

# Investigation of the Moisture Diffusion Process in Fibre-Reinforced Composites by Studying the Diffusivities in Hot-wet Temperature Resin-matrix

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**ABSTRACT :** Moisture diffusion or uptake is one of the phenomenon observed in fibre reinforced composites exposed to marine ambience or water body structures. The materials are exposed to variations in temperatures and humidity. Moisture uptake depends upon the nature of the resin, porosity, temperature, humidity, salt water concentrations, fibre orientation, fibre volume fraction, void content, resin matrix interface, interfacial bonding. Moisture is known to react with one or more of the matrix constituents and hydrolyses the polymer bonds which leads to dissolution of water-soluble molecules and thereby plasticizing the matrix and lowering the glass transition temperature ( $T_g$ ). Moisture absorption produces debonding of the fibre matrix interface and thus deteriorates the mechanical properties of the composites. It also causes swelling of the matrix phase and weakening/breaking of the matrix/fibre bond, formation of micro-cracks due to environmental stresses and polymer-solvent interactions. Hence the rate of deterioration is governed by the rate of moisture absorption and percentage of moisture content present. This affects the short-term and long-term durability of the composites. Hence determination of moisture content and rate of moisture diffusion is necessary to understand the kinetics of moisture diffusion. In this study three types of Fibre reinforced composites, glassfibre/polyester, glassfibre/vinylester and glassfibre/epoxy resin laminates are fabricated by Hand lay-up process and compacted in a Hotpress. An experiment is performed to compute the diffusion co-efficients at different times in hot-wet temperature of different fibre/resin combinations and theoretically evaluated by Fick's law of diffusion.

**Keywords -:** Diffusivity, Hand lay-up, Hotpress, Moisture diffusion, resin.

## 1. INTRODUCTION

In recent times glass fibre based composites have found extensive use in water body structures, civil, marine and aerospace applications. Three types of resins are very significant and largely used due to their least moisture absorbing properties.

Numerous studies have indicated the characterizing of moisture absorbing properties like diffusion, by observing the absorption content percentage over a period of time. At low temperature, the moisture absorption percentage has been studied for a fixed increase in weight percentage. A.M.Visco et.al. studied accelerated ageing of sea water absorption at 60°C. In this study, the moisture diffusion percentage is analysed by computing the diffusion coefficients at 90°C water immersion and theoretically evaluated using Fick's second law of diffusion.

## 2. Fabrication of Fibre reinforced composites

Initially a The fabrication of the Fibre reinforced composites was done by Wet Hand lay-up method and compacted in a hot press. As large number of specimens were required for experimental purpose a large mould of 1m x 1m was selected for the purpose. Teflon sheet was placed in the mould. A gel coat of the releasing agent (paraffin wax) was applied to the sheet for easy removal of the composite. Known amount of the resin and hardener was weighed using an electronic weighing balance in a container and mixed thoroughly by stirring for about twenty minutes till a resin system of uniform mixing is achieved. Rule of mixtures was followed to determine the amount of fibre and resin required. A wt. percentage of 60:40 was followed in preparation of the fibre/matrix laminate. A layer of 2D woven glass fabric was placed on the mould and the resin system is poured onto it. A putty blade was used manually for the flow and levelling of the resin system by applying uniform pressure until the fabric is covered by the resin system. Similarly a number of glass fabric layers were placed one over the other inter-layered with the resin system. The number of layers is decided by the thickness of the laminate required and calculated. Finally a Teflon sheet applied with a releasing agent (paraffin wax) was used to close the top surface of the mould to get a smooth surface on both the sides. Then the prepared wet lay-up composite was compacted using a hot press of 5 Ton capacity at 115°C for two hours. The composite laminate was then kept in a temperature

chamber and cured at 115<sup>0</sup> C for two hours. The dried composite is cut using a cutting machine for specimens as per ASTM standard dimensions.

2.1. Hot press

The hot press used was of 5 Ton capacity and hydraulically operated with temperature controller with a mould size of 1m x 1m and temperature range upto 150<sup>0</sup> C. Hot press is used for uniform distribution of the resin system over the glass fibres and for proper interfacial bonding between the fibre/matrix interface. By applying uniform pressure in the hot press at high temperature, any presence of voids occurred during the hand lay-up process will be eliminated, thereby achieving a perfectly compacted laminate, smooth on both the sides. By applying uniform pressure at high temperature, the resin system will be distributed uniformly and compacted by squeezing out the extra resin under pressure and thereby a uniform thickness of the required size of 3mm is achieved. Also any moisture present during the hand lay-up process will be removed by evaporating at high temperature and air traps will be nullified.

2.2. Steps for preparation of fibre reinforced composite using hand lay-up process with hot press.

1. Teflon sheet is placed on the mould surface.
2. A gel coat of the releasing agent (paraffin wax) is applied over the Teflon sheet and waited for a few minutes.
3. Known amount of resin and hardener which was calculated is weighed in an electronic weighing balance in a container separately.
4. The hardener is mixed with the resin and thoroughly mixed by stirring rigourously for about twenty minutes.
5. Glass fabric of size 1m x 1m is cut, and placed over the teflon sheet.
6. The prepared resin system is poured over the glass fabric and uniformly applied using a putty blade on the surface till the resin covers the glass fabric.
7. Similarly the glass fabrics are layered one over the other and properly inter mixed with the resin system till the required number of layers is achieved.
8. The top surface is closed by a Teflon sheet applied with the releasing agent (paraffin wax).
9. The composite thus prepared is compacted using a hot press. For our experiment it was compacted for two hours at 115<sup>0</sup> C.
10. Then it is placed in a temperature chamber for curing, maintained at 115<sup>0</sup> C for 2 hours to dry.
11. The dried composite is cut for the specimens of required dimensions as per ASTM standards using a cutting machine.

3. Experiment

The experiment was conducted for the three types of laminates, Glass fibre/polyester(GF/poly), glassfibre/vinylester(GF/VE)glassfibre/epoxy(GF/EP).

The specimens of the three types of laminates were marked as PL1, PL2, PL3 for GF/poly laminates; VE1, VE2, VE3 for GF/VE laminates; EP1, EP2, EP3 for GF/EP laminates. The cut edges of the specimens were sealed using a Teflon sealant and dried for 24 hours. The dry weight of the specimens of the three types of laminates were recorded using an electronic balance. These specimens were immersed in hotwater maintained at 90<sup>0</sup>C in a hotwater bath maintained at a controlled temperature of 90<sup>0</sup>C. The specimens were removed from the water bath at regular intervals of time and wiped with a cloth to remove any moisture present on the surface and weighed using an electronic balance and the wet weight of the specimens were recorded. This procedure was followed to record the wet weight of the specimens at different time intervals[1]. TABLE.1 shows the wet weights of the specimens measured at different intervals of time. The absorbed moisture content (%) was calculated using the relation:

$$M\% = [M_w - M_d / M_d] * 100 \tag{1}$$

Where M<sub>d</sub> is the dry weight of the specimen, M<sub>w</sub> is the wet weight of the specimens at different time intervals. A sample size of three was taken for the experiment.

The moisture content (%) was determined for the three samples and the average value was taken. Same procedure was followed to determine the moisture content (%) for the other types of laminates. A Graph was plotted for Moisture Content (%) against Time along y-axis and x-axis respectively.

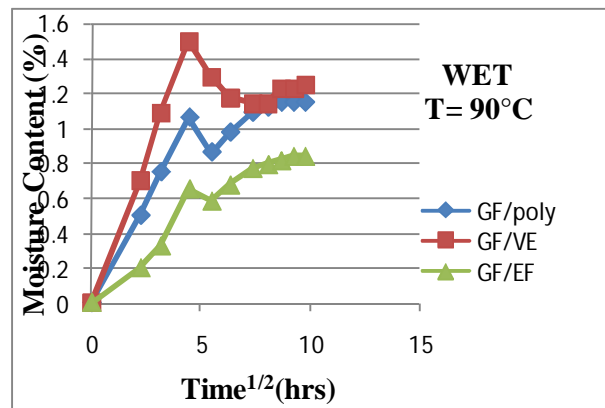


Fig 1. Graph of moisture content (%) vs time for three types of laminates- GF/Poly, GF/VE, GF/EP.

Since same readings were obtained after 95 hours, these readings were taken for calculations. Moisture content (%) after 95 hours, of the three types of laminate composites are:

$$M_m\% \text{ GF/Poly} = 1.1483\%$$

$$M_m\% \text{ GF/VE} = 1.2463\%$$

$$M_m\% \text{ GF/EP} = 0.8419\%$$

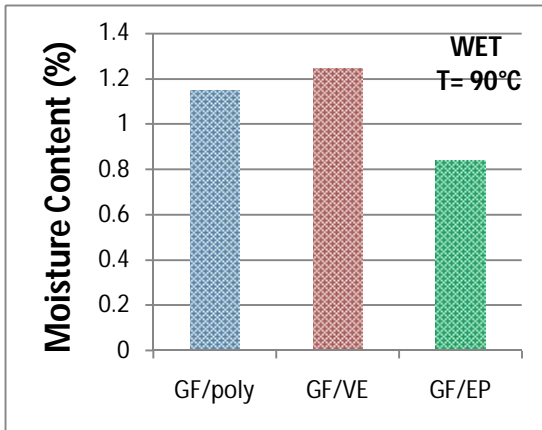


Fig 2. Bar chart showing moisture content (%) of the three types of laminates- GF/Poly, GF/VE, GF/EP after 95 hours in hotwater at 90°C.

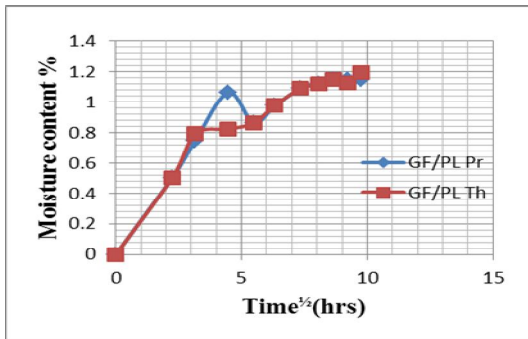


Fig 3. Graph shows practical and theoretical curve of GF/Poly laminate.

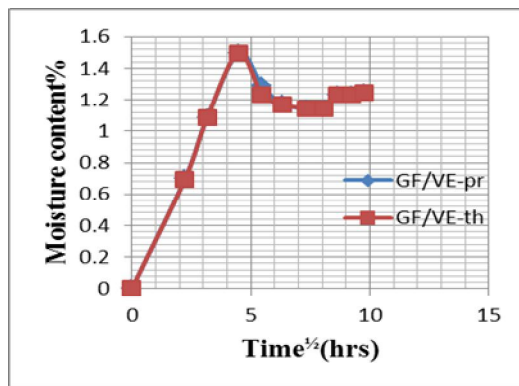


Fig 4. Graph shows theoretical and practical curve of GF/VE laminate.

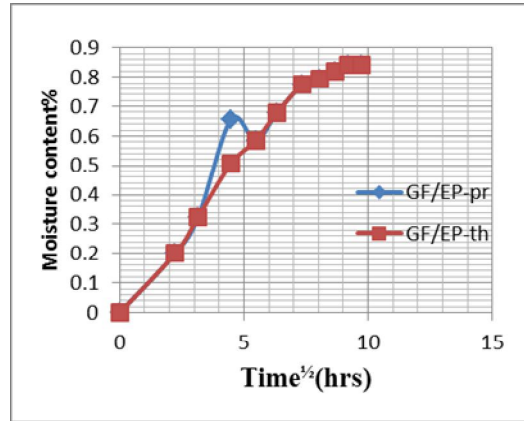


Fig 5. Graph of theoretical and practical curve of GF/EP laminate.

### 3.1. Fick's law of diffusion

The present investigation is the effect of temperature on moisture uptake or diffusivity factor.

Fick's second law, in one-dimensional form,

$$\frac{\partial C}{\partial t}(z,t) = D_z * \frac{\partial^2 C}{\partial x^2}(z,t) \quad (0 \leq z \leq h, t > 0) \quad (2)$$

Where, C = concentration of diffusing moisture. t=time, x is the position in diffusing direction. D<sub>z</sub> is moisture diffusion coefficient along thickness, h is the thickness of the specimen.

When a dry laminate of composite of uniform thickness 'h' is exposed to moisture, the sample mass increases due to water uptake, the moisture uptake (or mass gain) M<sub>t</sub> is obtained as,

$$\frac{M_t}{M_m} = [1 - \sum \left( \frac{8}{(2n+1)^2} * \exp\left\{ -\frac{D_z(2n+1)^2 * \pi^2 t}{h^2} \right\} \right)] \quad (3)$$

The approximate solution to this eqn. is given by:

$$\frac{M_t}{M_m} = 4 \left[ \frac{D_z t}{\pi h^2} \right]^{1/2} \quad (4)$$

Now the diffusion co-efficient can be calculated from the initial slope, after re-arranging the terms,

$$D_z = \pi \left[ \frac{h}{4M_m} \right]^2 * (\text{slope})^2 \quad (5)$$

$$\text{Slope} = \left[ \frac{M_t - M_a}{\sqrt{t_b} - \sqrt{t_a}} \right] = \frac{4M_m}{h\sqrt{\pi}} \sqrt{D} \quad (6)$$

Also, the time required to attain maximum moisture content (99.9%) can be expressed as:

$$t_m = \left[ \frac{0.698 h^2}{D_z} \right] \quad (7)$$

The diffusion co-efficient D is calculated using the relation:

$$M_t = M_i + [(M_m - M_i) * \left(\frac{4}{h}\right) * \sqrt{\frac{Dt}{\pi}}] \quad (8)$$

Where,  $M_i$  is initial moisture content in the composite,  $M_m$  is saturation moisture content,  $h$  is thickness, 't' is time,  $D$  is diffusivity in the direction of thickness.  $M_t$  is moisture content at any time 't'.

Here  $M_i = 0$ , i.e.,

$$M_t = \frac{4M_m}{h} \sqrt{\frac{Dt}{\pi}} \quad \text{or} \quad D^{1/2} = \frac{\sqrt{\pi h M_t}}{4\sqrt{t M_m}} \quad \text{mm}^2/\text{sec.} \quad (9)$$

The diffusivity factor or diffusion co-efficient  $D$  of the three types of laminates at different time intervals are shown in TABLE 2.

TABLE 2. Diffusivities of GF/Polyester ,GF/Vinylester and GF/Epoxy FRP Composite laminates.

Time (hours)	Specimens		
	Diffusivity factor at hotwater temperature 90°C in mm <sup>2</sup> /sec		
	GF/Polyester (x10 <sup>-6</sup> )	GF/vinylester (x10 <sup>-6</sup> )	GF/Epoxy (x10 <sup>-6</sup> )
5	18.6	30.9	5.54
10	28.8	37.2	7.35
20	21.0	35.3	1.486
30	9.24	17.5	7.902
40	8.87	10.85	7.97
54	8.2	7.65	7.659
65	7.179	6.36	6.73
75	6.54	6.39	6.183
85	4.379	5.639	5.78
95	5.16	5.16	5.16

Time to attain maximum moisture content for the three types of laminates are:

$$t_m \text{ (GF/Poly)} = \frac{0.698 * 3^2}{5.16 * 10^{-6}} = 338 \text{ hours.}$$

$$t_m \text{ (GF/VE)} = \frac{0.698 * 3^2}{5.167 * 10^{-6}} = 338 \text{ hours.}$$

$$t_m \text{ (GF/EP)} = \frac{0.698 * 3^2}{5.16 * 10^{-6}} = 338 \text{ hours}$$

#### 4. DISCUSSION

It is observed from the graph shown in “Fig.1”, the diffusion curve is linear in the initial stages obeying Fick’s second law of diffusion and during this phase, the diffusion co-efficient  $D$  increases with the passage of time at a constant controlled temperature[4]. During this phase the absorbed moisture content(%) also increases with the increase in time[2]. This linear variation is according to the earlier studies and can be predicted by Fick’s second law of diffusion. Also there is a linear increase in the moisture absorption during this phase[5]. The diffusion co-efficient  $D$ , increases in the initial stages, and shows greater absorption of moisture, and hence the wet weight of the specimens of the three types of laminate composites also shows higher values. There is a variation in diffusivity factors after the initial stage, indicating lower absorption of moisture and which stabilizes after passage of time.

After the initial moisture absorption, it is observed from the graph, that the moisture absorption varies, and a non-linear type of variation is observed in the second phase, and cannot be predicted using Fick’s second law. After passage of time, the system stabilises and maintains a constant level of absorption pattern, which can be considered as saturation state[6-7]. With further passage of time it can be concluded that the system attains equilibrium with the external surroundings and tries to achieve 99.9% moisture content% [3].

The values of Diffusivities recorded shows, that the diffusion co-efficient  $D$  is not a fixed constant for a controlled temperature, but varies slightly with the passage of time. The diffusivity of glassfibre/epoxy laminate is very low when compared to the glassfibre/vinylester and glassfibre/polyester laminates. Also the absorbed moisture content(%) is lower, compared to the glassfibre/vinylester and glassfibre/polyester laminates. Glassfibre/epoxy laminates offers much more resistance to water absorption and hence slows down the deterioration of the laminates and predicts increased life expectancy, in terms of moisture degradation. The other two types of laminates GF/VE and GF/Poly shows higher values of diffusion co-efficient  $D$  and lower resistance to water absorption.

The viscoelastic nature of polymer shows non-fickian diffusion after the initial stage and moisture absorption in composites is mainly due to resin matrix and permeable fibres show very little moisture absorption. The factors influencing moisture degradation in composites: Swelling of the matrix phase, presence of residual stresses at and near the interfaces, weakening or breaking of the adhesion bond between the fibre and the matrix, and polymer-water interaction mechanisms governing the moisture diffusion process in composites[12].

Also it is seen that the rate of diffusion increases in the initial stages which can be related to the increase in activation energy as given by the Arrhenius expression:

$$R(T) = A \exp\left[\frac{-E_a}{RT}\right] \tag{10}$$

R is Universal gas constant=8.3144 Jmol<sup>-1</sup>K<sup>-1</sup>

$$E_a = -RT \ln\left[\frac{k}{A}\right] \tag{11}$$

A is the frequency factor, k is the coefficient of reaction rate, T is temperature in kelvin.

Table 1

Specimens	Dry weight	10 hours	20 hours	30 hours	40 hours	54 hours	65 hours	75 hours	85 hours	100 hours
PL1	11.627	11.71	11.76	11.73	11.73	11.75	11.75	11.76	11.76	11.77
PL2	11.76	11.86	11.89	11.88	11.91	11.9	11.91	11.91	11.91	11.91
PL3	11.71	11.79	11.82	11.79	11.8	11.83	11.83	11.83	11.83	11.82
VE1	11.5	11.61	11.65	11.64	11.64	11.61	11.61	11.62	11.62	11.63
VE2	11.39	11.52	11.56	11.55	11.51	11.54	11.54	11.55	11.55	11.54
VE3	11.23	11.36	11.42	11.37	11.37	11.36	11.36	11.37	11.37	11.38
EP1	14.32	14.35	14.41	14.4	14.42	14.43	14.44	14.45	14.45	14.44
EP2	14.59	14.66	14.68	14.67	14.68	14.69	14.7	14.7	14.7	14.71
EP3	13.87	13.91	13.97	13.96	13.97	13.99	13.98	13.98	13.99	13.99

Diffusivity depends upon the nature of the resin matrix, fibre size, fibre orientation, fibre volume fraction, porosity and voids [8] & [9].

Since the diffusivity factors were stabilized after 95 hours for the three types of laminate composites, it is seen that the time to attain maximum moisture content for the three types of laminates is same for a constant controlled temperature. The theory and practical values are agreeable.

**5. Conclusion**

Diffusivity factor or diffusion co-efficient is very important and determines the flow across the concentration gradient for a fixed temperature. Diffusion occurs at the same constant temperature due to the movement across the interstitial spaces and also due to capillary action. The amount of moisture content or uptake depends upon the diffusivity or the diffusion co-efficient and varies

accordingly to temperature. The process of diffusion takes place due to hydrolysis and plastization of the immediate neighbouring molecules in the resin matrix, and the swelling due to the absorption of moisture, which initiates a concentration gradient in the immediate neighbouring molecule, which finally initiates a diffusion process across the laminate. The presence of fibres slows down the movement of the molecules and hence lowers the diffusivity factors after the initial stage.

**6. Limitations and Future work**

Here diffusivities were studied across the direction along the thickness of the specimen, and 3-dimensional diffusion analysis can be studied. Further experiments can be studied for non-linear diffusion process and literatures can be made available for the same.



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