Investigation of Moisture Diffusion Process in Fibre Reinforced Composites by Computing Diffusivity Factors along 3-Perpendicular Directional Axes of 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 the previous study, one dimensional accelerated diffusion process, along the thickness of the laminates was studied by computing the diffusivity factors at different time intervals. In this study, 3-directional accelerated diffusion process is studied by fabricating three types of Fibre reinforced composites; glass fibre/polyester, glass fibre /vinylester and glass fibre/epoxy resin laminates 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, along the directions of thickness (D_z),*
length (D_x) and width (D_y) is computed of different fibre/resin combinations and theoretically evaluated by Fick's law of diffusion.

1. INTRODUCTION

In recent times glass fiber 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 were done on moisture diffusion at elevated temperature [1], and in this study, 3-perpendicular directional axes moisture diffusion is studied and evaluated theoretically using Fick's second law of diffusion.

1.1. Fick's second law of 3-dimensional diffusion.

For a thin composite plate, the water concentration in the thickness z-direction is governed by 1-dimensional diffusion equation of Fick's second law:

$$\frac{\partial c}{\partial t}(z,t) = D_z \frac{\partial^2 c}{\partial^2 t}(z, t) \quad (0 \leq z \leq h, \ t > 0) \quad (1)$$

where, t is time, h is the thickness of the specimen, D_z is diffusion coefficient in z-direction.

The appropriate solution in the simplest form is given by:

$$M_t = \frac{4M_m}{\sqrt{h}}\sqrt{D_z t} \quad (2)$$

where, M_t is moisture content at any time 't', M_m is maximum moisture content at time 't'. In the initial stages of the diffusion process, it obeys Fick's law, and hence when applied to each side

independently, along the 3-directional axes, it can be written as:

$$M_t = \frac{4M_m}{\sqrt{L}} \sqrt{D_x t} \tag{3}$$

where, L is length of specimen

$$M_t = \frac{4M_m}{\sqrt{w}} \sqrt{D_y t} \tag{4}$$

where, w is width of specimen

$$M_t = \frac{4M_m}{\sqrt{h}} \sqrt{D_z t} \tag{5}$$

where, h is thickness of specimen

In 3-directional diffusion, the diffusion coefficient D_x, the diffusion coefficient D_y and the diffusion coefficient D_z are significant in ascertaining the diffusion process, and hence gives an idea about the moisture content in the matrix laminate. Therefore determining the diffusion coefficients D_x, D_y and D_z gives a clear picture of the moisture diffusion in the matrix laminate over the boundary conditions, (here it is time), for a constant controlled temperature.

2. Experiment

Initially, 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 115^0 C for two hours. The

composite laminate was then kept in a temperature chamber and cured at 115^0 C for two hours. The dried composite is cut using a cutting machine for specimens as per ASTM standard dimensions.

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 150^0 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.

The experiment was conducted for the three types of laminates, Glass fibre/polyester(GF/Poly), glass fibre/vinyl ester(GF/VE), glass fibre/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 90^0C in a hotwater bath maintained at a controlled temperature of 90^0C. 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 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. The moisture content (%) was calculated using the relation:

$$M_t = \frac{M_w - M_d}{M_d} * 100 \tag{6}$$

A Graph was plotted for Moisture Content (%) against Square root Time along y-axis and x-axis respectively.
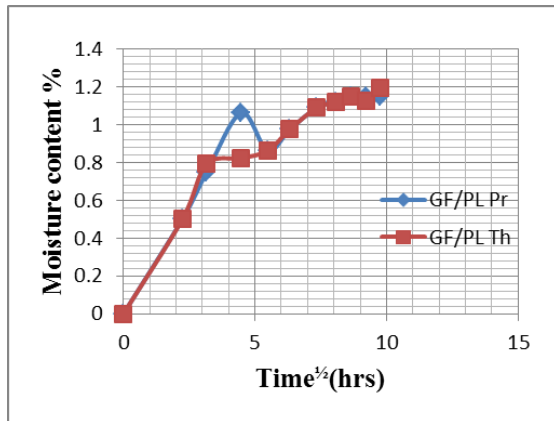

Fig.1.Graph of moisture content% vs Square root Time in hours of GF/Poly at T=90^{0}C, Wet.
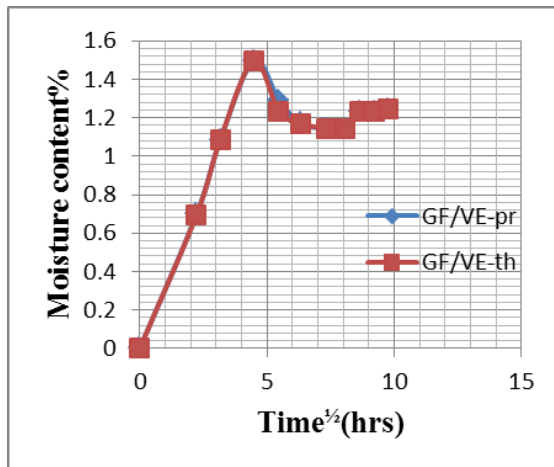

Fig.2. Graph of Moisture Content% vs Square root Time in hours of GF/VE at T=90^{0}C, Wet.
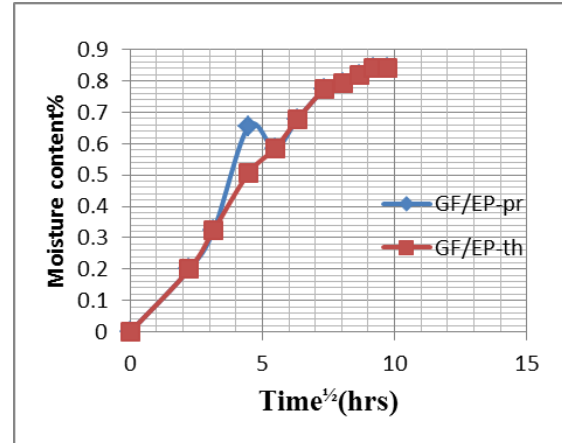

Fig.3. Graph of Moisture Content% vs Square root Time in hours of GF/EP at T=90^{0}C, Wet.

The Diffusivity factor or Diffusion co-efficient D_x, D_y, D_z of the three types of laminates at different time intervals are shown in TABLE.2

TABLE 2. Diffusion Coefficients of the Three types of Laminates at Different Time Intervals.

	Specimens Diffusivity factors at hot wet temperature 90^{0}C in mm^2/sec								
Time (hours)	Glassfibre/Polyester			Glassfibre/vinylester			Glassfibre/epoxy		
	D_x	D_y	D_z (x10^{-6})	D_x	D_y(x10^{-4})	D_z (x10^{-6})	D_x	D_y (x10^{-4})	D_z (x10^{-6})
5	0.0349	8.2726	18.6	0.0581	13.764	0.0104	0.0104	2.4623	5.54
10	0.0392	9.2819	20.88	0.06987	16.537	0.0138	0.0138	3.2671	7.35
20	0.0394	9.3426	21.0	0.06642	15.721	0.0279	0.0279	6.6087	14.86
30	0.0173	4.1084	9.24	0.02466	7.785	0.0148	0.0148	3.5124	7.902
40	0.0166	3.945	8.87	0.02039	4.8265	0.0149	0.0149	3.5435	7.97
54	0.0154	3.6449	8.2	0.01437	3.4017	0.0143	0.0143	3.4041	7.659
65	0.0135	3.1907	7.179	0.01194	2.828	0.0126	0.0126	2.9928	6.73

75	0.01229	2.9088	6.54	0.012	2.8046	0.0116	0.0116	2.748	6.183
85	0.01229	2.5666	4,379	0.01058	2.5064	0.0108	0.0108	2.5691	5.78
95	0.01229	2.2964	5.16	0.0097	2.2964	0.0097	0.0097	2.2964	5.16

Table1.Weights of Specimens at Different Time intervals

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	14.44	14.44	14.45	14.45	14.44
EP2	14.59	14.66	14.68	14.67	14.68	14.7	14.7	14.7	14.7	14.71
EP3	13.87	13.91	13.97	13.96	13.97	13.98	13.98	13.98	13.99	13.99

3. DISCUSSION

For a thin composite rectangular plate, in the early stages of diffusion, the approximate solution is given by:

$$\frac{M}{M_m} = \frac{4}{h\sqrt{\pi}}\sqrt{D_z t} \qquad (7)$$

$$\frac{M}{M_m} = \frac{4}{L\sqrt{\pi}}\sqrt{D_x t} \qquad (8)$$

$$\frac{M}{M_m} = \frac{4}{w\sqrt{\pi}}\sqrt{D_y t} \qquad (9)$$

for Fick's second law of diffusion, taken independently along 3-directions. In the early stages of diffusion process, it obeys Fick's law, and hence (7), (8) and (9) can be applied to each side independently [14].

The extended form for 3-directional diffusion in a thin rectangular plate, can be written as:

$$M_t = 4M_m\left[\frac{\sqrt{D_x}}{L} + \frac{\sqrt{D_y}}{w} + \frac{\sqrt{D_z}}{h}\right]\sqrt{\frac{t}{\pi} * \frac{1}{3}} \qquad (10)$$

Where, M_m is maximum moisture content, Dx is diffusivity factor along x-direction, D_y is diffusivity factor along y-direction, D_z is diffusivity factor along z-direction, L is length of the specimen, w is width of the specimen, h is thickness of the specimen, t is time, M_t is moisture content at any time 't'. The theoretical diffusivity factors D_x, D_y and D_z can be calculated using the relation, (7), (8) and (9) respectively. Similarly the moisture content, M_t, at any time 't' can be computed using the relation (10). Separate graphs are plotted for the three types of laminates, GF/Poly, GF/VE, GF/EP; for the practical and theoretical values of M_t against Time.

It is observed from the graphs of the three types of laminates, as shown in "Fig.1", "Fig.2" and "Fig.3", the practical and theoretical values match each other and the practical and theoretical graphs are almost similar, which shows that it aligns well with the Fick's law of diffusion process quantitatively.

Also the diffusion curve varies linearly in the initial stages obeying Fick's law of diffusion during the I stage where the diffusion coefficients D_x, D_y and D_z increases with the passage of time at a

constant controlled temperature [4]. Also there is a linear increase in the moisture absorption during this phase [5].

After the initial moisture absorption, it is observed from the graphs, of the three types of laminates, that there is a non-linear type of variation in the second phase, where the diffusion is lesser. After passage of time, the system stabilizes and maintains a constant level of absorption pattern, which can be considered as a saturation state [6]&[7], where in, no further increase in weight of the specimens is observed. And 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 time taken to attain maximum moisture content can also be determined by the empirical relation, $t = \dfrac{0.698 h^2}{D}$

The values of the diffusivities computed shows that, D_x, D_y and D_z varies slightly with the passage of time. Comparison of diffusion co-efficient in the three types of laminates are shown in the bar chart.
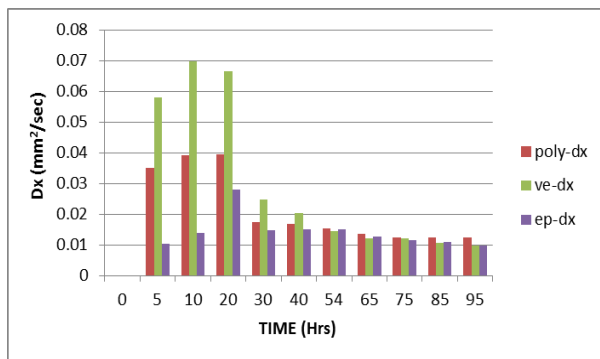

Fig.4.Comparison of Diffusion Co-efficient D_x in Three types of Laminates along x-direction.
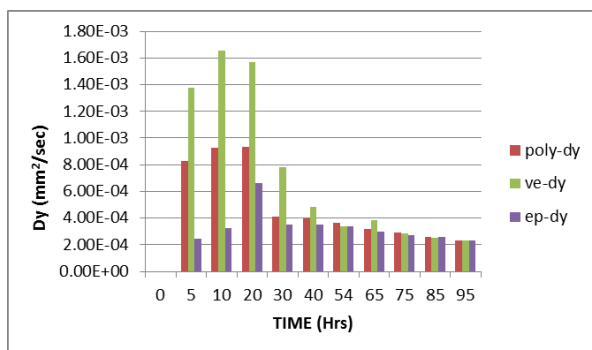

Fig.5.Comparison of Diffusion Co-efficient D_y in Three types of Laminates along y-direction.
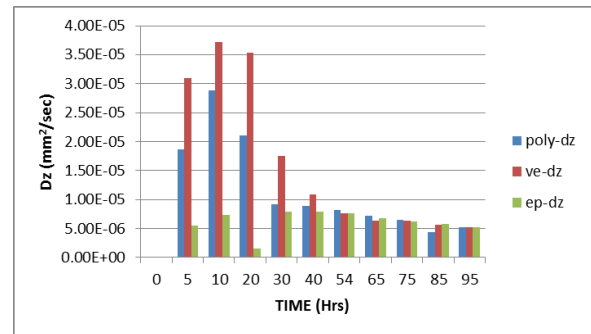

Fig.6.Comparison of Diffusion Co-efficient D_z in Three types of Laminates along z-direction.

The D_x, D_y and D_z values of GF/EP laminate is very low when compared to the GF/VE and GF/Poly laminates and also the absorbed moisture content % is also lower compared to GF/VE and GF/Poly laminates. The 3-directional analysis shows that GF/EP laminates offers much more resistance to water absorption and hence slows down the deterioration of the laminates and shows increased life expectancy in terms of moisture degradation. The other two types of laminates GF/VE and GF/Poly shows higher values of diffusion coefficient D_x, D_y and D_z and lower resistance to water absorption.

Also it is seen that the rate of diffusion increases at higher temperatures, which can be related to the increase in activation energy as given by the Arrehenius expression:

$$R(T) = A.exp.\left(\dfrac{-E_a}{KT}\right) \qquad\qquad (11)$$

where, E_a is $-RT.ln\left(\dfrac{K}{A}\right)$, R is universal gas constant=8.3144 J/mol/K, A is frequency factor, T is temperature in Kelvin, K is coefficient of reaction rate.

4. CONCLUSION

Diffusivity factor is very important and determines the flow across the concentration gradient for a fixed temperature,(10) can be used to determine accurately the amount of moisture content or uptake along the 3-perpendicular axes directions. Also the graphs of practical and theoretical values of M_t as computed by (6) and (10) are similar. The process of diffusion takes place due to hydrolysis, and the increase in weight of the specimens is due to the retention of water or moisture of the neighbouring molecules of the resin matrix. Due to the change in the concentration levels of the neighbouring molecules, and when it reaches the max. level, movement takes place across the laminate which can be explained by the 3-direction analysis of weight gain of the specimens. The presence of fibres slows down the movement of

molecules and hence lowers the values of D_x, D_y and D_z after the initial stage. Also it should have sufficient energy to diffuse through the fibres which have higher density than the resin matrix. At lower energies the water absorption takes place through the resin matrix and much of the deterioration or degradation takes place in the resin matrix. At higher temperatures the values of diffusion coefficients are also higher, and the rate of moisture absorption is greater and hence the time taken to attain maximum moisture content is also less.

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