Influence of Water Ageing on Mechanical Performance of Glass Fiber Reinforced Polyester (GFRP) nanocomposites

S M Vinu Kumar1*, V Hariprasad2, K L Senthil kumar1
1Department of Mechanical Engineering, Bannari Amman Institute of Technology, Sathy, Tamilnadu, India
2Department of Aeronautical Engineering, Bannari Amman Institute of Technology, Sathy, Tamilnadu, India,
Corresponding Author: vinukmr1988@gmail.com

Abstract. The current paper discusses about the effect of water ageing on mechanical properties of unfilled and nano-SiC filled Glass/Polyester (G-P) composites. G-P and its nanocomposites were synthesized using hand layup technique followed by compression moulding curing process. Kinetics of water absorption undergoing in each composites has been studied. Results showed that addition of nanofiller in pure G-P composites reduces the water uptake after attending its equilibrium level. Mechanical properties of the moisture absorbed sample exhibited low strength compared to dry or unexposed composites. In overall, amongst the fabricated composites, 4.5 wt.% nano-SiC Filled G-P composites showed better mechanical properties.

1. Introduction

Fiber Reinforced Polymer based composites are in huge demands for making aerospace components, automotive parts, satellite vehicles parts, marine parts and so on and so forth whenever there is a demand for replacing the heavy metallic material. The main mottos of synthesizing composites are to impart high strength (being low weight materials) and offer outstanding performance during its service as a component. Most of the composites which are in present services are generally made up of synthetic fiber reinforced types. Though its usage has become threat to the environment still it is best choice for applications, since yet to develop alternate natural fiber reinforced composites which could give best performance as synthetic one. Then It doesn’t mean synthetic fiber reinforced composites (SFRP) are not having any issues. SFRP composites are facing environmental challenges, particularly when they are out to moisture, hydrothermal, corrosion, saline condition, UV with humidity. According to Huang, et al [1] when glass fiber reinforced composites exposed to moisture absorption for long duration water molecules will tends to enter the voids existing between fiber and matrix phase and deteriorate the mechanical performance of the composites. This happens due to poor interfacial adhesion occurred between primary and secondary phase and also due to hydrophilic group present in synthetic fiber especially glass fiber. Yan et al [2] concluded that mechanical performance of the flax fabric/epoxy composites degraded water, seawater and alkaline ageing. Tual et al [3] developed the carbon/epoxy composites for turbine blade. Their work inferred that mechanical properties of the composites are reduced during sea water ageing. Exhaustive studies revealed that pores/voids in the laminates can be reduced by incorporating filler/particles into the matrix phase. These fillers are either chemically bonded or physically tangled to polymer phase in micro and nano form. Most of the fillers
used for fabricating polymer hybrid composites are Inorganic in nature due to ease of availability and low manufacturing cost.

From the exhaustive literature survey it is found that glass fabric reinforced Polymer composites may be appropriate choice for making marine and low weight structures compared to other conventional/SFRP materials. Although there are plenty of works reported on Mechanical properties on Glass/Polyester composites, to our capacity no work has been reported on the effect of sea water ageing on mechanical performance of Nano-SiC filled Glass/Polyester composites. Thus the objective of this paper is to understand the influence of the water ageing on Tensile, flexural, Hardness, and Impact properties and also sea water diffusivity of nano-SiC filled Glass/Polyester composites. Finally, performance of the nanocomposites has been evaluated and compared with that of neat/Unfilled Glass-Polyester composites.

2. Materials and Method

2.1. Materials

In the present investigation unidirectional E-Glass fibers were purchased from the Local vendor, Chennai, Tamilnadu India. Nanofiller-SiC were procured from Universal Carborundum India Pvt Ltd, Kochi, Kerala, India. Unsaturated Polyester resin and its accelerator and catalyst were supplied by Vasa Vibala Resin Pvt Ltd, Chennai, Tamilnadu India.

2.2. Preparations of composite Laminates

Pre-calculated amount of polyester resin is mixed with 1.5 % MEKP catalyst as prescribed by vendors. SiC powder was dried in a muffle furnace at 150° C for about 1 hr before mixing it with the resin. Later 1.5 % Cobalt Naphthenate accelerator added to Resin and Filler mixture to initiate the curing process.

![Figure 1](image) Process of Fabrication of unfilled and Nano-SiC filled Glass/Polyester (G-P) composites

Steps followed in fabrication of the hybrid laminates is shown in the figure 1. At an outset Resin and Filler mixture impregnates each layer of E-glass fabric layer (of size 220×220 mm) by laying down on the surface of the mold one above the other until desired thickness is achieved. Metallic hard roller and brush facilitates degassing and ensures the uniform distribution of the resin. Each fabricated laminates were cured under pressure of 35 bar using hydraulic press for 24 hrs. Further laminates are removed from the mold and cured for 48 hr at room temperature before use of the composites. All laminates for the mechanical tests were prepared from the eight layer of the E-glass fabric except the hardness test for which 16 layers of fabric were used. All laminates of the hybrid composites were processed at a
weight fraction of 60% (±1.5). Thickness of Laminates maintained uniform thickness of 3.2 mm using a spacer. Finally, neat and SiC-Filled G-P composites are successfully fabricated and composition of the composites has been detailed in Table 1.

| Sl. No | Composite Designation | Quantity of Constituents (wt %) |
|--------|------------------------|---------------------------------|
| 1      | G-P                    | E-Glass Fabric 60 Polyester matrix 40 Nano-SiC filler |
| 2      | 1.5 G-P                | 65 38.5 1.5 |
| 3      | 3.0 G-P                | 65 37 3.0 |
| 4      | 4.5 G-P                | 65 35.5 4.5 |

2.3. Water Absorption test

Water absorption test were carried out on fabricated G-P based composites in accordance to ASTM D 570-98. At least three test specimens were taken from each composite having a dimension of length 6.4 cm and width 1.2 cm. specimens were Immersed in the sea water aqueous solution whose pH=8 was maintained at room temperature. Before immersing the specimen, its weight has to be determined using high precision digital weighing balance. After an Interval of 24 hours, Specimen should be taken off the sea water bath and weight has to be measured by wiping out of the surfaces of specimen using tissue papers. This process should be continued till weight gained by composites attains saturation levels.

Percentage in Weight gain is calculated by using following equation (1)

\[ W(t) = \frac{W_x - W_o}{W_o} \times 100 \]

Where \( W_x \) is the Mass gained by the specimen in regular interval of time during ageing and \( W_o \) is the initial mass before ageing. \( W(t) \) is the moisture gain in percentage.

When composites immersed for several period of time, weight changes in composites with respect to time was plotted to study effect of moisture on composite system. Diffusion coefficient is calculated using initial slope obtained from the plot drawn between moisture gain and square root of time using Equation (2). Where ‘m’ is the slope calculated from the graph and ‘t’ is the thickness of the sample[4].

\[ D = \pi \left( \frac{r^2 m^2}{16 W_o^2} \right) \]

Besides, sorption coefficient which is equilibrium sorption of the penetrant and it is calculated using equation (3). Where \( W_\infty \) and \( W_t \) is the percentage of water uptake at equilibrium stage and at time ‘t’[4-7].

\[ S = \frac{W_\infty}{W_t} \]

Net effect of the sorption and diffusion coefficient can be determined using Permeability coefficient using equation (4)[4-7]

\[ P = D \times S \]

3. Characterization of the composites

3.1. Barcol Hardness Test

The Hardness of the neat and Nano-SiC filled G-P composites determined as per ASTM D2583.
The specimens were positioned and loads had applied over it using hard Indenters. Nearly 10 indentions are made and its average value have been computed to assign final hardness number to the individual composites

3.2. Tensile Strength and Flexural Strength
Tensile test was carried out as per ASTM D-638 in universal testing machine (capacity 100kN). Specimen dimension for tensile test is shown in the Figure 2. During the test, machine's cross head speed of 4 mm/min was maintained. In order to evaluate flexural property, three-point bending test was carried as per ASTM D790 in universal testing machine. In this test effective length of 58 mm and cross head speed of 2 mm/min have been selected. Dimension of the specimen for conducting bending test is shown in the Figure 3.

3.3. Impact strength:
Toughness of the composite determined using Impact test. Izod impact test was employed under ASTM D256. Specimen should be cut in accordance to standard as shown in Figure 4. The striking velocity of pendulum used in the test is 4 m/sec.

Figure. 2 Dimension of the Tensile specimen prepared as per ASTM D-638

Figure. 3 Dimension of the Fexural speciemn prepared as per ASTM D-790

Figure. 4 Dimension of the Impact (Izod) specimen prepared as per ASTM D-256.
4. Results and Discussion

4.1. Water absorption Behavior of the Neat and Nano-SiC filled G-P hybrid composites:

![Figure. 5(a) Water absorption gain in percentage against time (square root of hour) (b) EMC curve obtained different composition of fabricated composites.](image)

Water absorption behavior of G-P composites at various loading of nano-SiC particles is shown in the Figure 5(a). As the ageing time of composites in sea water increases, moisture uptake by the composites also increases up to saturation point. Beyond this point composites are no longer in the position to absorb any moisture or water molecules. This can be witnessed in the present work and is depicted in the Figure 5(a). From the plot it is interesting to observe that, as the nano filler addition increased from 1.5wt.% to 4.5wt.%, water absorption capacity decreases. From the plot 5(b) it is noted that EMC (Equilibrium moisture content) of composites reduced as the nano filler loading increases. This is attributed to strong interfacial adhesion imparting by the filler to matrix phase which in turn improves the fiber matrix region there by curtailing down the void content [5]. According to Anjum et al [8] voids can pave the way for the water molecule to enter through capillary action there by increase the water absorption rate. Therefore, it is essential to make sure that void in the laminate is least. Furthermore, moisture uptake attains the equilibrium state after initial take off, so this pattern is said to have followed Fickian Diffusion process [6].

| Fabricated hybrid nanocomposites | Sorption Coefficient (S) | Diffusion Coefficient (× 10^4 mm²/sec) | Permeability Coefficient (P) (× 10^-4 mm²/sec) |
|----------------------------------|--------------------------|----------------------------------------|-----------------------------------------------|
| G-P                              | 0.04315                   | 1.28845                                | 0.431592                                      |
| 1.5 G-P                          | 0.0272                    | 4.75667                                | 3.691173                                      |
| 3 G-P                            | 0.0558                    | 2.82833                                | 2.675603                                      |
| 4.5 G-P                          | 0.0236                    | 0.447917                               | 0.032344                                      |

There are three important factors under Fickian Diffusion process responsible for moisture absorption in composites and they are diffusion coefficient (D), Sorption coefficient (S) and permeability coefficient (P) and these factors are calculated using Equations 2, 3, and 4 respectively. Calculated value has been presented in the Table 2. Diffusion coefficient (D) is one of the most
essential parameter considered in the Fickian Diffusion Model. It shows about the ability of the water molecule penetrating the composites materials. Diffusion coefficient increases when initial nanoparticle loading increased to 1.5wt.% and decreases when filler loading increases further from 3 wt.% to 4.5 wt.%.. Lowest diffusion coefficient was found for 4.5 G-P nanocomposites because filler improves the interfacial adhesion between matrix and itself. Apart from that, filler also reduces the gap/void existing between Fiber-Matrix thereby reduces the velocity of water molecule entering the laminates [5]. Thus water absorption of 4.5 G-P nanocomposites is low as compared to other fabricated composites. Another important factors considered in kinetics of water diffusion is sorption coefficient and permeability coefficient. Sorption coefficient of 4.5 G-P nanocomposites showed lowest value compared to other composites since minimum void in the composite resist the absorption of water molecules. Permeability coefficient of the nano hybrid composites behave little differently. It follows the same trend of Diffusion coefficient except by the 3 G-P nanocomposites. Lowest Permeability coefficient exhibited by the 4.5wt.% Filled nano-SiC/G-P composites.

4.2. Effect of Water Absorption on Hardness

Figure 6 presents the hardness of the various fabricated hybrid composites when they are subjected to different environmental condition. It is observed that, as the wt.% addition of nano-SiC particle increases, the hardness of the hybrid composites also increases. Same trend has been observed for the moisture exposed sample. Highest hardness number had exhibited by 4.5 G-P nanocomposites in both dry and moisture environments.

![Figure 6 Barcol Hardness of the Unfilled and Nano-SiC filled G-P composites at dry and moisture condition](image)

4.3. Effect of Water absorption on Tensile Strength

Figure 7 shows the tensile strength of the various fabricated hybrid composites under dry and moisture condition. It is seen in the figure that 25.95% improvement in the tensile strength was noted when 4.5wt.% of nano SiC filler added into pure G-P composites. Addition of nanofiller forms the chemical bonding and as well as physical tangling with polyester and it further fills the gap between fiber-matrix which leads to overall strong interfacial bonding among the reinforcements[9]. When the composites are subjected to tensile load, matrix phase receive the load and transfer the same to glass fiber through nano particles. Thus when composites exhibit better tensile property it means there exist a strong bonding between the reinforcements. Further when the composites exposed to moisture condition, it follows the same trend as seen in dry condition. Moisture exposed sample showed less strength compared to non-exposed sample because water molecules penetrated inside the composites allows the glass fiber to swell along with matrix phase and weaken/damage the fiber-matrix interface hence strength of the composites reduces[10].
4.4. Effect of water absorption on Flexural Strength:

Flexural strength of the unfilled and nano-SiC filled G-P composites under dry and moisture exposed condition has been presented in Figure 8. It is observed that addition of nano filler into the G-P composites increases the bending strength of the composites. Unfilled G-P composite showed 110 MPa and for the same, when nano-SiC filler was added, bending rose to 158 MPa, that means 34.9 % improvement in the flexural strength was noted. Flexural strength is purely depending upon the fiber property since it is load bearing member of the laminates. When the composites are subjected to flexural test then bottom surface of the material experiences compression stress and top surface experiences tensile stress[11, 12]. Therefore, samples should have strong fiber–matrix interface to resist the bending load. From the plot it can be seen that 4.5 G-P nanocomposites has shown better flexural strength which means fiber-matrix interface as result of filler’s chemical bonding imparts strong bonding and also it reduces void [11]. Further from the plot it can also be seen that, moisture exposed samples showed less strength compared to unexposed samples however it follows the same trend as observed in the dry sample. Difference in the flexural strength of the exposed composites with dry samples is very marginal. Moreover, when composites exposed to water immersion, moisture
uptake increases. When void percentage in the sample increase, strength of the composite decreases because water molecule will get trapped between these voids causes the matrix and fiber to swell thereby weakens the interface badly, thus failure of the fiber in the composites takes at low loading during mechanical test[13]. Therefore, it has to ensure during fabrication that, voids should be minimal. However, it is impracticable to avoid the void formation while synthesizing thermoset based polymer composites. Figure 9 shows voids are predominantly observed in the 1.5 G-P nanocomposites. Flexural and tensile strength are fiber sensitive and water molecule diffused inside the composites further deteriorates the matrix-fiber interface which leads to early debonding of fiber phase. Water absorbed by synthetic fiber such as glass fiber and carbon fiber is less as compared to natural fiber however water molecules penetrating inside the matrix network accelerates the matrix cracking for pre-mature failure thus flexural and Tensile strength decreases[14, 15].

![Figure 9](image.png)

**Figure 9** Voids formation in 1.5 wt.% nano-SiC filled G-P composites

4.5. Effect of water absorption on Impact strength:

Impact strength of unfilled and nano-SiC Filled G-P composites is shown in the Figure 10. Impact strength of 4.5 G-P nanocomposites exhibited 14.6 % improvement compared to unfilled G-P composites. This may be due to the uniform distribution on nano-SiC particles in polyester resin which transfer the load to the fiber via matrix phase. During water immersion, sample absorbs water molecules which accelerates interface degradation of fiber-Matrix-filler eventually leads to reduction in impact strength of the hybrid composites. It is interesting to see the effect of moisture on 4.5 G-P nanocomposites. Only 1.34% decreased in the impact strength was noted compared to unexposed sample because water molecule trapped in the gap existing between matrix and fiber also resist the impact energy to produce high impact values [11, 12].

![Figure 10](image.png)

**Figure 10.** Impact Strength of the Unfilled and Nano-SiC filled G-P composites at dry and moisture condition.
Conclusions:

Moisture absorption property of the Glass fiber reinforced polyester composites with and without nanofiller SiC has been studied. From the Characterization studies following conclusions has been drawn:

1. Moisture absorption studies showed that reinforcement of nanofiller SiC in to pure G-P composites offers resistance to the moisture absorption. Amongst the fabricated composites, 4.5 wt. % nano-SiC filled composites exhibited low moisture uptake.

2. Moisture absorption endured by the unfilled and Nano-SiC filled G-P composites follows Fickian Diffusion Behavior. Addition of Nano-SiC fillers reduces the EMC from 7.5% to 4.1% in sea water ageing condition.

3. Tensile strength, Flexural strength, Impact strength of the unexposed composites showed better strength compared to water absorption samples.

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