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# *CHARACTERIZATION OF HYGROTHERMAL DIFFUSION PARAMETERS IN FIBRE-REINFORCED POLYMETRIC COMPOSITES*

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## Introduction :

The combination of very high specific strength and stiffness, controllable thermal expansion, corrosion resistance and outstanding electrical properties has resulted in the use of fibre-reinforced plastic (FRP) in many applications. Currently, almost every aero-scope company is developing products made with fibre-reinforced composite materials. In the near future, aircraft will be built with a very high percentage of components made from composite materials [1, 2]. The final stage is the ‘all-composite airplane’ that many people have dreamed of building for several year.

One of the key questions in using composite materials as air-craft components is the degradation of the material due to moisture absorption through long years of service. The mechanical properties of composites which are controlled by the matrix or the matrix/fibre interface, for example shear, flexural, compression, and axial (± 45) tensil strength and stiffness, maybe affected by the absorbed moisture, especially when measured at high temperature. In service, moisture absorbed from the environment causes an average increase of weight by about 1 – 4% in composite components [3].

Deformation is also possible upon change of temperature and upon absorption of moisture. The matrix material is much more susceptible to hygrothermal deformation than the fibre. The temperature change and moisture absorption result in the development of hydrothermal strains that may change mechanical properties [4].

## Hygrothermal Diffusion :

It is well known from the theory of specific heat that atoms in a crystal oscillate around their equilibrium positions, occasionally, these oscillations become violent enough to allow an atom to change sites. It is these jumps from one site to another which give rise to diffusion in solids [5]. Hygrothermal diffusion usually takes place in presence of thermal and moisture gradients. The atoms will then diffuse or migrate from the region of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise of temperature. The concentration gradient of moisture is developed due to non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerate the process of diffusion [6].

Transport phenomena in polymers are generally explained by a number of free volume-based theories. The free volume is defined as the difference between the measured volume of a polymer and the occupied volume. The latter is the volume occupied by the actual mass of a molecule plus the volume it occupies because of thermally dependent vibration. The free volume is a result of ‘holes’ and ‘voids’ caused by packing irregularity. The amount of moisture absorbed depends mainly on the relative humidity, whereas the rate of diffusion depends mainly on the temperature [7]. The basic similarity between the thermal and moisture diffusion was earlier recognized by Fick [8] following the work of Fourier [9]. Fick’s law is generally applicable to rubbery polymers but often fails to describe the diffusion process in glassy polymers. The transition from a glassy to rubbery state occurs at glass transition temperature. Once it has been established that diffusion is Fickian, the moisture history in the materials can be calculated readily [3].

## Non-fickian Diffusion :

However in case of glassy polymers the diffusion behaviour cannot be described by the classical law of Fick. This is particularly so when swelling of the composites becomes insignificant. The anomalous behaviour is often termed as non-Fickian behaviour [10]. Thisanomally is primarily due to change in the polymer structure on solubility and diffusion mobility. Internal stresses are developed, as the diffusion proceeds. Polymers may contain a wide spectrum of relaxation time associated with structure change. Below the transition temperature i.e., at the glassy state, the absorption process is influenced by motions of chain molecules. The chain molecules, in this case, move at about the same rate or slower than the motivating diffusion process. Above the transition temperature (rubbery stat), the chain molecules relax at a faster rate. The relative rates of diffusion and polymer relaxation may be classified into three major categories [11]. When the diffusion rates are much slower than those of relaxation, the diffusion is said to be Fickian. Non-Fickian or anomalous behaviour pertains to the situations when the diffusion and relaxation rates are comparable. The third category refers to the diffusion progresses when the diffusion rate is much faster compared to the relaxation rates.

Figs.1(a) to (d) show that different types of absorption and desorption characteristics [12]. The Fickian behaviour is observed in Fig.1(a). The characteristic behaviour shown in Fig.1(a) is termed as Pseudo-Fickian, when both absorption and desorption characteristics have the same general shapes and disposition. The absorption curve is sigmoidal in shape with a single point of inflexion as shown in Fig.1(c). The point of inflexion is at about 50% of equilibrium absorption, after which this absorption rate becomes faster. The initial rate of absorption is more rapid and becames slower after interaction of the two curves. A two-stage absorption behaviour is shown in Fig.1(d) in which initial absorption is rapid.

It is however interesting to note that many polymeric composites that are used for aerospace applications exhibit the Fickian behaviour. Springer and others [3] investigated the behaviour of T300/5208 and AS3501-5 graphite composites under various hygrothermal conditions. Fig.2(a) and 2(b) show moisture absorption characteristics at T300/5208 laminates at 294K and 355K respectively. The Fickian behaviour is observed in the initial stage of absorption when the curves are linear. The non-Fickian diffusion behaviour is noted at much early stage if the temperature is raised from 294K to 355K. It is also noted that the relative humidity level $\phi$ also influence the on-set of non-Fickian behaviour. The lower the value of $\phi$, the lower is the values of $\bar{c} / c_\infty$ at which the non-linearity starts.

**Hypothermal Parameters :**

However, the present-day structural composites use organic fibre like Keviar, A900 polyethelene etc., along with various types of thermosetting and thermoplastic resins. The moisture absorption characteristics will certainly vary from material to material. Considerable attention has, therefore, to be given to investigate the hygrothermal response of polymeric composites for optimum and safe design applications. The characterization of hygrothermal diffusionparameters such as the moisture diffusion coefficient ($D_m$), the equilibrium moisture content ($M_m$), the thermal conductivity (K), the thermal diffusivity ($\frac{K}{PC}$), the coefficient of thermal expansion ($\alpha$), the coefficient of hygroscopic expansion ($\beta$) and various others experimental parameters need to be determined to accomplish the objectives.

**Determination of Hygrothermal Diffusion Parameters :**

Moisture Diffusion Coefficient ($D_m$) and Equilibrium Moisture Content ($M_m$) :

The following test procedure may be used to determine $D_m$ and $M_m$ [13].

(1) The test specimen has to be made in the form of a thin plate ($\frac{h}{S} << 1$ and $\frac{h}{R} << 1$) so that the moisture enters predominately through the RS surface (not the edges) of the plate (Fig.3).
(2) The specimen is completely dried in a desiccator and its dry weight $W_d$ is measured.
(3) The specimen is placed in a constant temperature, constant moisture environment and its weight W is recorded as a function of time.

(4) The moisture content (% wt. gain) $M = (w - w_d) \times \frac{100}{w_d}$ is plotted versus $\sqrt{t}$ as illustrated in Fig.4.

(5) The tests are repeated for different temperatures and different environmental moisture conditions.

The above procedure yields a series of curves similar to one shown in Fig.4. Initially (when $t < t_2$) all curves are straight lines, the slope (i.e., $\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}$) being proportional to the diffusivity of the material. After a long period of time the curves approach asymptotically maximum moisture content $M_m$. The value of $M_m$ is constant when the material is fully submerged in a liquid. It varies with the relative humidity $\phi$ when the material is exposed to moist air. In the latter case $M_m$ may be expressed as

$$M_m = a\phi^b \tag{1}$$

Where a and b are material constants.

The moisture diffusion coefficient $D_m$ is obtained from the initial slope ($t < t_2$) of the $M_m$ versus $\sqrt{t}$ curve.

$$D_m = \left(\frac{h}{4M_m}\right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \tag{2}$$

If the moisture entering the specimen through the 'edges' can be neglected, $D_x$ is given as

$$D_x = D \tag{3}$$

Including 'edge effects' for a homogeneous material $D_x$ is

$$D_x = D\left(1 + \frac{h}{S} + \frac{h}{R}\right)^2 \tag{4}$$

Recent experimental evidence suggests that the value of b in Eq.1 is near unity. The above relationship is only an approximation. In fact, $M_m$ varies with temperature.

Both increases and decreases in Mm have been noticed. The increase in Mm is due to cracks developing in the material and possibly due to non-Fickian diffusion. The decrease in Mm may be caused by loss of material due to leaching of cracking.

The moisture diffusion coefficient strongly depends on temperature. The relationship can be expressed by an equation of the form

$$D_m = D_o \text{ ex} \left[ - \frac{E}{RT} \right] \tag{5}$$

Where $D_o$ and E are the pre-exponential factor and activation energy respectively, and R is the gas constant (  = 1.987 cal/mol.K). For the graphite/epoxy composite (As/3501-5) a relationship between $D_m$ and T is shown in Fig.5[14]

The maximum moisture content $M_m$ may be estimated approximately from the max. moisture content of the resin$(M_m)_r$ . By assuming that the fibres do not absorb any moisture,

$$M_m = (M_m)_r \ (W_r) \qquad (6)$$

Where Wr is the wt. fraction (%) of resin.

The transverse diffusivity of the composite can be estimated from the diffusivity of the resin $D_r$. If all the fibres are parallel to the surface through which the moisture diffuses, then $D_m$ may be approximated by the expression [13].

$$D_m = D_r (1 - 2\sqrt{\pi} /V_f) \qquad (7)$$

Where $V_f$ is the fibre volume fraction ($V_f < 0.785$).

The mostute diffusion coefficient $D_m$ is also determined from the half-time of sorption process as [4]

$$Dm = \frac{0.04895 \ h^2}{t_{1/2}} \qquad (8)$$

$t_{1/2}$ is the time for which

$$\frac{\bar{C} - C_o}{C_\alpha - C_o} = \frac{1}{2} \qquad (9)$$

Thermal expansion co-efficient ($\bar{\alpha}$) and coefficient of Hygroscopic Expansion ($\beta$) :

An interferomatic dilatometer is generally used to carry out the experiment for the measurement of $\alpha$ [15]. The basic idea is to measure a very small change in the length of piece with a unit of a half-wave length of a certain ray. He-Ne gas Laser beam is chosen as incident light, because coherency of Laser is the key to autographic reconding of outputs. The temperature in the electric heating pot is measured by a chromel-alumel thermocouple.

Thermal expansion co-efficient is measured in a heating process only from the room temperature upto $140^0$C or $150^0$C with the heating rate of $1^0$C/min. Measurements are conducted three times for some sets of specimens. An averaged thermal expansion coefficient between $T_1{}^0$C and $T_2{}^0$C, $\bar{\infty}$ is calculated by the following formula :

$$\bar{\alpha} = \partial 1/[(T_2 – T_1) \ 1_1] \qquad (10)$$

$$= [(\lambda r/2) . (\int N/1_r) – (d\lambda_2 - d\lambda_1)] / T_2 – T_1) \qquad (11)$$

When $\lambda$ is the wave length of the incident light, l is the length of a set of specimens, $\partial$N is the number of the waves in an autoreconded photo cell output. d$\lambda$ means the connection factor caused by a temperature change of the wave length of the incident light in the standard atmosphere : and the subscripts r, 1, 2 indicate the values at $15^0$C, $T_1{}^0$C and $T_2{}^0$C respectively.

The strange results may sometimes come because of the hygroscopic nature of the epoxy. It is a key point that a moisture change in the epoxy causes a change in length. $\alpha$ can also be obtained by carrying out experiment as per ASTM-D696-79. A fused-quartz-tube dilatometer can be used for the purpose.

The thermal expansion coefficient $\alpha$ is also related with the strain $e^T$ introduced by the temperature change $(T - T_0)$, i.e.,

$$e^T{}_i = \alpha (T - T_0) \tag{12}$$

The hygrothermal strain $e^H{}_i$ is related to the coefficient of hygroscopic expansion $\beta$ as given below [4].

$$e^H{}_i = \beta c \tag{13}$$

where c is the specific moisture concentration

$$c = \frac{H}{\rho} \tag{14}$$

where H is the moisture concentration and $\rho$ is the density. The determination $\beta$ essentially involves an accurate measurement of expansion in a moist environment. The equipments that are primarily needed are dilatometer and hygrothermal chamber. Here the specimen is conditioned in the hygrothermal chamber.

**Specific Heat (C) :**

Specific heat of a body is defined to be the heat required to raise unit mass of the body through $1^0$. So, if a body has a mass M, the heat required to raise its temperature by $t^0$C is H, then

$$H = m C t \tag{15}$$

The methods available for the determination of specific heat can be grouped as below [20] :

(1) Method of mixture :
  (a) Regnault's apparatus
  (b) Copper block calorimeter

(2) Electrical method :
  (a) Nernst and Lindemann calorimeter, particularly useful in low temperature region.

(3) Methods based on Latent heats :
  (a) Joly's steam calorimeter
  (b) Bunsen's ice calorimeter

Any of the above methods can be used to determine the specific heat, C of the composite system.

Thermal Conductivity (K) and Thermal Diffusivity ($\frac{K}{\rho C}$) :

The thermal conductivity is a measure of the speed at which heat is conducted through the material. The values of thermal conductivity of composites may be approximated from the known fibre and matrix properties ($V_f < 0.785$), as follows [3] :

$$K_{11} = (1 - V_f) K_r + V_f K_f \qquad (16)$$

$$K22 = (1 - 2\sqrt{V_f} / \pi)Kr + \frac{K_r}{B_k} [\pi - \frac{4}{\sqrt{1} - (B^2{}_k V_f / \pi)} \quad \tan - 1 \frac{\sqrt{1} - B^2{}_k V_f / \pi}{1 + B_k \sqrt{V_f / \pi}}] \qquad (17)$$

$$Bk = 2(\frac{K_r}{K_f} - 1) \qquad (18)$$

$K_{11}$ is the thermal conductivity parallel to the fibre direction ($\alpha = 0$) and $K_{22}$ in the transverse direction to the fibre ($\alpha = 90^0$). $K_r$ and $K_f$ are the thermal conductivities of the resin and the fibre, respectively. In the $\alpha$ direction,

$$K\alpha = K_{11} \cos^2 \alpha + K_{22} \sin^2 \alpha \qquad (19)$$

The thermal diffusivity ($\frac{K}{\rho C}$) of composite materials can be determined once K, $\rho$ and C are known.

## Conclusion :

In the preceding section various methods for determining important hygrothermal parameters have been briefly discussed. The determination of $D_m$ is fairly straight forward at the initial stage of moisture absorption, when the absorption rate is proportional to the square root of time. The values of diffusion coefficient so derived are valid in case of weak coupling of temperature and moisture. But the interdependent of temperature and moisture in case of non-Fickian behaviour requires further investigation.

The problem becomes more complicated when $D_m$ depends on the concentration history of constituents. A mathematical model of the form [16, 17]

$$\frac{\partial D_m}{\partial t} = \frac{\partial D_f}{\partial C} \quad \frac{\partial C}{\partial t} + \eta_0 e^{wc} ( D_s - D_m) \qquad (20)$$

Requires five adjustable parameters for determination of $D_m$ for describing moisture absorption and desorption with sigmoidal and pseudo-Fickian types of behaviour. These parameters are $\eta_0$, w, $a_0$, $b_0$ and $D_c$.

$$\text{Where} \quad D_f = D_s \exp(a_0 c) \qquad (21)$$

$$D_s = D_c \exp(b_0 c) \qquad (22)$$

However, this model has not been verified experimentally. A model for the two-stage absorption process has also been proposed in ref. [16]. Fvisch et al[17] proposed a model to describe the anomalous diffusion behaviour including the effect of internal stresses arising from the diffusional swelling within the matrix system :

$$\frac{\partial}{\partial x}[D_m(x, t, c)\,\frac{\partial c}{\partial x} - C_0 (B_m (x, t, c))] = \frac{\partial c}{\partial t} \qquad (23)$$

Where $C_0$ is a constant and $B_m$ the mobility coefficient.

The absorption characteristics of acetone in polyvinyl chloride was investigated in Ref.[18]. Fibre reinforcement has also strong influence on the moisture diffusion coefficient $D_m$ (Fig.6). Influence of externally applied on the moisture diffusion for SP-313 scotch ply at 333K is shown in Table 1.

| | Unstressed | Stressed (% of ultimate stress) | | |
|---|---|---|---|---|
| | | 25 | 45 | 65 |
| Dm (x $10^{-13}$ $m^2/s$) | 1.95 | 3.56 | 3.70 | 11.67 |
| $\bar{C}$ (% dry wet.) | 1.75 | 1.60 | 1.65 | 1.75 |

But it is to be emphasized that actual experimental diffusion behaviour can not always be describe by the mathematical models proposed so far, not only because of coupling between temperature and moisture but also due to many other reasons as cited above. Thus the problem of diffusion is polymeric fibre reinforced composites is to be solved approaching from two distinct directions :

1) to proposed a theoretical model (or models) that satisfactorily describe the diffusion behaviour in polymeric composites and
2) to devise the experimental programme (or programmes) that can evaluate the parameters.

**Nomenclature :**

| | |
|---|---|
| a | constant (dimensionless) |
| b | constant (dimensionless) |
| $\bar{c}$ | average moisture concentration ($g/mm^3$) |
| $c_o$ | ambient moisture concentration ($g/mm^3$) |
| $c_\alpha$ | moisture concentration at $t = t_\infty$ |
| $D_m$ | mass diffusivity ($mm^2/s$) |
| R | width of specimen (mm) |
| S | length of specimen (mm) |
| h | thickness of specimen (mm) |
| M | percent moisture content (dimensionless) |

| | |
|---|---|
| t | time (s) |
| $\bar{\alpha}$ | thermal expansion coefficient |
| $V_f$ | volume fraction of fibre |
| W | weight of material |
| $W_d$ | dry weight of material |
| $\beta$ | coefficient of hygroscopic expansion |
| $\alpha\rho\gamma$ | fibre orientation with respect to the x, y and z axis |
| T | temperature (K) |
| $\phi$ | percent relative humidity |
| $\beta$ | (dimensionless) |
| $\rho$ | density of material ($g/mm^3$) |

Subscripts :

| | |
|---|---|
| f | fibre |
| i | initial state |
| m | maximum saturation |
| r | matrix |
| 11 | in the direction parallel to the fibre |
| 22 | in the direction transverse to the fibre |

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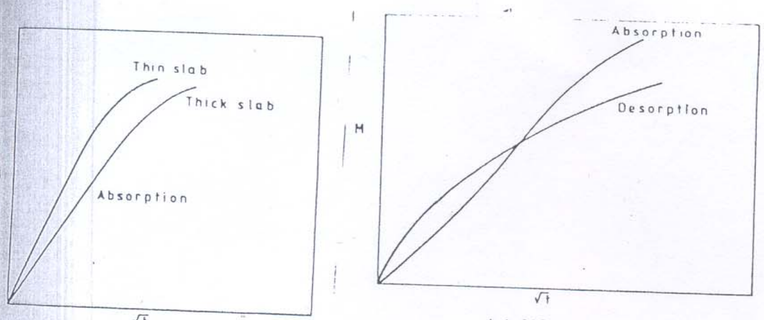
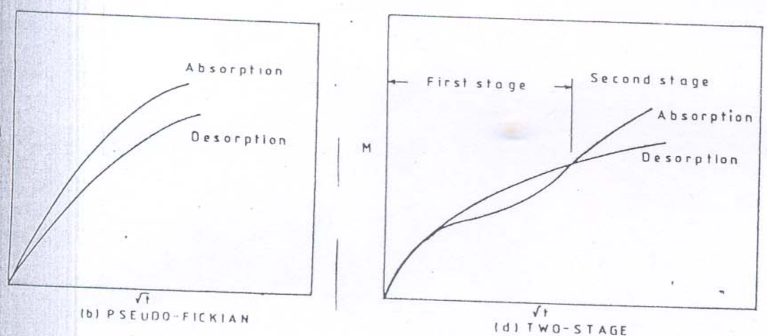
## Figure Description :

| | | |
|---|---|---|
| Fig.1 (a, b, c, d) | : | Types of absorption and desorption curves. |
| Fig.2 (a, b) | : | Moisture absorption in T300/5208 laminates. |
| Fig.3 | : | Geometry of test specimen. |
| Fig.4 | : | Illustration of the change of moisture content with the square root of time. |
| Fig.5 | : | Diffusivity as a function of temperature for the 3501-5 composites solids line is fit to data (Humidity) |
| Fig.6 | : | Arrhenius plot for graphite epoxy laminate. |



(a) FICKIAN

(c) SIGMOID

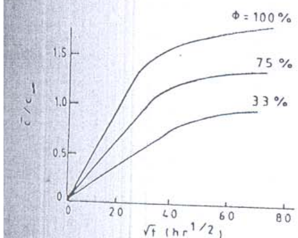


(b) PSEUDO-FICKIAN

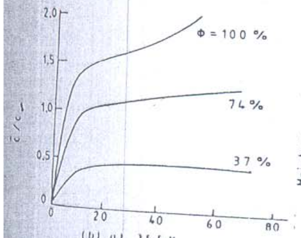
(d) TWO-STAGE

Fig.1.

Fig.1.Types of absorption and desorption curves



a) at 294 K



(b) at 355 K

Fig.2. Moisture absorption in T300/5208 laminates

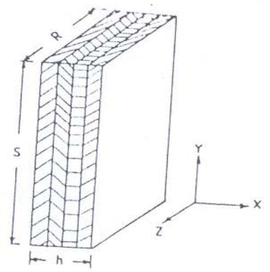


Fig. 3. Geometry of test specimen

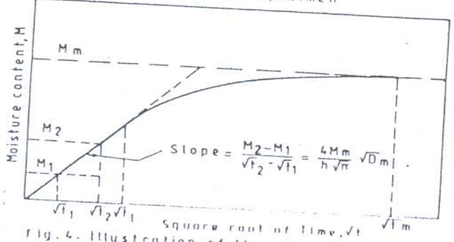


Fig. 4. Illustration of the change of moisture content with the square root of time

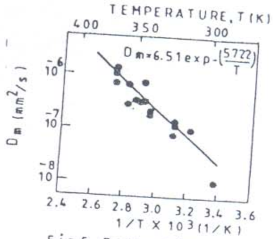


Fig.5. Diffusivity as a function of temperature for the AS/3501-5 composites solid line is fit to data (Humid air)

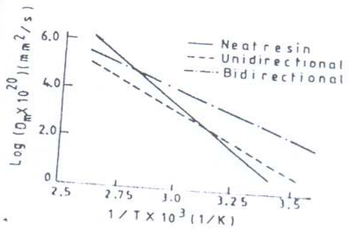


Fig.6. Arrhenius plot for graphite epoxy laminate