Prediction of Moisture Content and Mechanical Properties in FRP Composites

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Abstract

A model was developed to predict the moisture content and mechanical properties of fiber-reinforced plastic composites. This was compared with the Fickian model of diffusion and the cause of deviations was looked into. The degradation of residual properties due to moisture absorption has been predicted taking into consideration the empirical formula. The validity of these predictions depends on all degradation processes being simple function of absorbed water content.

[Key words: FRP composites, Fickian model, Fiber-matrix interface, Non-dimensional time]

Introduction

Mechanical performance of a fiber-reinforced plastic (FRP) composite is primarily dependent on three factors: 1. Strength and modulus of the fiber, 2. Strength and chemical stability of the resin, and 3. Effectiveness of the bond between resin and fiber in transferring stress across the interface. Anyone of the above factors can be a weak link, which may become the limiting factor in the composite mechanical properties. One of the problems preventing full utilization of polymer-matrix composites is their poor reliability in wet environments. All composites absorb moisture in humid atmospheres or when immersed in water. Absorption process generally follows Fick's law, according to which the mass of the absorbed water increases linearly with the square root of time. So the moisture content of the composite may be calculated using Fick's law. However, the experimental results show departure from Fick's law. To gain further insight on moisture sorption in composite laminates and moisture absorption behavior when classical Fickian diffusion behavior does not apply has been examined in this paper.

Literature Background

Depending on the matrix phase chemistry the penetrants, liquids or vapors that are absorbed in the bulk matrix and by the interface can cause degradation. For most thermoset (epoxy) composites, the absorption of moisture modifies the strength and stiffness. In contrast, for thermoplastic (PEEK, poly aryl-ether-etherketone) composites, experimental results show no significant effect of moisture on either longitudinal or transverse mechanical properties[1]. Moisture induced property degradation tends to correlate well with the sorbed moisture in matrix material and also on the affinity of water molecules for the molecule of a particular composite. Moisture related degradation is associated with chemisorption and reactivity characteristics of the permeating environment and matrix materials. Moreover, defects such
as voids, cracks and other microstructural inhomogeneities associated with the fiber/matrix interface contribute to severity of moisture effects in resin matrix composites.

Moisture absorption in composites differs in certain aspects from the classical diffusion described by Fick's law not only due to one-dimensional approximation but also due to certain other physical factors, which contribute to the kinetics. According to one dimensional diffusion law, average moisture concentration (weight percentage) after time $t$, in a specimen of width $2L$ is given by

$$M(t) = \frac{1}{L} \int_{-L}^{L} M(x,t)dx$$

$$M(x,t) = M_0 \left[ \sum (-1)^{n+1} \left( \text{erfc} \left( \frac{2n+1-x/L}{t^{*}} \right) + \text{erfc} \left( \frac{2n+1+x/L}{t^{*}} \right) \right) \right]$$

where

which can be simplified to

$$\frac{M(x,t)}{M_0} = 1 - 2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{Q_n} \cos \left( \frac{Q_n x}{L} \right) \exp \left( -Q_n t^{*} \right)$$

where

$$Q_n = (2n-1)/2$$

$$M(x,0) = 0$$

$$t^{*} = Dt/L^2 \text{ (Non dimensional time)}$$

$D$ = diffusion coefficient

For sufficiently short time $(0 < t^* < 0.55)$

$$M(t) = 2M_0 t^{*}/\pi$$

and for long time $(t^* > 1.32)$

$$M(t) = M_0 \left[ 1 - \frac{8}{\pi^2} \exp \left( -\frac{\pi^2}{4} t^{*} \right) \right]$$

Some characteristics of classical diffusion law are

1. It is concentration and history independent.
2. A clearly defined saturation level is attained.
3. A temporal dependence enters through a non-dimensional time.
4. If we plot moisture gain $M$ vs. $t^*$ it becomes a straight line up to 62% of saturation.

**The Proposed Model**

The moisture absorption kinetics depends on the type of surface of the fiber. If the surface area is such that it can mechanically hold the moisture then the kinetics closely follow the one
dimensional Fick's law, which is the case in the carbon fiber epoxy resins. In such cases due
to the presence of steps in atomic level (which is revealed in the microstructure), the
mechanical bonding results leading to ideal moisture absorption kinetics. But this is not the
case for glass fiber reinforced composites. To study the moisture absorption kinetics of these
composites whose behavior closely approaches the ideal behavior a programming was made
on the solution based on the one dimensional Fick's law.

When moisture absorption in composite materials deviates from classical Fickian diffusion
behavior, additional terms are required to account for the deviation. Such moisture absorption
relationship is approximated by the following expression

$$
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \Lambda \frac{\partial C}{\partial t} - \Gamma \frac{\partial C}{\partial t}
$$

The last two terms represent anomalies of classical Fickian diffusion where the $\Lambda(\partial C/\partial t)$ term
accounts for the increase in moisture content due to damage in the materials, such as
microcracking and delamination, that tends to trap water by physico-adsorption mechanisms[2]. The $\Gamma(\partial C/\partial t)$ term characterizes the degree of reduction in weight gained due
to mass loss by matrix resin dissolution. Needless to say, the solution to the above equation is
very complex and non-trivial. Nonetheless a distinction is made between the actual process and
theoretical process to analyze the cause of departure[3]. The general departures are

1. Saturation may not be fully attained.
2. The process may be concentration dependent.
3. The process may depend upon the history of composite:
4. The coefficient of diffusion ($D$) is not constant but changes with temperature.

When the composite absorbs moisture it swells and stresses are generated within it resulting
an increase in coefficient of moisture diffusion. This becomes significant when the moisture
quantity increases. The coefficient of diffusion with moisture absorption can be expressed as

$$
D_{ef}(t) = D[1 + dM^2(t)]
$$

of coefficient of diffusion.

In classical models moisture and water molecules are considered free ones. But actually they
are bonded with hydrogen bonds (even in vapor phase at room temperature). This tries to
lower the diffusion of water molecules to the composite[4]. Therefore, the effective moisture
concentration may be represented as

$$
(M_w)_{ef} = b M_w
$$

Where

$M_w$ = atmospheric moisture concentration
$b$ = dimensionless constant ($0 < b < 1$)

Classical model also assumes that the saturation level is attained instantaneously throughout
the specimen, which is not so. The actual process becomes ideal process after a certain period
of time ($t_s$) and taking this time shift factor into account:

$$
t_{ef} = (t - t_s), \quad t_s < t
$$

Again, in actual practice coefficient of diffusion changes with temperature because the higher
the temperature higher is the kinetic energy. This increases the mobility of molecules

$$
D(T) = D_k \exp \left( \frac{\Delta H_k}{kT} \right)
$$
...ing in higher diffusion coefficient[5]. Taking Maxwellian distribution of energy for fiber molecules, the coefficient of diffusion may be written as

$$D(R) = D_0[1 + dM^2]$$

where $D(R)$ is the coefficient of diffusion at absolute temperature $T_R$. Incorporating all these equations to Fick’s law and putting

The final moisture content can be represented as[6]

$$\frac{M(I)}{M_f} = b\left[1 - \frac{t}{t_f}\right]\exp\left(\frac{A/T_R - A/T}{2}\right) + \frac{d}{2}\left[b\left(M_f\right)^2\left[1 - \frac{t}{t_f}\right]\exp\left(\frac{A/T_R - A/T}{2}\right)\right]^{\frac{1}{2}}$$

where $A$, $b$ and $d$ are constants.

Individual effects of parameters $d$, $b$ and $T$ (through $A$) is shown with the help of non-dimensional plots. With the help of these graphs it is possible to explain the difference in experimental data and one-dimensional Fickian prediction.

The prediction of property changes[7] has been attempted based on the fact that property changes are directly dependent on the true absorbed water content in the laminates as already reported. The predictions are made on the basis of the moisture absorbed in the second model with modifications. Therefore, the only time factor involved was the time required to reach the desired absorption level. Consequently the effects observed are related to the temperature of immersion and the time taken at that temperature to reach the stated absorption level which is again brought from the modified model. The apparent dependence of mechanical properties on the absorption level alone is at least partly attributed to the opposing effects of high temperature and the short time required for reaching given absorption level at those temperatures. However, some damage mechanism (such as osmotic cracking) appears to depend directly on water content.

In this context two steps are necessary to predict material properties.

1. The prediction of water absorption kinetics at temperatures outside the experimental range.
2. The establishment of empirical relationship between water content and mechanical properties.

The first data can be directly borrowed from the second model. Since the fibers don't absorb water and the absorbed water is concentrated within the matrix phase, the quantity of water absorbed in interfacial voids increases slowly as debonding progresses but is not thought to be a very significant fraction of the total. A curve-fitting program is used to compare curves of various shapes with the experimental plots of residual properties against true water content. The property values at any time are taken to be the average of those resulting from exposures at a range of temperatures. The best-fit curves are obtained with the equations of the form

$$P = a\left(1 - e^{-b(1-c)t}\right) + d$$

where $P$ is the residual property and $a$, $b$, $c$ and $d$ are empirical constants. In other cases, related expressions involving two exponential expressions are used. Using the equations and assigning values to $a$, $b$, $c$ and $d$ it is possible to predict the residual mechanical properties of
laminates such as tensile strength in dry and wet conditions, intra and inter laminar strength, failure strain, tensile modulus in wet and dry conditions.

Results and Discussion

To study the moisture absorption kinetics of these composites whose behaviour closely approaches the ideal behaviour a programming was made on the solution based on the one dimensional Fick's law. Fig. 1 shows the variation of moisture content with time both plotted in non-dimensional parameters $M'(t')$ vs. $t'$. It is the theoretical absorption curve though most of the composites are found to deviate from this. But as an exception the carbon fibre reinforced epoxy resin closely matches with it due to it's uneven fibre surface which results in strong mechanical bonding between the fibre and matrix. But glass reinforcements have wide deviation from this curve.

![Image of one-dimensional Fick's Law Solution](image)

Fig. 1 One-dimensional Fick's Law Solution

Individual effects of parameters $d$, $b$ and $T$ (through $A$) are shown with the help of non-dimensional plots from figs. 2 to 4. With the help of these graphs it is possible to explain the difference in experimental data and one-dimensional Fickian prediction. Fig. 2 show that the parameter $d$ tends to increase the moisture content above the classical value. A higher value of $d$ means a higher degree of concentration dependence and hence the predictions of the proposed equations deviate more from the classical predictions. This effect becomes more prominent at higher concentrations. The effect of parameter $b$ is shown in fig. 3. Since $b$ appears due to hydrogen bonding between the molecules of water in the environment it's effect is to lower the moisture concentration in the material. For the classical model $b$ takes the value 1. For lower values of $b$ the predicted moisture content tends to fall below the classical value and $(M/M_c)$ falls below unity. Fig. 4 shows the effect of temperature. It is indicated that, if temperature dependence of the coefficient of diffusion is neglected and the constant value $D_R$ is used in the Fick's model, it's prediction depart considerably from the values obtained from the proposed modification. If the test temperature $T$ is higher than the reference temperature $T_R$, the classical model gives much lower value of $M(t)$ than the modified model.
Comparison of Proposed and Classical Models: Effect of Parameter β with J. T. = 1.2 and 0.95

Comparison of Proposed and Classical Models: Effect of Parameter T. with β = 0.05
From the above results it is realized that at small concentration levels effect of parameter dominates over the effect of d and hence $(\text{MM}_{f})$ is less than unity. Whereas at higher level of concentration, the concentration dependence dominates over the hydrogen bonding factor and $(\text{MM}_{f})$ value becomes more than one. Depending on whether the hydrogen bond effect or concentration dependence dominates the diffusion process, the actual data may be below or above the classically predicted value. Although the quantitative accuracy of the suggested modifications are yet to be tested, it satisfies the minimal condition of viability and is able to explain the departures of the Fickian model with the reported experimental data. The degradation of residual properties due to moisture absorption has been predicted taking into consideration the empirical formula. The validity of these predictions depends on the degradation processes being simple function of absorbed water content.

References