during the absorption and desorption cycle

3.3. Interphase between CF and epoxy

Figure 10(a-f) shows the interphase region formed between the CF and epoxy for (a,b,c) Pristine laminate (d,e,f) 0.4GNP laminate for both unaged and hygrothermally aged specimens. From **Figure 10(a and c)** it is observed that the thickness of the interphase region in case of 0.4GNP laminate ($\sim 2.34 \pm 0.02 \mu m$) is larger than the Pristine laminate ($\sim 0.98 \pm 0.1 \mu m$). The higher thickness of the carbonaceous interphase region in case of 0.4GNP laminate results from the spray coating of hydrophobic non-functionalized GNP's on to the CF surface prior to laminate manufacturing. It is observed that the thickness of the interphase region decreases with hygrothermally ageing time. In case of pristine laminate, the decrease happens monotonically ($\sim 10\%$ over the first 15 days and $\sim 12\%$ over the next 15 days of hygrothermal

ageing period) while in case of 0.4GNP laminate it seems to decrease by ~40% over the first 15 days of hygrothermal ageing and remains stable thereafter. However, the interphase thickness of 0.4GNP laminates even after 30 days of hygrothermal ageing is larger than that of the Pristine laminate in the 'Unaged condition'. Hence, the 0.4GNP laminate with a thicker interphase region resulting from the coating of hydrophobic non functionalized GNP is expected to show better resistance to water molecules than the pristine laminate. A possible reason for the decrease in the interphase region of pristine laminate could be local swelling of epoxy caused by water molecules with hygrothermal ageing which affects the integrity of the interphase region. Along with the swelling of epoxy, in case of 0.4GNP laminate, it is expected that the hydrophobic GNP could be repelled by incoming water molecules to condense into agglomerates and form into a thinner interphase which is facilitated by the high temperature of the hygrothermal ageing bath.

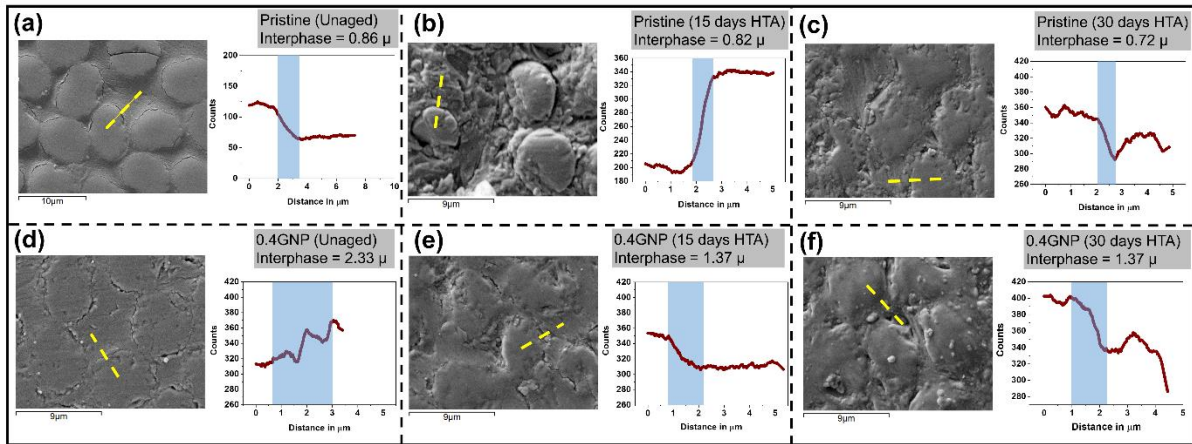


Figure 10 Representative images for evaluation of the interphase region formed between the CF and epoxy for (a,b,c) Pristine laminate (d,e,f) 0.4GNP laminate for unaged and hygrothermally aged specimens

Figure 11 presents a schematic of the water absorption scenario in case of Pristine and 0.4 GNP laminate. In case of 0.4 GNP laminates, a coating of GNP surrounds the CF which results in the formation of a hydrophobic carbonaceous interphase. The presence of this interphase region presents barriers to the transport of water molecules in the epoxy matrix and especially in the region surrounding the CFs which results in 0.4GNP laminates being more water resistant. However, as shown in *Figure 12*, it is observed that the percentage improvement in water resistance of 0.4 GNP laminate over the pristine laminate decreases as hygrothermal ageing progresses; from ~17% of the end of 5 days of hygrothermal ageing to about 5.5 % at the of 30 days of hygrothermal ageing. The reduction in the water resistance

ability of 0.4GNP laminate over the pristine laminate (as shown in *Figure 12*) would result from the shrinkage of the CF-GNP-Epoxy interphase region.

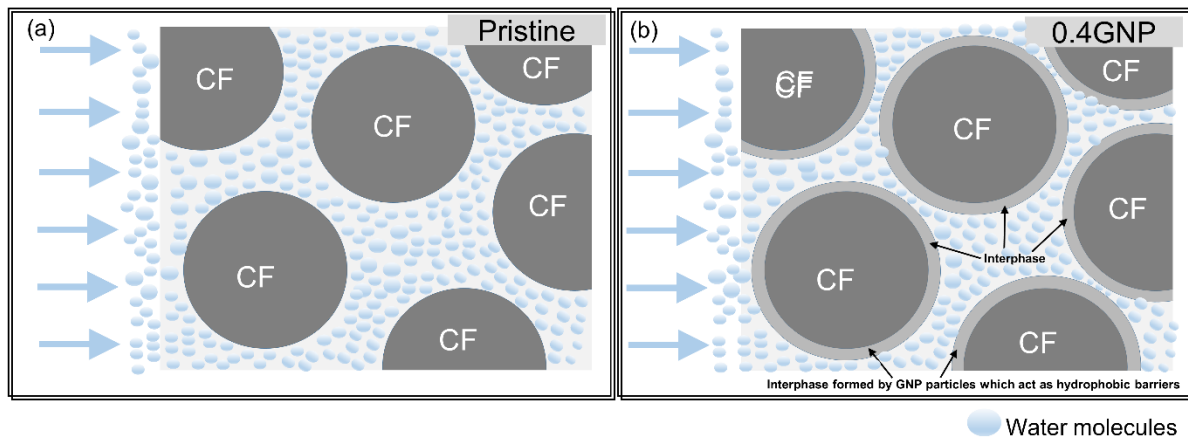


Figure 11 Schematic of the water diffusion and degradation process in pristine and 0.4GNP laminate

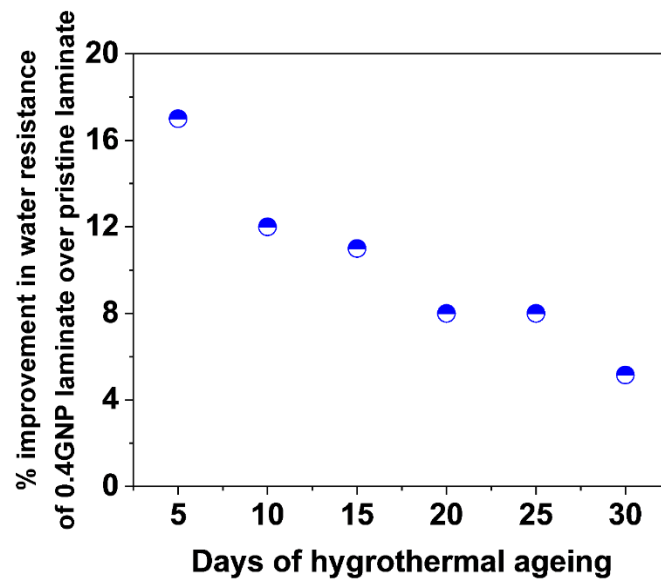


Figure 12 Change in % improvement in water resistance of 0.4 GNP laminate over Pristine laminate with days of hygrothermal ageing

3.4. Gel content measurements

Figure 13 presents the gel content (proportional to the cross-link density) of laminate specimens and its change with GNP addition and hygrothermal ageing. For the unaged condition, all the laminates showed a higher gel content of ~99% with the gel content being a bit lower for 0.4 GNP laminates as compared to Pristine. At the end of 15 days of hygrothermal

ageing, the decrease in gel content of the Pristine laminate is higher than 0.4 GNP laminate. While at the end of 30 days of hygrothermal ageing, the gel content of Pristine was similar to that at the end of 15 days. Over the first 15 days of hygrothermal ageing 0.4GNP laminate showed a negligible decrease in gel content while it showed a larger decrease in the gel content (and hence the cross-link density) between 15 to 30 days of hygrothermal ageing. Hence, the degradation of the laminate in terms of decrease in gel content (cross-link density) of the polymeric constituents is delayed with GNP addition.

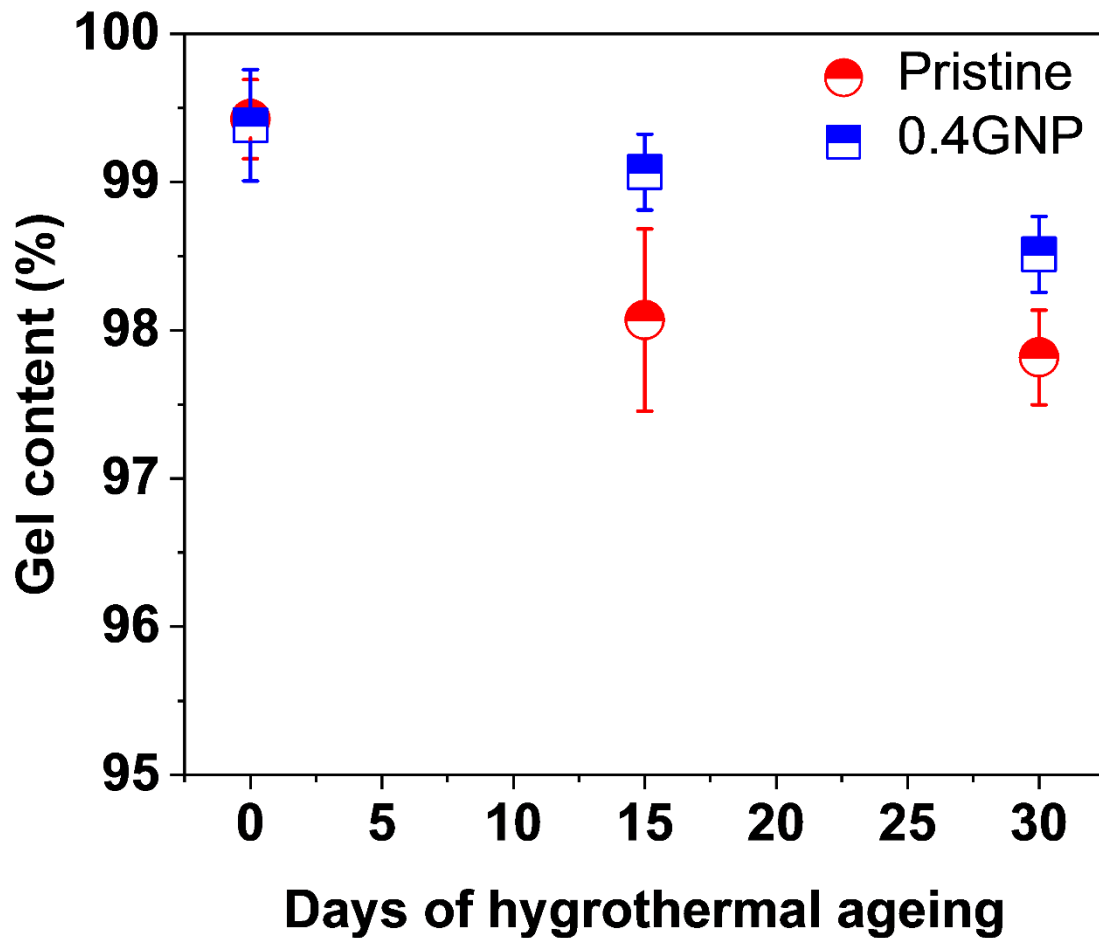


Figure 13 Change in gel content of the laminate with hygrothermal ageing

3.5. Dynamic mechanical analysis

Figure 14(a,b) presents the $\tan\delta$ -temperature curve for unaged specimens and hygrothermally aged specimens obtained from the DMA data and *Figure 14(c)* presents the change in the glass transition temperature with hygrothermal ageing time as evaluated from the peak of the $\tan\delta$ -temperature curve. From *Figure 14(a,b)* and *Figure 14(c)* it is evident that the glass transition temperature (T_g) decreased by $\sim 2^\circ\text{C}$ with GNP addition. A prior study by

Karthicksundar et al [44] on glass fiber epoxy composites with carbon powder as nano-fillers have shown that addition of nano-fillers causes a small decrease in the T_G which could possibly be due to a poor nano-filler epoxy interface, interaction of nano-fillers with the radius of gyration of epoxy chain and due to some possible impurities introduced by the nano-fillers. Jarrett and Korkees [28] observed a very small change in T_G ($< 1^\circ\text{C}$) after GNP addition. They attributed the rather very small decrease in T_G to the good thermal stability of GNPs. **Figure 14** shows that with hygrothermal ageing T_G only decreases in case of pristine specimen while 0.4GNP specimens does not record a decrease in the T_G . However, the decrease in T_G for pristine laminate with hygrothermal ageing is very small $< 1.5^\circ\text{C}$. As previously studied by Mishra and Singh[36], hygrothermal ageing at elevated temperature ($\sim 75^\circ\text{C}$) could lead to a minimal decrease in T_G as the plasticization caused by hygrothermal ageing is counteracted by the development of a secondary cross-link network through complex hydrogen bonding of water molecules with polar groups of epoxy.

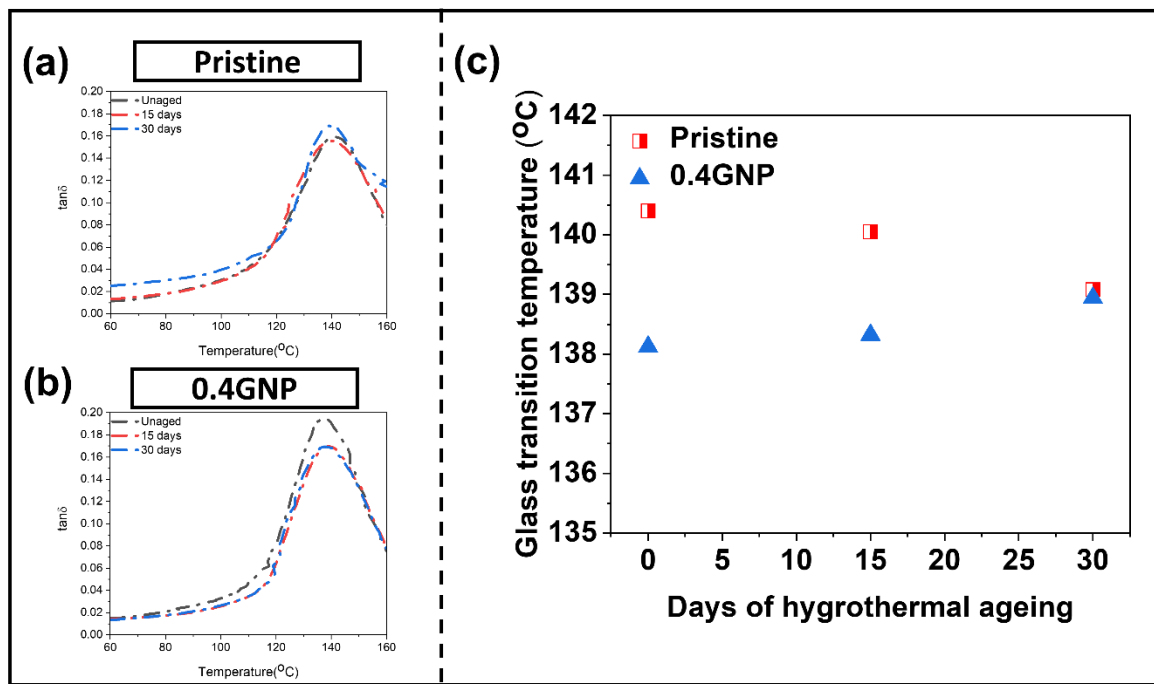


Figure 14 Plots for change in (a,b) $\tan\delta$ as a function of temperature with increasing hygrothermal ageing (c) Change in the glass transition temperature with hygrothermal ageing time for Pristine and 0.4GNP laminates

3.6. Tensile test

Figure 15(a) presents the ultimate tensile strength (UTS) of pristine and 0.4GNP laminates for unaged and hygrothermally aged conditions and **Figure 15(b)** presents the

percentage strain at failure of pristine and 0.4GNP laminates for unaged and hygrothermally aged conditions. All the tests were performed on specimens that were removed from the hygrothermal ageing bath and desorped/dried for a long duration (in excess of 30 days) till the point where a saturation in mass was obtained over a period of 72 days. Each data point on the plot is the average of 4 tensile tests. In the as prepared condition, the 0.4GNP laminate showed almost 12% improvement in UTS and ~ 13 % improvement in failure strain over the pristine condition. The increment in tensile strength of the 0.4GNP laminate can be explained by the mechanical locking provided by the GNP fillers (where GNP fillers and epoxy can be mechanically locked together enhancing interfacial bonding). and the formation of a carbonaceous interphase/interphase at the CF/epoxy as explained previously[2,3,45]. The formation of an interphase not only strengthens the epoxy matrix in the vicinity of the CF but also results in efficient load transfer between the epoxy and the CF[18].

As the hygrothermal ageing progresses, it is seen in *Figure 15* that the UTS of the laminates decreases drastically even after 15 days of hygrothermal ageing with ~ 25% decrease for Pristine and ~ 35% decrease for 0.4GNP laminate. The UTS further decreases at the end of 30 days of hygrothermal ageing but this time the decrease in UTS is less as compared to the decrease in UTS after 15 days of hygrothermal ageing (~5% decrease over 15 to 30 days of hygrothermal ageing). It is also observed that the UTS of the laminates: falls within the same standard deviation (for 15 days of hygrothermal ageing and also for 30 days of hygrothermal ageing) and hence the enhancement in strength initially achieved through 0.4 wt % GNP addition is completely lost. Along with a decrease in tensile strength, the tensile strain at failure also decreases with hygrothermal ageing. However, the % strain at failure is always higher for 0.4GNP laminate even after 30 days of hygrothermal ageing.

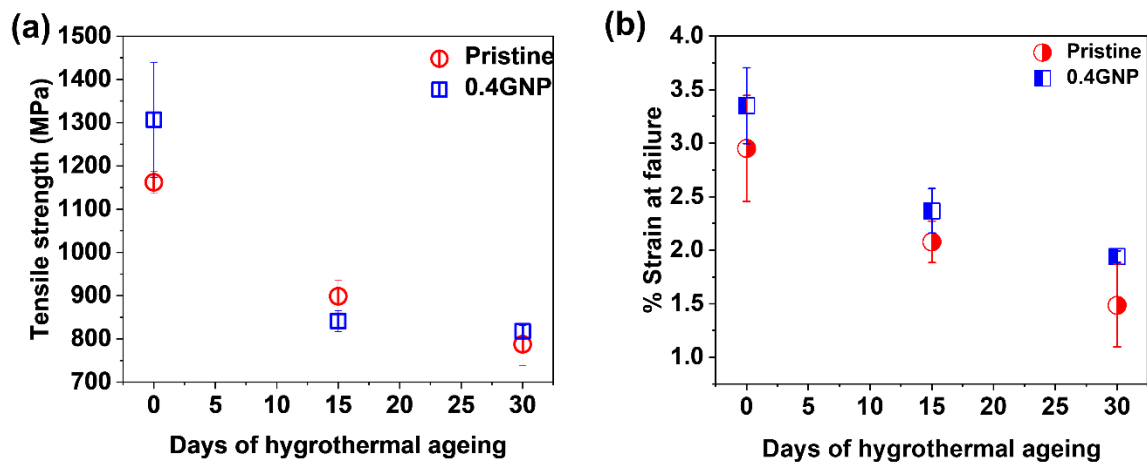


Figure 15 (a) Variation of ultimate tensile strength with hygrothermal ageing for Pristine, and 0.4GNP laminates (b) Variation of % strain at failure with hygrothermal ageing for Pristine, and 0.4GNP laminates

Figure 16(a,b,c) presents a representative set of tensile stress-strain curve for Pristine, and 0.4GNP for as prepared condition, after 15 days hygrothermal ageing and after 30 days of hygrothermal ageing. It is observed that along with a change in tensile strength, the nature of the stress-strain curve also changes. In case of “Unaged” specimens (**Figure 16(a)**), the specimen reaches the UTS after which a complete failure of the specimen happens and the stress drops to zero. After 15 days (**Figure 16(b)**) and 30 days (**Figure 16(c)**) of hygrothermal ageing, the load does not drop to zero immediately after attaining UTS, rather, it happens in steps. The step by step decrease in the tensile stress happens due to ply-by-ply failure. The fracture of the first ply or set of plies leads to the first load drop event which corresponds to the UTS. The damage of one ply decreases the load bearing ability of the composite and with further straining, failure is triggered in subsequent plies accompanied by formation of steps on the stress-strain curve until complete failure happens. The ply-by-ply failure is often triggered by a narrow band of the epoxy rich region which exists between two plies. It is shown previously that the tensile strength and fracture toughness of epoxy decreases with hygrothermal ageing [46] and hence, it is expected that the strength of the epoxy in-between plies would also have decreased with hygrothermal ageing. Also, plasticization that builds up in the epoxy with hygrothermal ageing would weaken inter ply bonding and the difference in the swelling behavior of the epoxy rich and the fiber rich region would lead to generation of internal stresses and de-bonding. The de-bonded regions would further allow for the intake of more water molecules. The dominance of the degraded epoxy rich regions in triggering the failure under uni-axial tensile loading completely canopies the effect of GNP addition. Hence,

there is no effect of GNP addition on the tensile strength after long duration of severe hygrothermal ageing.

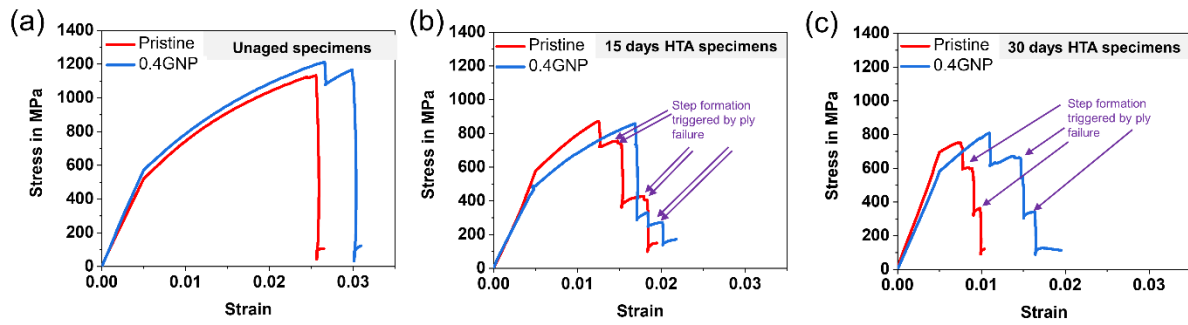


Figure 16 Tensile stress-strain curve for Pristine and 0.4GNP for (a) Unaged specimens, (b) desorped specimens after 15 days of hygrothermal ageing (c) desorped specimens after 30 days of hygrothermal ageing

3.7. ILSS

Figure 17 shows the change in the ILSS with hygrothermal ageing time for Pristine, and 0.4GNP laminates. The ILSS increased with GNP addition in the unaged condition by around 7% . However, as hygrothermal ageing progressed the ILSS of all the three laminate reduced and the enhancement in the ILSS achieved with GNP addition was completely lost. The decrease in ILSS was large over the first 15 days of hygrothermal ageing (~10% for pristine and ~20% for 0.4GNP) and minimal over the next 15 days of hygrothermal ageing. Thus, for both the tensile strength and the ILSS, the effect of GNP addition was completely lost after severe hygrothermal ageing. **Figure 18** presents a representative load-displacement curve generated during the ILSS test. It is observed that for unaged specimens, the load decreases monotonically once the peak load is reached whereas for aged specimens, the load-displacement curve is rather tortuous post possibly triggered by multiple inter-ply delamination.

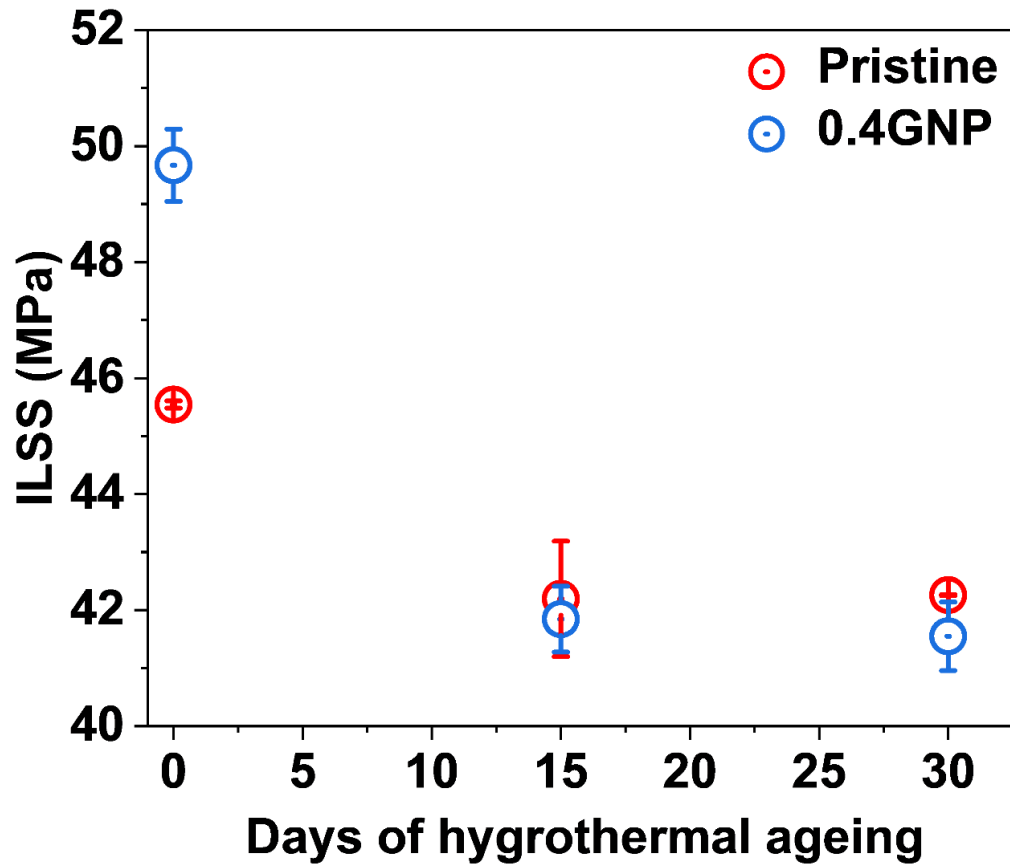


Figure 17 Change in ILSS with hygrothermal ageing time for Pristine and 0.4GNP laminates

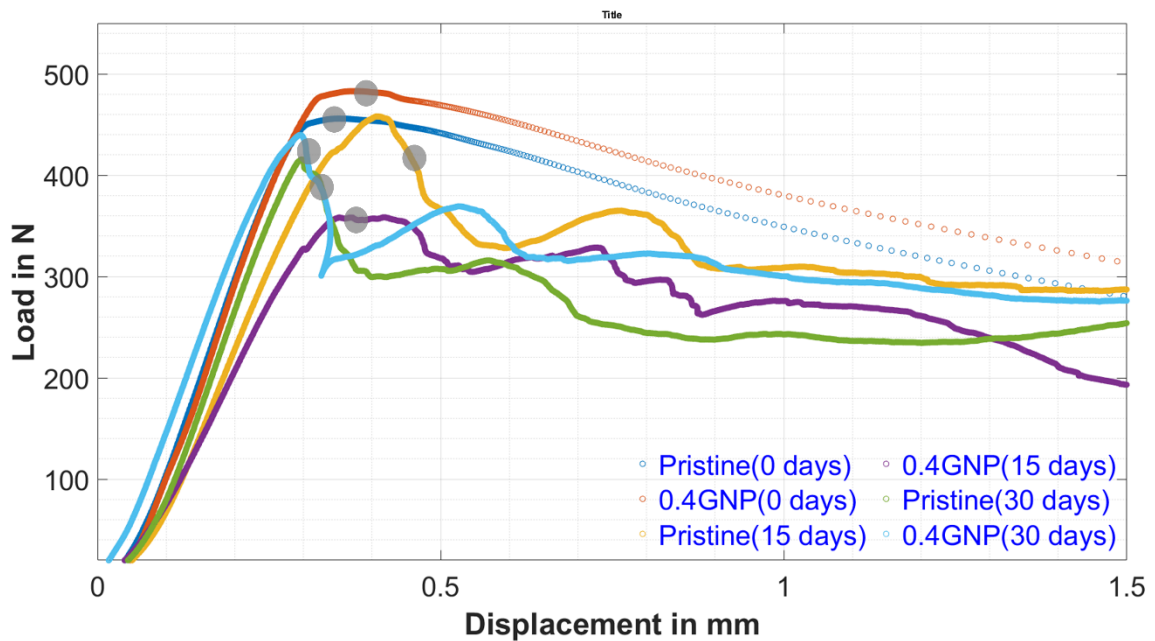


Figure 18 Representative load-displacement curve generated during the ILSS test. The black circles indicate the regions where the side-section images recorded during the ILSS tests and presented in Figure 18

Figure 19(a-f) presents the side-section images of the ILSS specimens captured during the ILSS test just after the first drop in load had occurred. For the unaged specimens, especially for 0.4GNP laminates, the first load drop was triggered by a crack initiated just under the loading nose. Multiple inter-ply delamination accompanied the initiated crack. In case of pristine specimen, the load drop was mostly triggered by multiple delamination. The addition of GNP was able to delay the delamination and hence resulted in a higher value of ILSS for 0.4GNP laminates. However, as hygrothermal ageing progressed, initiation of delamination was seen in all the specimens which was triggered at a much lower load. This indicates that the thin film of epoxy in-between ply had become weak with hygrothermal ageing and is responsible for its failure.

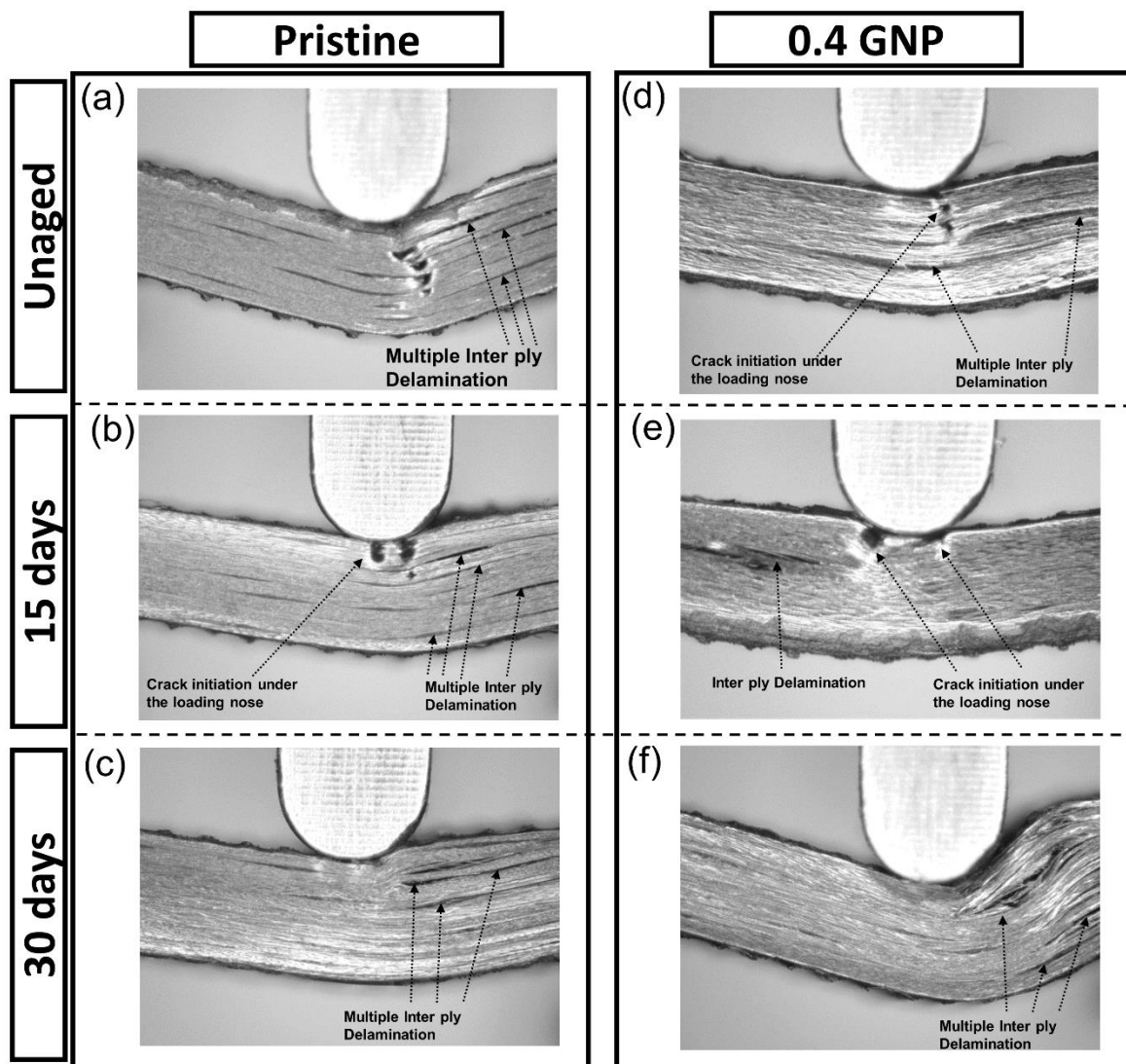


Figure 19 Side section of the ILSS test specimens captured during the ILSS test after the first load drop in the load-displacement curve for unaged and hygrothermally aged specimens.

(a,d) Unaged specimens, (b,e) desorped specimens after 15 days of hygrothermal ageing (c,f) desorped specimens after 30 days of hygrothermal ageing.

3.8. Fractography of tensile tested specimens

The tensile test fracture surface was done along two planes as show in the schematic in *Figure 20*. The first plane (Location 1) was perpendicular to the tensile axis whereas in Location 2 the plane was along the tensile axis. Location 1 shows the deformation of the CF and epoxy as well as the extent of CF pullout while Location 2 shows inter-ply deformations. In all the tensile test specimens it was possible to find regions corresponding to Location 1 and 2. *Figure 20*(a-f) presents the fracture surface at Location 1 for Pristine and 0.4GNP laminate for Unaged (*Figure 20*(a,d)), 15 days hygrothermal ageing (*Figure 20*(b,e)) and 30 days hygrothermal ageing (*Figure 20*(c,f)).

The fracture surface at Location 1 of unaged specimens (*Figure 20*(a,d)), indicates that there are some regions where the epoxy is adhered to the CF and some regions where there is pullout of CF. It is observed that the extent of pullout of CF decreases and the adherence of epoxy is more for 0.4GNP laminate. This is because of the increasing mechanical locking presented by the spray coated GNPs on to the CF surface and the presence of an interphase region which efficiently transfers stress between epoxy and CF. After 15 days of hygrothermal ageing (*Figure 20*(b,e)), the extent of CF pullout in case of pristine laminate is higher than 0.4GNP laminate. For 0.4GNP laminate, we still see epoxy adhered to the CF over a large area on the fracture surface. Although 0.4GNP laminate showed a lower degree of CF pullout, its tensile strength decreased to the same value as Pristine. This supports the fact that the fracture of laminate under tensile loading was dominated by the degraded inter-ply epoxy rich region: failure from the weakest link. After 30 days of hygrothermal ageing (*Figure 20*(c,f)), all the laminates showed appreciable CF pullout and there were negligible area fraction of regions where the epoxy was adhered to the CF. This implies that the interface of the CF and epoxy is degraded and the effect of GNP is completely lost on the mechanical properties after 30 days of hygrothermal ageing at 75°C. This is also inferred from the decrease in the interphase thickness of 0.4GNP laminate as shown in *Figure 10*.

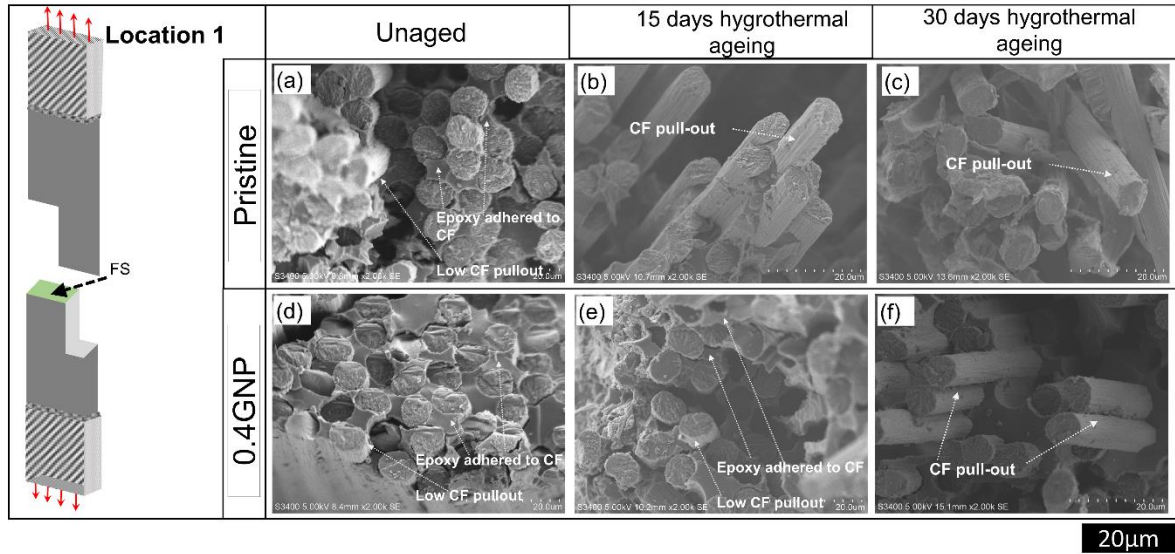


Figure 20 Tensile test fracture surface at Location 1 for Pristine, 0.2GNP and 0.4GNP laminate for Unaged (a,d), 15 days hydrothermal ageing (b,e) and 30 days hydrothermal ageing (c,f)

The fracture surface at Location 2 (*Figure 21* (a-f)), indicates that with hydrothermal ageing, the epoxy rich regions in between the plies have swelled up leading to the formation of inter-ply voids. The cracks generated in the epoxy rich regions for both pristine and 0.4GNP specimens, after 30 days of hydrothermal ageing, is possibly due to internal stresses caused during swelling or the disproportional expansion between the epoxy rich and fiber rich regions. Thus as ageing progresses, the weakest link in the composite becomes the inter-ply regions.

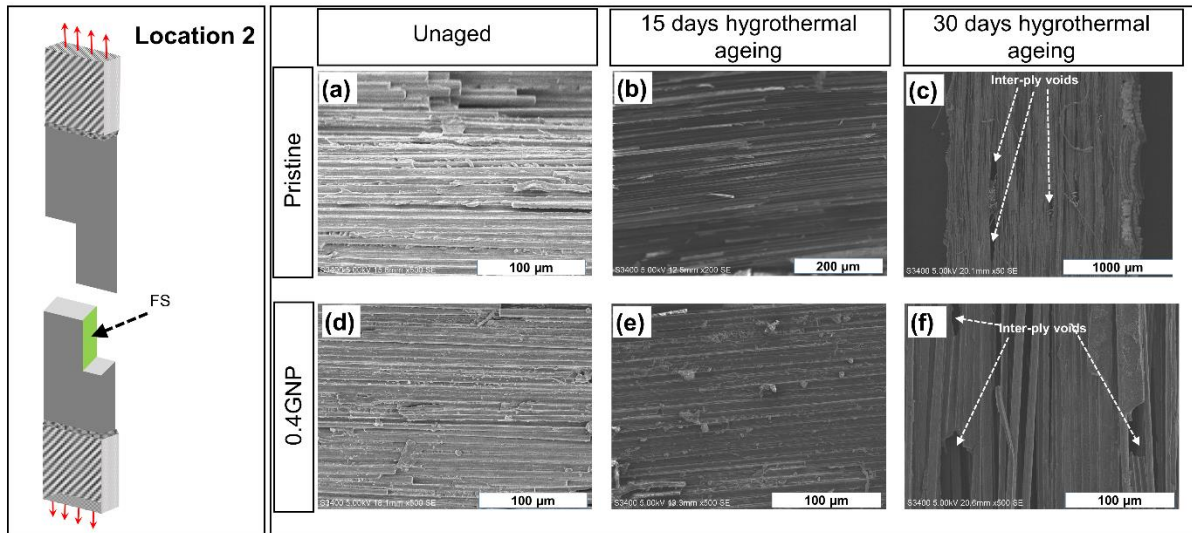


Figure 21 Tensile test fracture surface at Location 2 for Pristine and 0.4GNP laminate for Unaged (a,d), 15 days hygrothermal ageing (b,e) and 30 days hygrothermal ageing (c,f)

3.9. Side section SEM micrographs of ILSS tested specimens

Figure 19 presented the side section of stereo zone microscope image of the ILSS tested specimens just after the attainment of the peak load as marked in **Figure 18**. **Figure 22** presents the SEM micrographs of the side section (Insert 1 **Figure 22**) of ILSS tested specimens acquired using an SEM after completion of the ILSS tests. It is observed that in all the cases multiple delamination are triggered and the delamination type of event triggered during the ILSS tests increases with hygrothermal ageing. In the crack initiation region, it is observed in **Figure 22(d)** that the extent of fibre pull out for 0.4GNP laminate is lower than the fibre pull out in case of pristine specimen (**Figure 22(b)**). After 15 days of hygrothermal ageing, along with delamination, we also observe cross-ply failures in the case of pristine specimen (**Figure 22(e)**). After 30 days of hygrothermal ageing, we observe numerous delamination for both pristine and 0.4GNP specimen and the extent of CF failure and cross-ply failure is reduced both for pristine and 0.4GNP specimen. This is because the delamination which are triggered by the weakened epoxy reached region allow for stress relaxations and prevent other modes of failure.

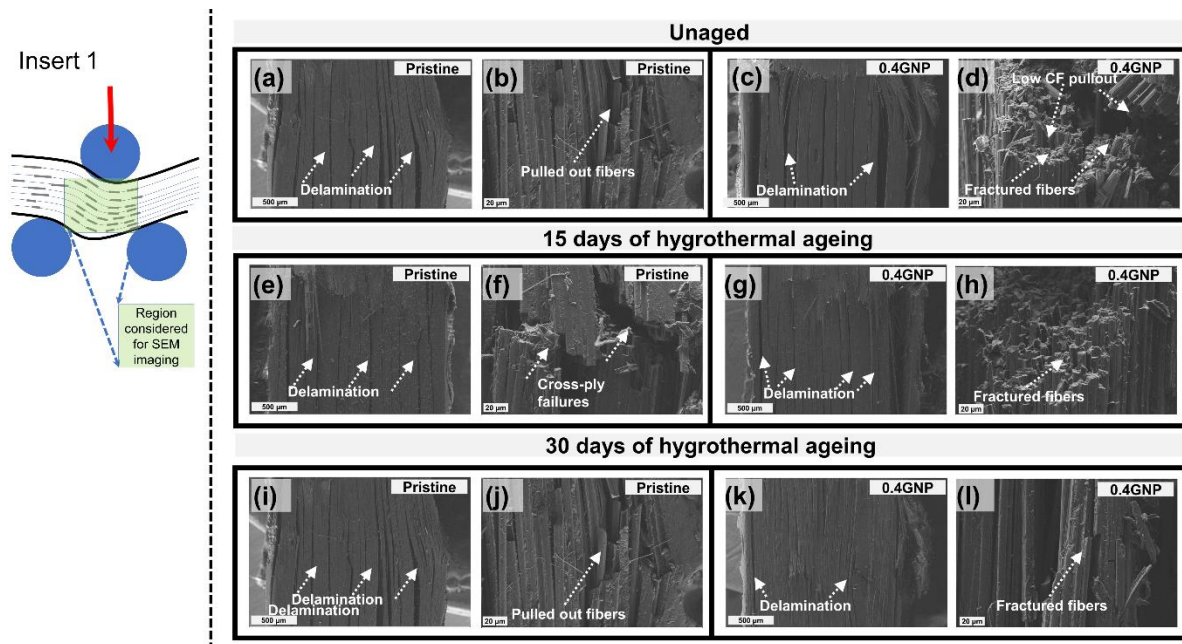


Figure 22 SEM micrograph of the side section of ILSS tested specimens for Pristine (a,b,e,f,i,j) and 0.4GNP laminate (c,d,g,h,k,l) for Unaged (a,b,c,d), after 15 days of hygrothermal ageing (e,f,g,h) and after 30 days of hygrothermal ageing (i,j,k,l).

4. Conclusion

A lot of research on enhancing the mechanical properties of composites focuses on enhancing the interfacial/interphase properties of carbon fiber and epoxy. This leads to substantial enhancement in the initial strength of the composite. However, it becomes extremely important to understand how much of the strength enhancement is retained after the composite is put into service especially in cases where the service environment is hot and humid. In this study it is observed that the strength enhancement in laminates achieved through GNP coating of CF fabrics was completely lost after 15 days of hygrothermal ageing at 75°C in water. Hence, it becomes very important for structural design engineers to consider the degradation in mechanical properties of laminates due to environment.

In the present study we have investigated the change in the structural and mechanical properties of laminates subjected to aggressive hygrothermal ageing. The CF used in the laminates were spray coated with GNP as nano-filler and Pristine CF was used as a control. The following conclusions have been drawn from the study

- 1) The dispersion of GNPs on to the CF fabric through spray coating was uniform up to 0.4 wt % of GNP addition. Beyond 0.4 wt %, agglomerates of GNPs were observed forming of the CF fabric. Formation of agglomerates are detrimental to mechanical properties.

- 2) The addition of GNPs on to the CF fabric rendered the CF fabric hydrophobic as measured through contact angle based measurements. The hydrophobicity of the CF fabrics increased up to 0.4 wt % of GNP addition and decreased thereafter with higher wt % of GNP addition possibly due to formation of agglomerates.
- 3) 0.4GNP laminate offered better resistance to hygrothermal ageing than Pristine laminate. This is possibly due to the higher content of hydrophobic non-functionalized GNP and the formation of a thicker carbonaceous CF-Epoxy interphase region.
- 4) The tensile strength in the unaged condition increased by almost 12% for 0.4GNP laminate as compared to the Pristine laminate. This could be due to the better mechanical locking provided with 0.4 wt % of GNP addition and the formation of a carbon rich CF-Epoxy interphase/interphase. With hygrothermal ageing, the enhancement in tensile strength of laminate achieved through GNP addition was completely lost and the fracture was triggered by the degraded thin layer of epoxy regions present between plies.
- 5) The fracture surface of the tensile tested specimens showed an increase in CF pullout with hygrothermal ageing. The degree of CF pullout was lower in case of 0.4GNP specimens for unaged and 15 days of hygrothermal ageing. However, after 30 days of hygrothermal ageing, the CF pullout was exaggerated for all specimens.
- 6) The ILSS in the unaged condition increased by almost 5% for 0.4GNP laminate as compared to the Pristine laminate. Similar to the tensile strength, with hygrothermal ageing, the enhancement in ILSS achieved with GNP addition was completely lost and the failure was triggered by multiple interply delamination.

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Declaration of competing interest

A section of the manuscript is submitted as a patent. Mishra, K., & Singh, A . Patent number 202321004351 , Hygrothermal ageing resistant carbon fiber reinforced epoxy based composite

materials and method for fabricating thereof. Excluding this we declare that there are no known competing financial interests or personal relationships that could have influenced the work presented in this article.

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