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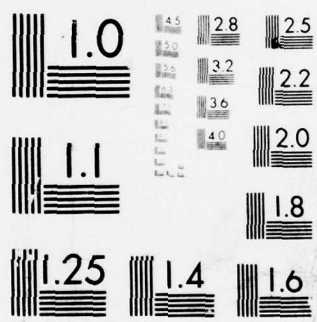

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LEVEL II

STRUCTURAL INELASTICITY XIX.

A Review of Moisture Diffusion in Composites.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The effect of moisture diffusion in composite materials is reviewed. Pertinent equations are listed and various special solutions are given. Extensive references are quoted. Several suggestions are made for future research in the area.

A REVIEW OF MOISTURE DIFFUSION IN COMPOSITES

1. Introduction. The effect of environment may be severe in polymeric composites. It may lead to reduced strength and even final failure through deterioration of polymers by chemical reactions such as scission of polymer chains or dissolution or by swelling. Scission and dissolution are the more severe processes. Scission may be caused by substantial energy input such as nuclear radiation which may break intramolecular bonds. Dissolution, on the other hand, causes errosion through solution of the polymer in a gaseous or liquid environment.

Swelling is an altogether different phenomena. It is caused by diffusion of moisture or organic vapour into the polymer. Although it is a weaker process than scission or dissolution, it can considerably degrade the physical properties of the polymer. With increasing uses of polymeric composites in marine and aerospace structures, radomes, and various other structures, under conditions which include exposure to humid weather or actual water, the influence of moisture in composites constitutes a major concern and should be thoroughly investigated.

Polymers are generally amorphous, crystalline or partly crystalline organic materials. Molecules of repetitive, comparatively low molecular weight units of one or more groups (monomers) are combined through primary valence bonds to form independent large molecules (macromolecules) in some sort of a chain. These large chainlike macromolecules are grouped together by an additional bond (intermolecular bond) to form

the complete polymeric structure. Thus, in polymers these macromolecules constitute the basic structural units that may have irregular and often complex shapes. Whereas the inter-atomic (intramolecular) bond, within the molecule are strongly covalent, the bonding between the molecules (intermolecular) may be relatively weak Van der Waals bonds, strong hydrogen bonds, or crosslinks between atoms of adjacent chains.

Diffusion is a process by which migration of atoms takes place between two or more substances. It is basically statistical in nature, and the path of migration (penetration) is highly random and unpredictable. In metals and ceramics, migration of atoms commonly occurs through migration of vacancies, migration of interstitialcies, and place exchange as indicated in Fig. 1. In polymers,diffusion of small molecules (diffusate) may take place as a result of random Brownian movements of the diffusate. The diffusion mechanism becomes very complicated when the molecules of the diffusate are about the same size as, or larger than, the chain segments that contribute most to heat motion in polymers.

In case of moisture diffusion, the micromolecules of the penetrant enter between the macromolecules of the polymer and make direct polymer-to-polymer contact impossible. This gradually loosens and finally breaks the bond between the macromolecules (i.e., intermolecular bond). The immediate effect of moisture diffusion in polymers however is change in dimensions i.e., swelling. As swelling progresses, a polymer which is initially strong may become rubberlike. So the moisture acts as a plasticizer, lowering the glass transition temperature of a polymer and loosening segmental motions at any given temperature.

Several other important considerations may arise because of moisture diffusion in polymers. 1) Since diffusion depends on frequency of molecular jumps, the diffusion coefficient will be dependent on the concentration of the penetrant. 2) The swelling of the polymer will eventually cause stressing and relaxing, and redistribution of chain segments through the entangled mass. Sometimes, the rate of swelling will be too great to maintain the most probable distribution of chain segments. Hence the diffusion coefficient changes with time when the chains are relaxing. 3) Non-Fickian diffusion may occur when the diffusion and relaxation rates are comparable. This diffusion anomaly is observed in case of glassy polymers, especially when the diffusate causes excessive swelling of the polymer. On the contrary, diffusion is reasonably Fickian (the rate of diffusion is much less than that of relaxation) in rubbery polymers (e.g., elastomers), as the rubbery state adjusts quickly to changes due to diffusion. 4) The coupling of heat and moisture may complicate the diffusion process. In a real situation, it will probably be extremely difficult to separate the effect of one from that of the other. This is because polymers are very susceptible to the influence of temperature.

With this brief introduction on general behavior of polymers and their response to moisture diffusion, let us now examine the characteristics of some polymers that are used in fabrication of composite structural members. These mostly fall under two

groups: thermoplasts and thermosets. Thermoplasts such as polyethylene, polystyrene, nylon, etc. possess an ability to be repeatedly formed by heat and pressure. A thermoplast softens upon heating at a temperature above the glass transition temperature but regains its strength upon cooling. With the increase in temperature the random motion of the atoms about their equilibrium positions increases and results in breakage of weaker bonds (i.e., secondary bonds) and the material begins to flow. New secondary bonds are formed upon cooling, and the material reverts to its original structure. Thus, a thermoplastic material softens upon heating, but does not decompose unless the temperature is high enough to break the primary covalent bonds.

On the other hand, thermosets or thermosetting plastics decompose before softening upon heating. The polymerisation process in thermosets is irreversible. Because of the three dimensional network of covalent bonds and crosslinks, the thermoset polymers are fairly rigid and stronger than thermoplasts. At high temperatures, however, the covalent bonds may break leading to destruction of the network structure and thus decomposition of the polymers. Epoxy, polyester, phenolic, silicone and, polyimide form the most commonly used resins of this group.

In the following sections we review and comment on some aspects of moisture diffusion studies in composites, and suggest some problem areas for future research.

2. Some results of moisture diffusion. Let us now review and extend some results of moisture diffusion representing Fickian behavior.

Fick's Equation for Three-dimensional Isotropic Medium:

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial M}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial M}{\partial y}\right) + \frac{\partial}{\partial z}\left(D\frac{\partial M}{\partial z}\right) \tag{1}$$

where D may be a function of time, spatial coordinates, and moisture concentration M.

If D is independent of x, y, and z, Eq. (1) reduces to

$$\frac{\partial M}{\partial t} = D\left(\frac{\partial^2 M}{\partial x^2} + \frac{\partial^2 M}{\partial y^2} + \frac{\partial^2 M}{\partial z^2}\right) \tag{2}$$

If D is also independent of moisture but depends only on time,

$D = f(t).$

Then we may introduce a new time-scale T such that

$dT = f(t)dt$

and Eq. (2) becomes

$$\frac{\partial M}{\partial t} = \frac{\partial^2 M}{\partial x^2} + \frac{\partial^2 M}{\partial y^2} + \frac{\partial^2 M}{\partial z^2} \tag{3}$$

Fick's Equation for Three-dimensional Anisotropic Medium

$$\begin{aligned}\frac{\partial M}{\partial t} &= \frac{\partial}{\partial x}\left(D_{11}\frac{\partial M}{\partial x} + D_{12}\frac{\partial M}{\partial y} + D_{13}\frac{\partial M}{\partial z}\right)\\ &+ \frac{\partial}{\partial y}\left(D_{21}\frac{\partial M}{\partial x} + D_{22}\frac{\partial M}{\partial y} + D_{23}\frac{\partial M}{\partial z}\right)\\ &+ \frac{\partial}{\partial z}\left(D_{31}\frac{\partial M}{\partial x} + D_{32}\frac{\partial M}{\partial y} + D_{33}\frac{\partial M}{\partial z}\right)\end{aligned} \tag{4}$$

where the D_{ij}'s may be functions of time, spatial coordinates, and M.

When D_{ij}'s are independent of position, Eq. (4) reduces to

$$\frac{\partial M}{\partial t} = D_{11}\frac{\partial^2 M}{\partial x^2} + D_{22}\frac{\partial^2 M}{\partial y^2} + D_{33}\frac{\partial^2 M}{\partial z^2} + (D_{23}+D_{32})\frac{\partial^2 M}{\partial y\,\partial z}$$

$$+ (D_{31} + D_{13})\frac{\partial^2 M}{\partial z\,\partial x} + (D_{12} + D_{21})\frac{\partial^2 M}{\partial x\,\partial y} \tag{5}$$

Transformation of Eq. (5) to principal axes of diffusion results in

$$\frac{\partial M}{\partial t} = D_x\frac{\partial^2 M}{\partial x^2} + D_y\frac{\partial^2 M}{\partial y^2} + D_z\frac{\partial^2 M}{\partial z^2} \tag{6}$$

Note that here x, y, z axes now represent principal axes of diffusion and D_x, D_y, D_z are principal diffusion coefficients.

If we make the further transformation of Eq. (6)

$$x_1 = x\sqrt{(D/D_x)},\quad y_1 = y\sqrt{(D/D_y)},\quad z = z\sqrt{(D/D_y)} \tag{7}$$

where D is any function of t and M, we obtain

$$\frac{\partial M}{\partial t} = D\left(\frac{\partial^2 M}{\partial x_1^2} + \frac{\partial^2 M}{\partial y_1^2} + \frac{\partial^2 M}{\partial z_1^2}\right) \tag{8}$$

Equation (8) has the same form as Eq. (2), and hence some anisotropic problems may be reduced to the corresponding isotropic problems.

Note that, for an orthotropic fiber-reinforced medium, Eq. (6) can also be written as

$$\frac{\partial M}{\partial t} = D_L\frac{\partial^2 M}{\partial x_1^2} + D_{T1}\frac{\partial^2 M}{\partial y_1^2} + D_{T2}\frac{\partial^2 M}{\partial z_1^2} \tag{9}$$

where L represents the fiber direction, and T's represent mutually perpendicular directions normal to the fiber direction, Fig. 2. In case of square, hexagonal, or random array of fibers, it is usually assumed that

$D_{T1} = D_{T2} = D_T$

Moisture Diffusion Through-the-Thickness. If diffusion takes place only through the thickness, Fick's equation reduces to

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial z}\left(D\frac{\partial M}{\partial z}\right) \tag{10}$$

Let us now introduce the following simplifications for convenience:

i) D may not be a function of z, if we consider only macro-properties.

ii) D does not depend on M.

iii) D is also independent of time.

Thus, assuming D to be constant, Fick's equation is simplified to

$$\frac{\partial M}{\partial t} = D\frac{\partial^2 M}{\partial z^2} \tag{11}$$

We now investigate the solution of Eq. (11) for different cases [1]*.

A. Constant Diffusion Coefficients

We consider diffusion through the thickness of a plane sheet of unidirectional composite.

Case I: Surface concentrations constant but different, and initial distribution $M_i(z)$, Fig. 3.

If $M = M_1$, $z = 0$, $t \geq 0$

$M = M_2$, $z = h$, $t \geq 0$

$M = M_i(z)$, $0 < z < h$, $t = 0$

*Numbers in square brackets refer to the list of references collected at the end of the report.

the solution of Eq. (11) is given by

$$M = M_1 + (M_2 - M_1)\frac{z}{h} + \frac{2}{\pi}\sum_{p=1}^{\infty}\frac{M_2\cos p\pi - M_1}{p}\sin\frac{p\pi z}{h}\cos(-Dp^2\pi^2 t/h^2)$$
$$+ \frac{2}{h}\sum_{p=1}^{\infty}\sin\frac{p\pi z}{\pi}\exp(-D\pi^2 p^2 t/h^2)\int_0^h M_i(z)\sin\frac{p\pi z}{h}dz \tag{13}$$

If $M_i(z) = 0$ or constant, the integral in (13) can be easily evaluated.

Case II: Surface concentrations constant and equal, and uniform initial distribution M_0, Fig. 4.

This is a symmetric problem about the mid-plane. Hence the solution (13) becomes

$$\frac{M - M_0}{M_1 - M_0} = 1 - \frac{4}{\pi}\sum_{p=0}^{\infty}\frac{(-1)^p}{2p+1}\exp\{-D(2p+1)^2\pi^2 t/h^2\}\cos\frac{(2p+1)\pi z}{h} \tag{14}$$

If M^*_t denotes the total amount of diffusing moisture which has entered the sheet at time t, and M^*_∞ the corresponding quantity after infinite time (i.e., after infinite time the moisture content of the whole sheet assumes that of the surfaces),

$$\frac{M^*_t}{M^*_\infty} = 1 - \sum_{p=0}^{\infty}\frac{8}{(2p+1)^2\pi^2}\exp\{-D(2p+1)^2\pi^2 t/h^2\} \tag{15}$$

Case III: Surface concentrations constant but different, and uniform initial distribution, Fig. 5. Starting at time $t = 0$ the concentration changes according to

$$M = M_1 + (M_2 - M_1)\frac{z}{h}$$
$$+ \frac{2}{\pi}\sum_{p=1}^{\infty}\frac{M_2\cos p\pi - M_1}{p}\sin\frac{p\pi z}{h}\exp(-Dp^2\pi^2 t/h^2)$$
$$+ \frac{4M_0}{\pi}\sum_{q=0}^{\infty}\frac{1}{2q+1}\sin\frac{(2q+1)\pi z}{h}\exp\{-D(2q+1)^2\pi^2 t/h^2\} \tag{16}$$

As t approaches infinity, the above equation reduces to the linear concentration distribution

$$\frac{M-M_1}{M_2-M_1} = \frac{z}{h} \qquad (17)$$

Case IV: Variable surface concentrations.

The surface concentrations $M_1(t)$ and $M_2(t)$ are functions of time, Fig. 6. The solution to the problem of diffusion is given by Carslaw and Jaeger [2]. For emperical values of $M_1(t)$, $M_2(t)$ and $M_i(z)$, three integrals arise which have to be evaluated graphically or numerically. In certain cases, however, where the surface concentration can be represented by a mathematical expression, the solution is considerably simplified.

Example 1: $M_1(t) = M_2(t) = M_0\{1-\exp(-\beta t)\}$, and the initial concentration is zero, Fig. 7.

The situation usually arises when an instantaneous change is attempted in an experiment. The solution is

$$\frac{M}{M_0} = 1 - \exp(-\beta t)\frac{\cos z(\beta/D)^{1/2}}{\cos \frac{h}{2}(\beta/D)^{1/2}} - \frac{16\beta h^2}{4\pi}\sum_{p=0}^{\infty}\frac{(-1)^p \exp(-D(2p+1)^2\pi^2 t/h^2)}{(2p+1)\{\beta h^2 - D\pi^2(2p+1)^2\}}\cos\frac{(2n+1)\pi z}{h} \qquad (18)$$

provided β is not equal to any of the values $D(2p+1)^2\pi^2/h^2$.

Hence the total amount M^*_t of diffusing substance is obtained by integrating (16) with respect to z between $-\frac{h}{2}$ to $\frac{h}{2}$.

$$\frac{M^*_t}{hM_0} = 1 - \exp(-\beta t)(4D/\beta h^2)^{1/2}\tan(\beta h^2/4D)^{1/2} - \frac{8}{\pi^2}\sum_{p=0}^{\infty}\frac{\exp\{-(2p+1)^2\pi^2 Dt/h^2\}}{(2p+1)^2[1-(2p+1)^2\{D\pi^2/(\beta h^2)\}]} \qquad (19)$$

Example 2: $M_1(t) = M_2(t) = kt$ (i.e., linear variation with time) and the initial concentration is zero. The solution is

$$\frac{DM}{kh^2/4} = \frac{Dt}{h^2/4} + \frac{1}{2}\left(\frac{4z^2}{h^2} - 1\right) + \frac{16}{\pi^3}\sum_{p=0}^{\infty}\frac{(-1)^p}{(2p+1)^3}\exp\{-D(2p+1)^2\pi^2 t/h^2\}\cos\frac{(2p+1)\pi z}{h}. \qquad (20)$$

The corresponding M^*_t is

$$\frac{DM^*_t}{kh^3/8} = \frac{2Dt}{h^2/4} - \frac{2}{3} + \frac{64}{\pi^4}\sum_{p=0}^{\infty}\frac{\exp\{-D(2p+1)^2\pi^2 t/h^2\}}{(2p+1)^4} \qquad (21)$$

B. Time-dependent Diffusion Coefficients

The time-dependence of the diffusion coefficient is discussed in the Introduction. Weitsman [3] solved a specific problem involving time-dependent diffusion coefficient. He observed that the diffusion coefficient becomes time-dependent, when the composite is subjected to a time varying temperature during a "thermal spike". In general, when D is a function of t only, the diffusion equation in one dimension becomes

$$\frac{\partial M}{\partial t} = D(t)\frac{\partial^2 M}{\partial z^2} \qquad (22)$$

Let us use the transformation

$$dT = D(t)\,dt,$$

$$\text{i.e., } T = \int_0^t D(t')dt' \qquad (23)$$

and then Eq. (22) reduces to

$$\frac{\partial M}{\partial T} = \frac{\partial^2 M}{\partial z^2} \qquad (24)$$

The previous solutions for constant D can therefore be utilized to evaluate M as a function of T and z. The relation (23) can then be used to convert T into t analytically or by numerical integration.

C. Concentration-Dependent Diffusion Coefficients

We now turn our attention to solution of Eq. (10), which is repeated below for easy reference.

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial z}\left(D \frac{\partial M}{\partial z}\right) \qquad (10)$$

The earliest treatment of this equation was given by Boltzmann [4]. For certain boundary conditions, Boltzmann reduced the above equation to an ordinary differential equation in terms of a single variable $\eta = z/2t^{1/2}$, provided D is a function of concentration only. Thus we have

$$\eta = \frac{1}{2} z/t^{1/2} \qquad (25)$$

Hence

$$\frac{\partial M}{\partial z} = \frac{1}{2t^{1/2}} \frac{dM}{d\eta}$$

and $$\frac{\partial M}{\partial t} = -\frac{z}{4t^{3/2}} \frac{dM}{d\eta}$$

Therefore,

$$\frac{\partial}{\partial z}\left(D \frac{\partial M}{\partial z}\right) = \frac{\partial}{\partial z}\left(\frac{D}{2t^{1/2}} \frac{dM}{d\eta}\right) = \frac{1}{4t} \frac{d}{d\eta}\left(D \frac{dM}{d\eta}\right)$$

so that

$$-2\eta \frac{dM}{d\eta} = \frac{d}{d\eta}\left(D \frac{dM}{d\eta}\right) \qquad (26)$$

Equation (26) is the starting point for many solutions [1, 5-12] of one-dimensional diffusion problems in infinite or semi-infinite media.

Let us now examine the boundary conditions for which the transformation (25) is valid.

Infinite Medium; Fig. 8.

$$M = M_1,\ z < 0,\ t = 0$$
$$M = M_2,\ z > 0,\ t = 0 \qquad (27)$$

The transformed boundary conditions are

$$M = M_1,\quad \eta = -\infty$$
$$M = M_2\quad \eta = +\infty \qquad (28)$$

Semi-infinite Medium; Fig. 9

$$M = M_0,\ z = 0,\ t > 0$$
$$M = M_1,\ z > 0,\ t = 0 \qquad (29)$$

so that

$$M = M_0,\quad \eta = 0$$
$$M = M_1,\quad \eta = \infty \qquad (30)$$

Thus, it has been possible to express both (27) and (29) in terms of η alone, as given in (28) and (30). In general, the transformation (25) can be used for diffusion and semi-infinite media when the initial concentrations are uniform and may be zero.

Finite Medium: Interestingly, Eqs. (25) and (26) are not applicable for through-the-thickness diffusion in a finite sheet of thickness h. The boundary conditions for a finite thick sheet may be

$$M = M_0,\ z = 0,\ z = \ell$$

Using the transformation (25), the second condition above results in

$$M = M_0, \quad \eta = \frac{1}{2} h/t^{1/2}$$

which is not expressible in terms of η only, but also involves t. However, Tsang [13-14] presented solution for one-dimensional diffusion through finite thickness, Fig. 10. The following non-dimensional variables are assumed first

$$\zeta = \pi z/h, \ \phi = (M-M_1)/(M_0-M_1), \ d = D/D_0 \tag{31}$$

The diffusion equation is then

$$\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial\zeta}\left(d \frac{\partial\phi}{\partial\zeta}\right) \tag{32}$$

subject to the conditions

$$\phi = 1, \ 0 \leq \zeta \leq \pi, \ t = 0$$

$$\phi = 0, \ \zeta = 0 \text{ and } \pi, \ t \geq 0 \tag{33}$$

Tsang then assumed an expansion of the form

$$\phi(\zeta,t) = \sum_{n=1}^{\infty} f_n(t) \ (2/\pi)^{1/2} \sin n\zeta \tag{34}$$

and proceeded to develop an approximate analytic solution having a simple form. The results are reasonably accurate for moderately concentration-dependent diffusion coefficients.

3. Approximate constitutive relations for a laminated composite.

D is again constant in each lamina, but may be different from lamina to lamina. It is observed [15] that the hygrothermal stresses are identically analogous to thermal stresses. The effect is dilatational; there exist coefficients of hygroscopic expansion β_i analogous to the coefficients of thermal expansion α_i, and the induced stresses are self-equilibrating across the

laminate thickness.

The through-the-thickness coordinate is represented by the z-axis. The constitutive relations for each layer are different and given by (for a non-principal coordinate system)

$$\sigma_i(z,t) = Q_{ij}[\epsilon_j - \alpha_j T(z,t) - \beta_j M(z,t)] \tag{35}$$

$$(i,j = 1,2,6)$$

where, Fig. 11,

Q_{ij} = anisotropic elastic constants

ϵ_j = strain components

α_j = coefficients of thermal expansion

β_j = coefficients of hygroscopic expansion

$T(z,t)$ = temperature distribution

$M(z,t)$ = moisture concentration distribution

z = distance measured from the mid-surface of the laminate

t = time

and i,j refer to Cartesian coordinates in plane stress. Thus $\sigma_1 = \sigma_x$, $\sigma_2 = \sigma_y$, $\sigma_6 = \tau_{xy}$, etc. Note that in Eq. (35) the following assumptions are made:

1. Linearly elastic material behavior
2. α_i and β_i are constant over the ranges of temperature and moisture.
3. The laminate is thin compared to other dimensions.

Force and Moment Resultants

$$N_i = \int_{-\frac{h}{2}}^{\frac{h}{2}} \sigma_i \, dz \qquad (i,j = 1,2,6) \tag{36}$$

$$M_i = \int_{-\frac{h}{2}}^{\frac{h}{2}} \sigma_i z \, dz \qquad (i,j = 1,2,6) \tag{37}$$

Hence applying (35) in the above relations and making use of summation relations [16] for stiffness coefficients, we obtain

$$N_i = (A_{ij} \overset{\circ}{\epsilon}_j + B_{ij}\kappa_j) - N_i^t - N_i^m \tag{38}$$

$$M_i = (B_{ij} \overset{\circ}{\epsilon}_j + D_{ij}\kappa_j) - M_i^t - M_i^m \tag{39}$$

where

$$A_{ij} = \sum_{k=1}^{n} Q_{ij}^{\;k} (z_k - z_{k-1})$$

$$B_{ij} = \frac{1}{2} \sum_{k=1}^{n} Q_{ij}^{\;k} (z_k^{\,2} - z_{k-1}^{\,2})$$

$$D_{ij} = \frac{1}{3} \sum_{k=1}^{n} Q_{ij}^{\;k} (z_k^{\,3} - z_{k-1}^{\,3}) \tag{40}$$

and

$$N_i^{\;t} = \int_{-\frac{h}{2}}^{\frac{h}{2}} Q_{ij}\alpha_j T(z,t)\,dz \tag{41}$$

$$N_i^{\;m} = \int_{-\frac{h}{2}}^{\frac{h}{2}} Q_{ij}\beta_j M(z,t)\,dz \tag{42}$$

$$M_i^{\;t} = \int_{-\frac{h}{2}}^{\frac{h}{2}} Q_{ij}\alpha_j T(z,t)\,z\,dz \tag{43}$$

$$M_i^{\;m} = \int_{-\frac{h}{2}}^{\frac{h}{2}} Q_{ij}\beta_j M(z,t)\,z\,dz \tag{44}$$

Evaluation of the integrals (41)-(44) requires the solution of classical heat conduction equation and boundary conditions.

$N_i^{\;t}$, $N_i^{\;m}$, $M_i^{\;t}$, and $M_i^{\;m}$ can also be expressed as a summation over the total thickness, if it is assumed that (like strain) the moisture and temperature distribution over a particular lamina are known functions of thickness and constants over the laminate plane. The constitutive relations for some specific cases (with this simplification) of moisture concentration have been derived by Pipes et al. [15].

Thus for the k-th layer,

$$N_{ik}^{\;m} = \int_{h_{k-1}}^{h_k} Q_{ij}^{\;k} \beta_j^{\;k} M(z,t)\,dz$$

$$= Q_{ij}^{\;k} \beta_j^{\;k} \int_{h_{k-1}}^{h_k} M(z,t)\,dz$$

$$= Q_{ij}^{\;k}\beta_j^{\;k}[m(z_k,t) - m(z_{k-1},t)]$$

where $m(z,t) = \int^{z} M(\xi,t)\,d\xi$.

Hence

$$N_i^{\;m} = \sum_{k=1}^{n} Q_{ij}^{\;k}\beta_j^{\;k}[m(z_k,t) - m(z_{k-1},t)] \tag{45}$$

Similarly,

$$M_i^{\;m} = \sum_{k=1}^{n} Q_{ij}^{\;k}\beta_j^{\;k}[z_k m(z_k,t) - z_{k-1}\, m(z_{k-1},t)$$

$$-n(z_k,t) + n(z_{k-1},t)] \tag{46}$$

where

$$n(z,t) = \int^{z} m(\eta,t)\,d\eta$$

Similar expressions can be obtained for $N_i^{\;t}$ and $M_i^{\;t}$. Note, again, that $m(z,t)$ and thereby $n(z,t)$ can be evaluated by solving the moisture diffusion equation along with appropriate boundary conditions.

4. Determination of diffusion coefficients.

Definition and Measurement

The measurement and theoretical prediction of D constitute the most important first step in describing the moisture diffusion process. The simplest definition of D for one dimensional case is given by the rate of transfer of the diffusate across unit area of section, divided by the space gradient of concentration at the section. Thus,

$$F = -D \frac{\partial M}{\partial z} \tag{47}$$

where F is the rate of transfer.

Fortunately, the moisture diffusion in polymeric composites is a two-component process i.e. a process involving diffusion between only two substances. When D is assumed constant and there is negligible swelling, an experimental method for evaluation of Eq. (15) will satisfactorily determine D. But the problem becomes significantly difficult when D is concentration-dependent associated with the swelling of the sheet. Crank [1] presented an elaborate discussion on various considerations for such cases. This will form useful guidelines for formulating a definite program for determination of D in cases of moisture diffusion in polymeric composites.

Edge Effects. When testing a finite size specimen in a moisture environment, it is quite likely that the moisture content of the specimen will be affected considerably because of diffusion

through the edges. This is particularly important during the early stage of diffusion.

In a test specimen (Fig. 12), usually the thickness (z-direction) is much smaller than the length (y-direction) and breadth (x-direction) of the specimen.

The moisture content due to diffusion through the the z-direction can then be determined from the results of the previous sections. But, if diffusions through the x- and y-plane are also considered, it will be appropriate to consider the medium semi-infinite.

Thus, say for a specific case when D is constant, the boundary conditions are

$$M = M_0, \quad 0 < x < \infty, \quad t = 0$$

$$M = M_1, \quad x = 0, \quad t > 0$$

Hence the solution [1] of

$$\frac{\partial M}{\partial t} = D_x \frac{\partial^2 M}{\partial x^2}$$

is

$$\frac{M-M_1}{M_0-M_1} = \mathrm{erf} \frac{x}{2\sqrt{(D_x t)}}$$

or,

$$\frac{M-M_0}{M_1-M_0} = 1 - \mathrm{erf} \frac{x}{2\sqrt{(D_x t)}} \tag{48}$$

The rate of transfer of the diffusing substance per unit area is proportional to the concentration gradient measured normal to the section, i.e.,

$$F = -D_x \frac{\partial M}{\partial x}.$$

Hence the weight of moisture entering along z-axis across the face (x=0)

$$M_x^{\,t} = \int_0^t -(bh)\ D_x\left(\frac{\partial M}{\partial x}\right)_{x=0} dt \tag{49}$$

From Eqs. (48) and (49),

$$M_x^{\,t} = 2bh\ (M_1-M_0)(D_x t/\pi)^{1/2} \tag{50}$$

Similarly,

$$M_y^{\,t} = 2ah\ (M_1-M_0)(D_y t/\pi)^{1/2} \tag{51}$$

If, however, the thickness is also comparable to the length and the breadth,

$$M_z^{\,t} = 2ab\ (M_1-M_0)(D_z t/\pi)^{1/2} \tag{52}$$

Hence, if the interaction of diffusion through different sides are neglected, and the moisture enters through all the six sides, the total weight of moisture is given by

$$M^t = 2(M_x^{\,t} + M_y^{\,t} + M_z^{\,t})$$

$$=4(M_1-M_0)\sqrt{\frac{t}{\pi}}\ [bh\ \sqrt{D_x}+ah\ \sqrt{D_y}+ab\ \sqrt{D_z}] \tag{53}$$

Similar results can be derived for other specific boundary conditions. It is, however, worth studying cases of edge effects in specimens when D is concentration dependent and there is appreciable swelling. References [5-12] may be useful for such study.

<u>Effective Diffusivity of Composite</u>. It is important to evaluate D in terms of constituent properties of the composite. This involves complex micro-level analysis of composites with associated boundary conditions. Shen and Springer [17] extended an early

work [18] to derive expressions for D parallel and normal to the fibers of a unidirectional composite by assuming the analogy of thermal conductivities. The diffusivities of the matrix and fibers are assumed constant. The transverse isotropy of the resulting composite is also assumed. They claimed good agreement with experiment. The results are however very much limited in application, as the moisture difference between two surfaces are assumed constant. In the absence of more reliable and significant contribution on this aspect, we reproduce Shen and Springer's results [17] for reference.

D_m = diffusivity of matrix

D_f = diffusivity of fiber

V_f = volume fraction of fiber

Then, in the case of square array packing of circular fibers (V_f < 0.785), Fig. 13

$$D_L = (1-V_f)D_m + V_f D_f$$

$$D_T = (1-2(V_f/\pi)^{1/2})D_m + \frac{D_m}{B_D}\left[-\pi\frac{4}{(1-(B_D^{\,2}V_f/\pi))^{1/2}}\tan^{-1}\frac{(1-(B_D^{\,2}V_f/\pi))^{1/2}}{1+(B_D V_f/\pi)^{1/2}}\right]$$

$$\text{where } B_D \equiv 2\left(\frac{D_m}{D_f}-1\right). \tag{54}$$

In most fibers, the diffusivity is comparatively small so that $D_f \ll D_m$. Hence,

$$D_L = (1-V_f)D_m$$

$$D_T = (1-2(V_f/\pi)^{1/2})D_m \tag{55}$$

<u>Off-axis Unidirectional Ply</u>. If the fiber direction makes angles θ_x, θ_y and θ_z with x, y and z axes, respectively (Fig. 14), the effective diffusivities in x, y, z directions are then given by

$$D_x = D_L \cos^2 \theta_x + D_T \sin^2 \theta_x$$
$$D_y = D_L \cos^2 \theta_y + D_T \sin^2 \theta_y$$
$$D_z = D_L \cos^2 \theta_z + D_T \sin^2 \theta_z \tag{56}$$

If the fibers lie in the xy-plane and make an angle θ with the x-axis,

$$D_x = D_L \cos^2\theta + D_T \sin^2\theta$$
$$D_y = D_L \sin^2\theta + D_T \cos^2\theta$$
$$D_{xy} = (D_T - D_L) \cos\theta \sin\theta$$
$$D_z = D_T \tag{57}$$

<u>Laminate</u>. Let h_k is the thickness of each layer

h is the total thickness i.e., $h = \sum_{k=1}^{n} h_k$

n is the number of layers

θ_k is the angle made by the fiber with the x-axis in the k-th layer

ϕ_k is the angle made by the fiber with the y-axis in the k-th layer ($\phi_k = 90° - \theta_k$)

The xy-plane is the plane of the laminate, and the z-axis is normal to the plane of the laminate. Then,

$$D_x = \frac{D_L}{h} \sum_{k=1}^{n} h_k \cos^2\theta_k + \frac{D_T}{h} \sum_{k=1}^{n} h_k \sin^2\theta_k$$
$$D_y = \frac{D_L}{h} \sum_{k=1}^{n} h_k \sin^2\theta_k + \frac{D_T}{h} \sum_{k=1}^{n} h_k \cos^2\theta_k$$
$$D_z = D_T \tag{58}$$

5. <u>Conclusions.</u> Reference [19] provides a list of several other current works on the effects of moisture in fiber-reinforced composites. *All of these show* that there is a growing awareness of the importance of this study. It is now well established that moisture and temperature may cause degradation of matrix-dominated flexural and strength properties. But the results are so scattered that hardly any generalized conclusion can be drawn as regard to the actual behavior of composites in a moisture environment. This is mainly because of the fact that the polymerisation process itself is a complicated one and never complete even for a single group of polymers. It varies considerably with the amount and nature of catalysts or curing agents, heat, pressure, manufacturing process, environmental conditions, and so on. All these will no doubt be responsible for finally governing the actual response of polymers to moisture and service temperatures. Therefore, a clear insight into the material behavior in the molecular level is essential to understand the basic phenomena of moisture diffusion and heat transfer.

Moreover, in fiber reinforced plastics, as the polymerisation or curing is carried out only in presence of fibers, the interface between the fiber and matrix plays a distinct and *significant role. Therefore* it is also emphasized that the material level study must include and identify the effect of fiber-matrix interaction in the polymerisation process. Once this is carefully done, it will be possible to sort out and connect the missing link that is so vital in predicting and correlating the real behavior of composites in both micro- and macro-levels.

From the mechanics view point, the study mainly concentrates in micro- and macro-levels. The analytical and experimental research should be planned to supplement each other and should consist of the major problem areas as listed below. These may again be sub-divided into several groups and sub-groups depending on the complexities and nature of the problems and materials (polymers and fibers) used. We however cite here only the major ones.

1. The coupled behavior of moisture diffusion and heat transfer in fiber composites including effects of interface and curing stresses for various fiber arrangements, namely, square and hexagonal (transverse isotropy) and rectangular (transverse orthotropy).

This is a micro-level investigation and will result in determination of diffusion coefficient, coefficients for hygroscopic expansion and thermal expansion, and their dependence on temperature and moisture.

2. Establishment of constitutive relations for a laminated composite system including hygrothermal effects.

This is essentially a macro-level study, but should include micro-level information regarding effects of interlaminar and residual stresses.

3. Study of strength characteristics and defining failure modes for unidirectional (micro) and laminate (macro) composites.

This is a complex problem area. We may start with any of the following approaches for our investigation. (i) Proceed with elastic solutions as in 1 and 2, assume a failure criteria

for each of the constituents or for the composite as whole, and then derive the scheme of progressive failure and predict final failure. (ii) Assign (or obtain) limit loads for the constituents and try to obtain a bound for the actual ultimate load for the composite as a whole.

However, it is again stressed that the correct interpretation of behavior at the material level will considerably improve the basic understanding and subsequent formulation of the failure mechanism in higher levels (micro and macro).

4. Solutions of specific boundary value problems of practical interest.

One should note that a realistic solution must include sufficient (if not all) information from the problem areas stated above.

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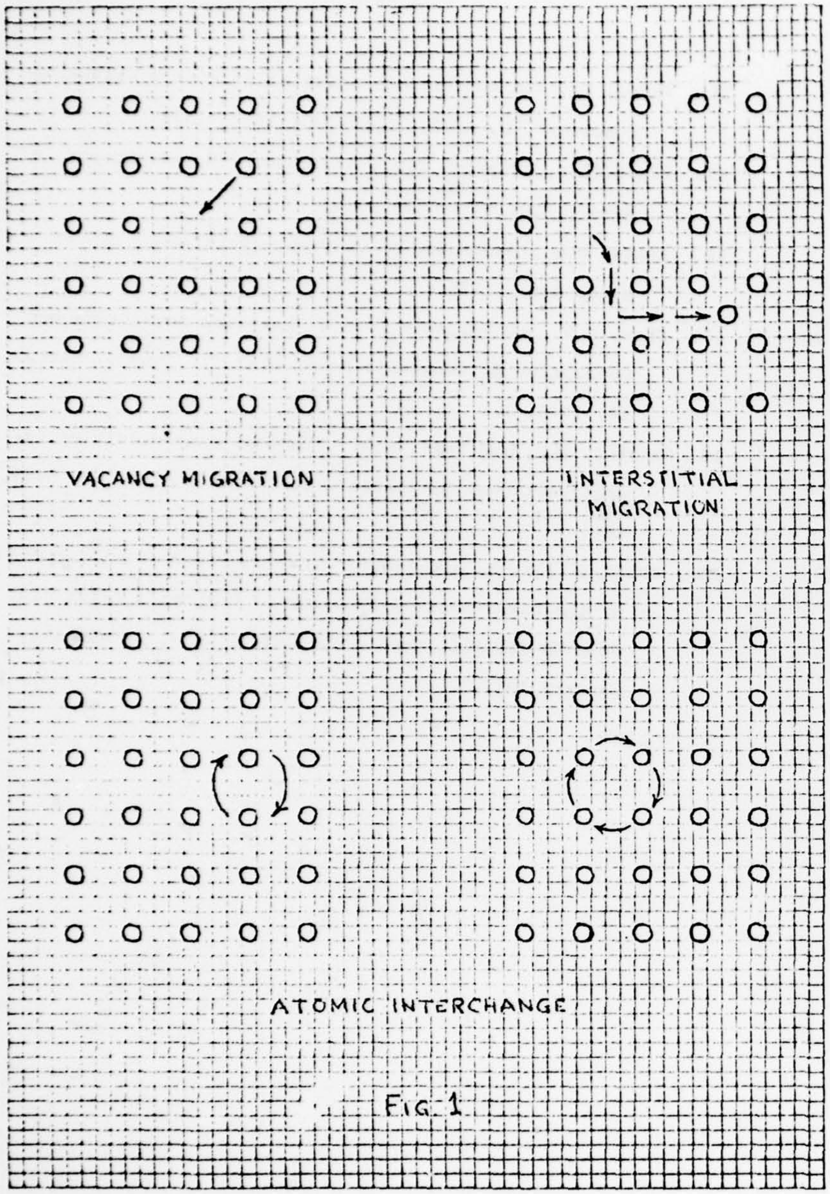

FIG. 1

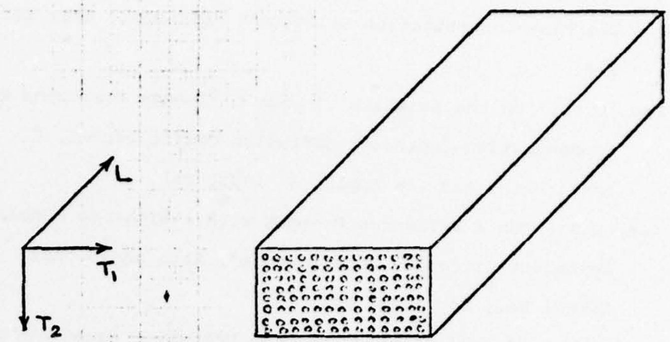

FIG. 2

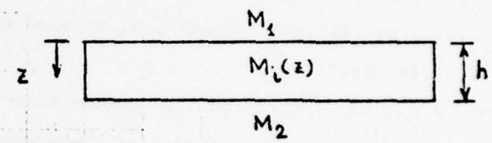

FIG. 3

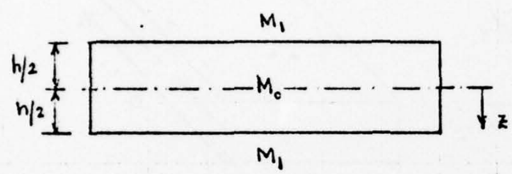

FIG. 4

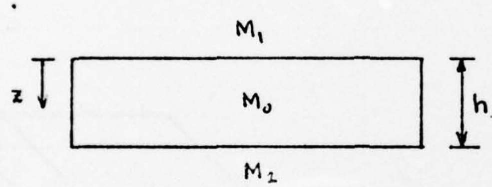

FIG. 5

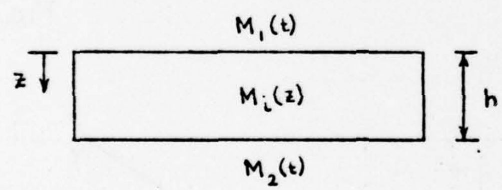

FIG. 6

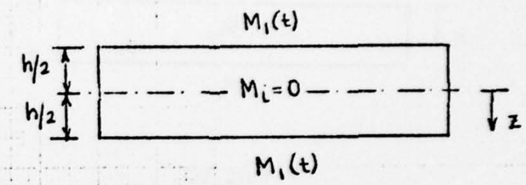

FIG. 7

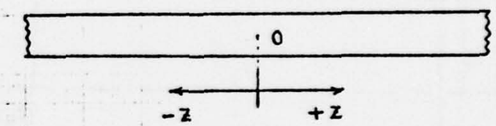

FIG. 8

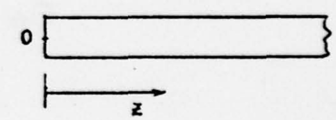

FIG. 9

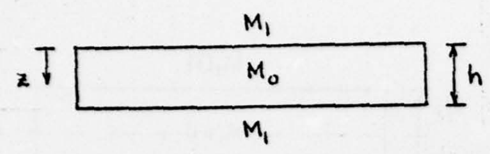

FIG. 10

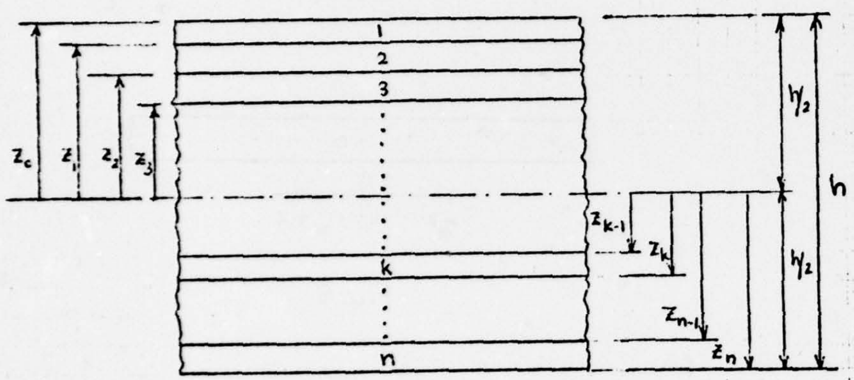

FIG. 11

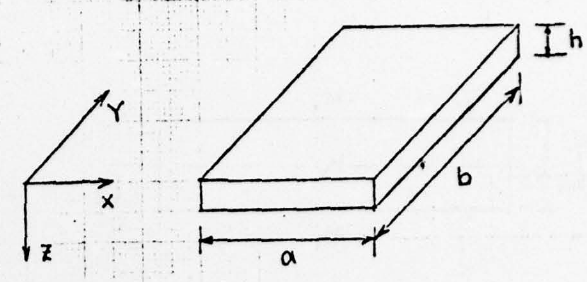

FIG. 12

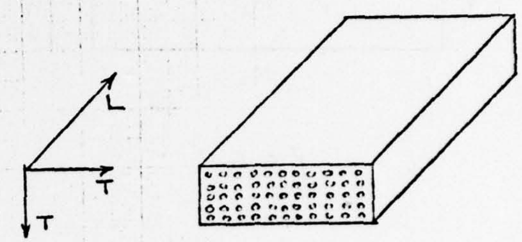

FIG. 13

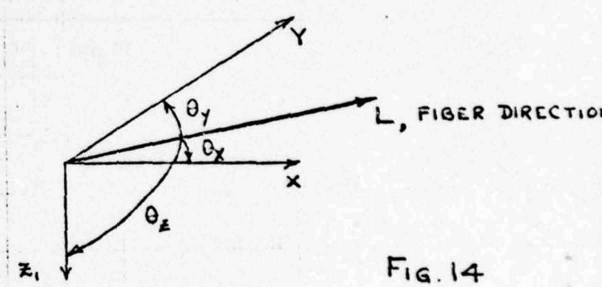

FIG. 14