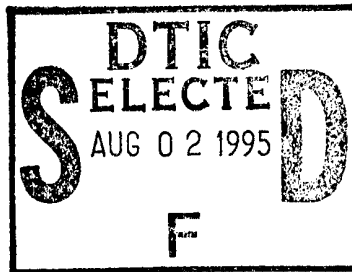4

# CONTRACT TECHNICAL REPORT

*"Effects of Fluids on Polymeric Composites - A Review"*
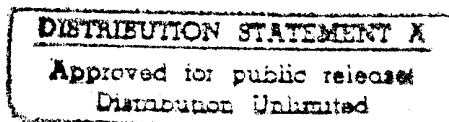
By

Y. Jack Weitsman

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This report presents a review of the effects of fluids on the response of polymeric composites. It contains a comprehensive listing of data regarding sorption processes, which are divided among several categories. Some categories are noted to be associated with reversible "benign" effects while others are correlated with irreversible phenomena that lead to property degradation and failure.

In addition, the report contains several chapters that deal with specific aspects of fluid effects on mechanical properties. These aspects include creep, durability, strength and fatigue.

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# EFFECTS OF FLUIDS ON POLYMERIC COMPOSITES - A REVIEW

Y. Jack Weitsman

## 1. INTRODUCTION

The sorption of solvents in polymeric composites and their effects on composites' performance are highly complex issues. Their study involves, in the least, the disciplines of polymer science and applied mechanics, where the former focuses on molecular-level interactions and the latter is concerned with mechanical response. A comprehensive review of this subject is a formidable task that may require an interdisciplinary team effort rather than an individual undertaking. The current review is based upon information gleaned from several hundred articles, while it is safe to assume that the total number of papers related to the current subject runs into the thousands.

What strikes the reader of articles related to fluid sorption and fluid effects in polymeric composites is the immense variety of materials and circumstances associated with the above subjects. To begin with, polymers are highly complex materials that vary in structure and physico-chemical properties, and polymeric composites adjoin an assortment of fibers with extremely intricate fiber/matrix interphases and interfacial bonding to an already knotty situation. The complexity is further compounded by the ingress of fluids of many kinds, which interact differently with the polymer, the fiber and the interphase matters within the composite.

The main issues associated with the mechanical performance of composites in the presence of fluids concern their dimensional stability, strength, fatigue response, and impact resistance. To a large degree these issues are only partially resolved at the present time even in the absence of fluids. Consequently, the best that can be expected from this review is the

1

gaining of a certain insight into the various phenomena associated with fluids in composites and the derivation of some guidelines towards evaluating their effects.

The kinetics of fluid sorption in polymers has been studied for about one and a half centuries, perhaps beginning with Fick (1855). Among the review articles on the subject one may cite several references (Rogers, 1965, 1985; Crank and Park, 1968; Stannett and Hopfenberg, 1972; Frisch and Stern, 1983), as well as several books (Crank, 1975; Ghez, 1988; Shewmon, 1983).

The effects of fluids on the creep response of polymers were studied intensively by several Russian researchers in the early 1970s. These studies are noted in a review article (Maksimov and Urzhumstev, 1977).

The interest in fluid sorption and fluid effects in polymers received in new impetus in the West during the mid 1970s with the advent of polymeric composites. Information regarding these investigations can be found in several review articles (DeIasi and Whiteside, 1978; Komorowski, 1983a, 1983b, 1983c, 1983d; Marom, 1989) as well as in three volumes of collected works (Springer, 1981, 1984b, 1988). Nevertheless, until recently the issue of fluid effects on composites has been considered of only secondary importance for the following reasons: at the "low tech" end, glass fiber composites were utilized in the boating industry. While such composites exhibit substantial sensitivity to fluids, these detrimental effects were overcome by over-design, with lesser concern for any possible waste in weight or performance. On the other hand, at the "high tech" end, carbon fibers formed the mainstay component of polymeric composites that were utilized for aerospace applications. While tight performance and design requirements were imposed in this case, carbon-fibers are largely immune to solvents and the

2

environmental exposures of practical concern were much less severe than in the boating industry.

It appears that the interest in environmental effects on composites may be rekindled due to new applications contemplated for these materials, which combine severe exposures and tighter design requirements. These new applications occur in the offshore oil industry, in naval submersibles and in the automotive industry. Since this review focuses on concerns related to the foregoing applications it is somewhat biased in that direction. For instance, it contains aspects of the stress corrosion cracking of glass and lists information regarding the effects of fuels and motor oils but omits reference to kevlar-fiber composites or to the detrimental effect of thermal spiking that are relevant to other applications.

## 2. SORPTION PROCESSES

(a) Basic Considerations. Linear, One Dimensional, Fickian Diffusion.

The simplest model for the diffusion of solvent into a solid is given by the linear Fick's Law (1855). Accordingly, the flux of the solvent, $\underline{F}$, is proportional to the (negative of) concentration grandient $\nabla m$. In the one dimensional case we have

$$F = -D \frac{\partial m}{\partial x} \tag{1}$$

where D is the diffusion coefficient.

The negative sign in equation (1) indicates that the flux is directed from high concentration to low concentration regions.

Conservation of mass states that

3

$$\frac{\partial m}{\partial t} = -\frac{\partial F}{\partial x} \tag{2}$$

Thereby, combining equations (1) and (2) we obtain the well known one dimensional version of Fick's law

$$\frac{\partial m}{\partial t} = D\frac{\partial^2 m}{\partial x^2} \tag{3}$$

It should be noted that the above equations can be derived from the statistics of a random walk process (e.g. Ghez, 1988).

The field equation (3) is accompanied by initial and boundary conditions, the simplest of which are

$$m(x, 0) = m_0 \qquad\qquad -L < x < L \tag{4}$$

and

$$m(\pm L, t) = m^b \qquad\qquad 0 < t < \infty \tag{5}$$

which correspond to a constant initial concentration and a fixed boundary concentration, respectively.

The solution of equation (3), with conditions (4) and (5), is well known (Crank, 1975) and is expressible in two well known alternate forms (Crank, 1975), which can be written compactly. Accordingly (Weitsman, 1981, 1991), the distribution $m(x, t)$ is given by

$$m(x, t) - m_0 f_0(x, t) = m^b f(x, t) \tag{6}$$

where

4

$$f_0(x,t) = \begin{cases} C(x,t) \\ or \\ 1 - E(x,t) \end{cases} \quad \text{and } f(x,t) = \begin{cases} 1 - C(x,t) \\ or \\ E(x,t) \end{cases} \quad (7)$$

In equations (6) and (7)

$$C(x,t) = 2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{P_n} \cos\left(\frac{P_n x}{L}\right) \exp\left(-P_n^2 \, t^*\right) \quad (8)$$

$$E(x,t) = \sum_{n=1}^{\infty} (-1)^{n+1} \left\{ erfc\left[\frac{2n-1-x/L}{(t^*)^{1/2}}\right] + erfc\left[\frac{2n-1+x/L}{(t^*)^{1/2}}\right] \right\} \quad (9)$$

where $P_n = (2n-1)\pi/2$, $erfc(z) = \frac{2}{\pi^{1/2}} \int_z^{\infty} - \exp(s^2)\,ds$, and $t^* = Dt/L^2$ is non-dimensional time.

The version which employs cosines, $C(x,t)$, converges rapidly for long times, while the series containing complementary error functions, $E(x,t)$, converges rapidly for short times.

For an initially dry plate exposed to a constant ambient boundary condition $m_b(\pm L, t) = 1$, the distribution $m(x,t)$, vs. the non-dimensional distance $x/L$ at various non-dimensional times $t^* = Dt/L^2$ is shown in Figure 1.

Extensions to time-varying diffusion coefficient D, which occur due to fluctuating temperatures, and for time varying boundary conditions, can be constructed by straight forward superposition on the basis of expressions (6) and (7) due to the linearity of the problem (Weitsman, 1991).

The total weight gain M(t) is given by

$$M(t) = \int_{-L}^{L} m(x, t)\, dx \qquad (10)$$

The detailed expressions (Crank, 1975) are omitted for the sake of brevity. The magnitude of M(t) is amenable to direct experimental measurement.

For initially dry plates with constant ambient conditions, the plot of relative weight gain $M(t^*)/M(\infty)$ vs. $\sqrt{t^*}$ is shown in Figure 2. ($t^* = Dt/L^2$ is the non-dimensional time in equations (8) and (9)). The above plot serves as a "base line" for comparison with actual data. Two locations of $M(t^*)/M(\infty)$ vs. $\sqrt{t^*}$ are marked on the above "base line" curve to within $\pm$ 1% error. Typical weight-gain data fall within a scatter band of 5% about their average values. Note the existence of a clearly defined saturation value $M(\infty)$. In addition, classical linear diffusion predicts a reflective symmetry between weight-gain data in initially dry specimens and weight-loss data upon drying of saturated coupons (no hysteresis).

(b) Weight-Gain and Diffusion data for Polymers and Polymeric Composites.

It was noted that in many circumstances weight gain data for the sorption and desorption of fluids in polymers do not concur with the predictions of Linear Fickian diffusion shown in Figure 2. Three types of "anomalous" weight-gain data in polymers are shown by curves "A", "B" and "S" in Figure 3 (Rogers, 1965). Some of these anomalies can be attributed to the inherent time-dependent response of polymers (Weitsman, 1990). On the other hand, moisture weight gain data in polymeric composites exhibit departures from linear Fickian behavior along curves "A", "B" and "S", as well as curves "C" and "D" in Figure 3. The deviations along curves "C" and "D" correspond to severe circumstances and are usually associated with irreversible damage and degradations.

Curve "A" in Figure 3, denoted as "Pseudo-Fickian", corresponds to the often encountered circumstance of a continuous gradual increase in weight-gain – never attaining equilibrium (e.g. Grayson and Wolf, 1985). Curve "B" in Figure 3 represents the so-called "Two-Stage Diffusion" behavior, while curve "S" is sometimes associated with a moving diffusion front (Nicolais, et al., 1991). However, curve "C" corresponds to a rapidly increasing moisture content within the composite, which is usually accompanied by large deformations, damage growth, material breakdown and/or mechanical failure.

Curve "D" in Figure 3 accords with weight-loss that is attributable to irreversible chemical or physical break-down of a material. Most commonly, weight losses occur in conjunction with hydrolysis, or the separation of side groups from the polymeric chains, or the dissociation of matter located at the vicinities of fiber/matrix interfaces.

Due to the wide variety of polymeric molecular structures and the large diversity in the polymeric composite material systems it is impossible to make specific predictions that correlate the disparate sorption processes typified by the six weight-gain plots shown in Figure 3 with particular causes. However, a comprehensive review of many data suggest the curves "C" and "D" in Figure 3 correspond most frequently to sorption processes that occur under severe circumstances, such as elevated temperatures, high external stresses or under exposure to high levels of ambient solvent concentrations. As already noted, these types of weight gain data are encountered much more frequently in composites than with "neat" polymers, except when the latter are undercured or contain non-stoichiometic amounts of curing agents. Furthermore, weight-gain data that correspond to curve "C" in Figure 3 are associated with substantial degradations in material properties (Springer et al.,

7

1981). They also portend shortened lives and impending failure of the material system. Loss of material integrity is associated with curve "D" in Figure 3.

Circumstances that correspond to weight-gain data categorized by the various curves in Figure 3 are listed in Table 1. Accordingly, the sorption behavior depends on the material system and, within the same material system, it varies with exposure conditions.

## TABLE 1: TYPES OF SORPTION DATA FOR VARIOUS MATERIALS AND EXPOSURES

| Type of Weight- Gain Date Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| LF | T300/5208 gr/ep | T < 60℃ | C. D. Shirrell, 1978 |
| A | "        " | T > 60℃ | "        " |
| A and/or B | Epoxy and AS/3501-5 gr/ep | Distilled water at 22℃ - 70℃; Humid air and water immersion | J. M. Whitney & C. E. Browning |
| LF | T300/1034 | "        " | C. H. Shen & G. S. Springer, 1981b; & T. Mohlin, 1988 |
| C | "        " | Distilled water at 90℃ | T. Mohlin, 1988 |
| B | Glass/polyester | Distilled water at 40℃ (no external load) | A. Lagrange, Ch. Melennec & R. Jacquement, 1991 |
| LF or A | "        " | Sea water at 40℃, various types of polyester | "        " |
| D | "        " | Distilled water at 40℃ and $\sigma = 0.5\,\sigma_{ult}$ | "        " |
| A or B | SMC-25, SMC-65, SMC-30 EA glass/polyester | 100% RH, 32℃ | A. C. Loos, G. S. Springer, B. A. Sanders & R. W. Tung, 1981 |

TABLE 1 (CONTINUED)

| Type of Weight-Gain Data Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| LF | SMC-25 | 100% RH, 50℃ | A. C. Loos, G. S. Springer, B. A. Sanders & R. W. Tung, 1981 |
| LF | SMC-25, SMC-65, SMC-30 EA | 40% RH, 65℃ | "         " |
| B | SMC-25 | 60% RH, 65℃ | "         " |
| D | "         " | 100% RH, 65℃ | "         " |
| D | SMC-65 | 100% RH, 50℃ and 65℃ and 60% RH at 65℃ | "         " |
| D | SMC-30 EA | "         " | "         " |
| A | SMC-25, SMC-65, SMC-30 EA | Distilled water at 23℃ | "         " |
| LF | "         " | Salt water at 23℃ | "         " |
| D | "         " | Distilled water at 50℃ | "         " |
| B | "         " | Salt water at 50℃ | "         " |
| A | "         " | Diesel Fuel at 23℃ and 50℃ | "         " |
| A or B | "         " | Jet fuel at 23℃ and 50℃ | "         " |
| A | "         " | Gasoline at 23℃ | "         " |

## TABLE 1 (CONTINUED)

| Type of Weight-Gain Data Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| A | SMC-25, SMC-65, SMC-30 EA | Aviation oil at 23°C and 50°C | A. C. Loos, G. S. Springer, B. A. Sanders & R. W. Tung, 1981 |
| LF | SMC-R25 | 100% RH and salt water at 23°C | G. S. Springer, B. A. Sanders & R. W. Tung, 1981 |
| D | " " | 100% RH at 93°C | " " |
| LF | " " | Diesel fuel at 23°C and at 93°C; Lubricating oil at 23°C; Antifreeze at 23°C and at 93°C | " " |
| B | " " | Lubricating oil at 93°C | " " |
| LF | SMC-R50 | 50% RH at 23°C and at 93°C and 100% RH at 23°C | " " |
| D | " " | 100% RH at 93°C | " " |
| A | " " | Salt water at 23°C | " " |
| D | " " | Salt water at 93°C | " " |
| LF | " " | Diesel fuel at 23°C; Lubricating oil at 23°C and 93°C | " " |

**TABLE 1 (CONTINUED)**

| Type of Weight-Gain Data Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| A or B | SMC-R50 | Diesel fuel at 93 ℃; Anti-freeze at 23 ℃ | G. S. Springer, B. A. Sanders & R. W. Tung, 1981 |
| D | "      " | Anti-freeze at 93 ℃ | "      " |
| LF | Glass/epoxy diamine hardener | 12%-100% RH, 25 ℃-90 ℃ | P. Bonniau & A. R. Bunsell, 1984 |
| A | Glass/epoxy dicyandiamide hardener | 28%-100% RH, 25 ℃-90% ℃ | "      " |
| D | Glass/epoxy anhidride hardener | 52%-100% RH, 90 ℃ | "      " |
| LF (?) | XMC-3 adhesive | 50% RH, water and salt water at 23 ℃ | G. S. Springer, 1981 |
| D | "      " | Water at 93 ℃ | "      " |
| B | T300/914 | 70%-98% RH at 50 ℃-70 ℃ | M. Blikstad, O. W. Sjoblom, & T. R. Johannesson, 1988 |
| LF | Cured or undercured epoxy | "Low" temperatures | V. B. Gupta, L. T. Drzal, & M. J. Rich, 1985 |
| A | "      " | "Intermediate" temperatures | "      " |

## TABLE 1 (CONTINUED)

| Type of Weight-Gain Data Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| C | Cured or undercured epoxy | "High" temperatures | V. B. Gupta, L. T. Drzal, & M. J. Rich, 1985 |
| B | Glass/epoxy | Water immersion at 80℃ | H. Hamada, Z. Maekawa, T. Morii, A. Gotoh & T. Tanimoto, 1991 |
| LF | Glass/vinylester acryl-silane surface treatment | Water immersion at 40°, 60°, 80℃ | T. Morii, T. Tanimoto, Z. Maekawa, H. Hamada & K. Kiyosumi, 1991 |
| LF | Glass/vinylester epoxy-silane surface treatment | Water immersion at 40℃, 60℃ | "          " |
| A | "          " | Water immersion at 80℃ | "          " |
| A | S glass/epoxy | Distilled water at 30℃-780℃ | A. Chateauminois, B. Chabert, J. P. Soulier, & L. Vincent, 1991 |
| C | "          " | Distilled water at 90℃ | "          " |

TABLE 1 (CONTINUED)

Type of Weight-

Gain Data

| Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| LF | E glass/epoxy | Water at 22℃ | B. Dewimille, J. Thoris, R. Mailfert, and A. R. Bunsell, 1980 |
| D | "        " | Water at 80℃-100℃ | "        " |
| A | Epoxy | Water at 22℃-100℃ | "        " |
| D | Glass/epoxy and hybrid glass/carbon epoxy | Water at 80℃ | H. Fukuda, 1986 |
| A | Vinylester | Water | H. Hojo, K. Tsuda, K. Ogasawara, & K. Mishima, 1982 |
| D | "        " | Salt water | "        " |
| A | S2 glass/epoxy | 75% RH at 75℃ - first exposure | S. Y. Lo, H. T. Hahn, & T. T. Chiao, 1982 |
| B | S2 glass/epoxy | 75% RH at 75℃ - second and third exposures | "        " |
| D | Swirl mat glass/PPS | Hot water | A. Y. Lou & T. P. Murtha, 1987 |
| A | gr/PPS | Non-impacted and pre-impacted exposed to jet fuel | C.-C. M. Ma, Y. H. Huang & M. J. Chang, 1991 |

TABLE 1 (CONTINUED)

Type of Weight-

Gain Data

| Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| LF | APC-2 | Non-impacted and pre-impacted exposed to jet fuel | C.-C. M. Ma, Y. H. Huang & M. J. Chang, 1991 |
| A | CF/epoxy | Sea water | L. M. Manocha, O. P. Bahl & R. K. Jain, 1982 |
| A | Hybrid CF/kevlar-epoxy | Sea water | "        " |
| D | gl/ep - gr/ep hybrid | Water immersion 70°C | M. A. French & G. Pritchard, 1991 |
| LF | Glass/UP | Distilled water at 23°C | G. Menges & H.-W. Gitschner, 1980 |
| C | Glass/UP | Distilled water at 40°C and 60°C * | "        " |
| A | CF/epoxy | Water and salt water at 60°C | Y. Nakanishi & A. Shindo, 1982 |
| A | Glass/polyester | Water immersion at 60°C with $\sigma < 0.3$ UTS | R. J. White & M. G. Phillips, 1985 |
| C | Glass/polyester | Water immersion at 60°C with $\sigma = 0.6$ UTS | "        " |

*Damage observed

TABLE 1 (CONTINUED)

Type of Weight-

Gain Data

| Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| LF | Epoxy | 97% RH, RT with $\sigma < 0.45$ UTS | M. C. Henson & Y. Weitsman, 1986 |
| A | AS4/3502 gr/ep | " " | " " |
| A | AF126-2 adhesive bond line | 75%-90% RH, 10°C-40°C | W. Althof, 1979 |
| A | FM73 adhesive bond line | " " | " " |
| A | gr/F155 | 95% RH at 49°C | D. L. Clark, 1983 |
| LF | gr/F185 | " " | " " |
| A | gr/F155-gr/F185 lay-up | " " | " " |
| LF | PEEK | Water at 36°C | L. Nicolais, A. Apicella, M. A. Del Nobile & G. Mensitieri, 1991 |
| A | " " | Water at 60°C | " " |
| B | " " | n-heptane at 36°C | " " |
| A | PEEK | Methylene chloride at -32°C | L. Nicolais, A. Apicella, M. A. Del Nobile & G. Mensitieri, 1991 |

TABLE 1 (CONTINUED)

Type of Weight-

Gain Data

| Sketched in Fig. 3 | Material System | Exposure | Reference |
|---|---|---|---|
| S | Several kinds of glass fibers in epoxy, polyester and vinylester | Methylene chloride at 36°C | L. Nicolais, A. Apicella, M. A. Del Nobile & G. Mensitieri, 1991 |
| Between S and LF | "      " | $CH_2$ $Cl_2$ at increasing activities | "      " |
| A | Several kinds of glass fibers and epoxy | Water at 90°C | C. A. M. van den Emde & A. van den Dodler, 1991 |
| C | E-glass roving in polyester and vinylester | "      " | "      " |
| D | Several kinds of glass fibers in epoxy, polyester and vinylester | Sulfuric acid solution at 90°C | "      " |
| B | Vinyl terminated polyether | Various levels of relative humidity and temperature | S. J. Barton & G. Pritchard, 1994 |

Very few data are available regarding moisture distribution with polymers or polymeric composites. Profiles were inferred from weight-gain measurements accompanying specimen sectionings (Althof, 1979). Alternately, profiles of water within AS/3501-5 gr/ep composites were recorded by radioactive measurements of $D_2O$ at several times during the diffusion process (Whiteside et al., 1984). Typical results of the latter technique are shown in Figure 4, where recorded distributions are compared with predictions of linear Fickian diffusion. Inspite of the scatter in the results shown in Figure 4 they tend to corroborate predictions which correspond to weight-gain data which follow curves "A" or "B" in Figure 3 (Cai and Weitsman, 1994).

Another departure from classical, linear behavior is noted when weight-gain data of initially dry coupons are compared against weight-loss data, recorded upon the drying of saturated specimens. Typical such data, shown in Figure 5 for AS4/3501 gr/ep coupons at various levels of applied stress (Henson and Weitsman, 1986), exhibit hysteresis loops that contradict classical predictions. Note the increase with stress in both saturation levels and widths of the hysteresis is loops.

(c) Causes and Models for Non-Fickian Diffusion.

There is a host of possible reasons for non-Fickian diffusion in polymers and yet additional probable causes when considering polymeric composites.

The fact that glassy polymers, with their highly complex molecular configurations, exist in a non-equilibrium thermo-dynamic state accounts for their inherent time-dependent behavior. The above time-dependence is compounded by additional temporal phenomena such as aging (Struik, 1978; Adamson, 1980), ongoing chemical reactions (Maksimov and Urzhumstev,

1977) and advancing cure. The time-dependence is accelerated by the fact the liquids tend to increase the free volume of polymers, thereby lowering their glass transition temperature (DeIasi and Whiteside, 1978; McKague, 1978; Browning, 1978). (Typically by 10°C for each 1% fluid weight gained in the polymer). The increased mobility of the molecular chains and side-groups is denoted as "plasticization". This is an essentially reversible phenomenon that can be accounted by means of the time-dependent diffusion model discussed below.

Many of the above considerations, that fall within the realm of polymer science, are discussed in several review articles (Rogers, 1965, 1985; Stannett and Hopfenberg, 1972; Hopfenberg and Stannett, 1973; Frisch and Stern, 1983; Windle, 1985) and texts (such as Crank, 1975, chapters 7 and 11).

Consequently, the time dependent diffusion process occurs conjointly with the time-dependent mechanical response of polymers, namely creep and relaxation. Accordingly the polymer requires time to approach its new equilibrium state commensurate with externally imposed boundary conditions (Crank, 1953; Long, 1960; Frisch, 1964, 1966; Crank and Park, 1968). More recently, the foregoing circumstance was modelled on the basis of fundamental principles of irreversible thermodynamics and continuum mechanics (Weitsman, 1990) to account for coupled moisture, thermal, and mechanical time-dependent behavior.

Essentially, the source of the non-Fickian sorption noted in curves "A" and "B" in Figure 3 was traced to a time-dependent boundary condition

$$m(\pm L, t) = m_0 + \sum_i m_i \left(1 - e^{-t/t_i}\right) \tag{11}$$

that holds even under exposure to constant ambient conditions, since the polymer cannot adapt instantaneously to the imposed external environment.

It has been shown (Weitsman, 1990; Cai and Weitsman, 1994) that solutions of equation (3) with initial condition (4) and boundary condition (11) (instead of (5)) can account for non-Fickian weight-gain data represented by curves "A" and "B" in Figure 3 and correspond to non-Fickian distributions such as shown in Figure 4.

The time-dependent re-configuration of the polymeric molecular structure may provide at least a partial explanation for the observed increase in the rate of moisture sorption between dry specimens and previously saturated and redried specimens (Mazor and Broutman, 1978; DeIasi et al., 1980; Lo et al., 1982).

In addition, it was noted that fluid saturation levels in polymers and polymeric composites may depend on the amplitudes of eternally applied loads. These saturation levels may increase with the magnitude of external tension (Henson, 1985), as shown in Figure 6. On the other hand, hydrostatic compression may increase or reduce the uptake levels of fluids since external compression tends to drive more fluids into the composite on one hand, while decreasing the free volume entrapped within the polymer on the other hand. Reduced saturation levels with pressure were noted by Avena and Bunsell (1988), while increased levels were observed in other cases (Williams and Gipple, 1991; Kosuri and Weitsman, 1995). A plausable explanation for the above observation is provided by a stress assisted diffusion theory, which accounted for viscoelastic effects (Weitsman, 1990).

Another approach to account for non-Fickian behavior is offered by the "Two-Phase Diffusion" model (Gurtin and Yatomi; Carter and Kibler, 1978; Apicella et al., 1981; Bonniau and Bunsell, 1984; Weitsman, 1990).

Accordingly, a portion n of the diffusing substance is entrapped within the polymeric molecules and becomes immobile while a remaining part, m, remains mobile and continues to diffuse into the polymer. In analogy with the flux concentration-gradient and conservation of mass equations (1) and (2) one obtains

$$D\frac{\partial^2 m}{\partial x^2} = \frac{\partial}{\partial t}(m + n) \tag{12}$$

with the initial condition (4) imposed on (m + n) and the boundary condition (5) applying to the mobile portion m only.

In addition, the rate of change of the immobile portion n is assumed to be governed by

$$\frac{\partial n}{\partial t} = \gamma m - \beta n. \tag{13}$$

It has been shown (Carter and Kibler ,1978; Bonniau and Bunsell, 1984) that the "Two-Phase Diffusion" model predicts weight-gains which correspond to curve "A" in Figure 3.

Another cause for non-Fickian diffusion is due to concentration dependent diffusivity D = D(m), which would render equation (3) to be non-linear.

All three foregoing circumstances predict the occurrence of hysteresis loops of the kind shown in Figure 5 (Henson and Weitsman, 1986). Similar hysteresis loops were noted by other investigators for absorption and desorption data of gr/ep composites (Whitney and Browning, 1978; Shirrel, 1978) and to a lesser extent in "neat" epoxy (Apicella et al., 1981; Henson and Weitsman, 1986; Barton and Pritchard, 1994). Usually, these loops indicate a

desorption process that is initially faster and subsequently slower than the absorption process – a circumstance that is conceptually consistent with the time-dependent boundary condition (11). It may be worth noting that analogous hysteresis loops were noted in the transverse strain of glass/epoxy composites subjected to cyclic environment (Lo et al., 1982).

A more intricate sorption process occurs when diffusion is accompanied by a chemical reaction. The chemical reaction can introduce an inert substance into the host material, in which case solvent absorption is accompanied by an enhanced weight gain. On the other hand, the chemical reaction may involve dissociation of matter, thereby diffusion induces weight losses (Crank, 1975).

A model for diffusion and chemical reaction which occurs at a moving front is represented by the thermal oxidation of silicon (Deal and Grove, 1965; Ghez, 1988) expressed by

$$S_i + O_2 \rightarrow S_i O_2 \tag{14}$$

The distribution $C(x, t)$ of the excess of $O_2$, when the moving oxidation front is located at $x = L(t)$, is sketched in Figure 7 (Adapted from Ghez, 1988).

In that figure $C(x,t)$ denotes the concentation of oxygen, with values of $C_0$ and $C_L$ at the outer boundary and at the oxide/silicon front, respectively. Also, $f_0$ denotes the flux of $O_2$ from the ambient into the oxide and $r$ is the rate of the reaction in equation (14). The concentration of $S_i O_2$ within the oxide layer is assumed constant, say $C_i$.

Conservation of oxygen mass at the moving boundary $x = L(t)$ gives

$$D \frac{\partial C}{\partial x}\bigg|_{x=L} + r + C_L \dot{L} = 0 \tag{15}$$

In view of the foregoing assumption of constanct $C_i$, the reaction rate is given by

$$r = C_i \dot{L} \qquad (16)$$

Assuming that r is linear in the oxygen concentration $C_L$

$$r = kC_L \qquad (17)$$

one obtains from equations (15), (16) and (17) that

$$D \frac{\partial c}{\partial x}\bigg|_{x=L} + kC_L(1 + C_L/C_i) = 0 \qquad (18)$$

If one further assumes a linear distribution of $C(x, t)$ in x, which corresponds to the steady-state case, and makes some further reasonable simplifications regarding the relative magnitudes of various terms in equations (15) - (18), the above expressions provide a relation for the velocity dL/dt of the moving front. Integration with respect to time t yields the parabolic expression

$$L^2/k_p + L/k_L = t \qquad (19)$$

where $k_L$ and $k_p$ are the linear and parabolic rate constants (see Ghez, 1988 for details).

A typical plot of the weight of a reaction product vs. $\sqrt{t}$, based upon equation (19) is shown in Figure 8, where predicted trends are compared against weight-gain data during the oxidation of unreinforced RBSN at 1000°C (Bhatt, 1992). The discrepancy may be attributed to the existence of a complex of oxidation reactions. Nevertheless, the above results can explain increasing weight gains for reactions which involve acquisition of matter, as well as weight-losses if reactions involve dissociation, with time. These weight changes occur in addition to what is attributable to diffusion, thereby,

in combination with curves "LF", "A", or "B", can predict trends consistent with curves "C" and "D" in Figure 3.

Moving fronts of chemically reacted matter were observed in the case of water-vapor induced corrosion of glass (Charles, 1958a) and also in glass fibers exposed to hydrochloric and sulphuric acids as well as to distilled water (Ehrenstein and Spaude, 1984). The latter observations showed that the rate of etching depended on temperature, as may be expected for thermally activated processes. Similar fronts, which separate reacted and non-reacted matter, were noted in glass-reinforced polyester exposed to sulphur, chlorine and other substances (Menges and Gitschner, 1980) and in neat APS/epoxy mixtures, with distinct APS (coupling agent) to epoxy molar ratios, exposed to water (Hoh et al., 1990). Such observations were also reported for PEEK resins (Nicolais et al, 1991) and noted in glassy polymers under various circumstances (Alfrey et al, 1966).

Unfortunately, most of the above observations of reaction fronts were not accompanied by weight-gain or weight-loss data. An exception occurs in the case of the corrosion of glass/vinyl ester composites reacting with NaOH and HCl solutions (Hojo et al., 1982). In that circumstance weight-loss data seem to confirm the suggestion that curve "D" in Figure 3 corresponds to a dissociation of matter caused by chemical reactions.

Unlike the reversible "plasticization" phenomenon which may be related to weight-gains along curves "A", "B" and LF in Figure 3, chemical reactions may destroy the back-bones of polymer chains and dissociate them into separate segments. This phenomenon, denoted as "hydrolysis", is irreversible and would usually result in the leaching of matter and weight loss (curve "D" in Figure 3). Alternately, hydrolysis may have the contrary

effect of inducing micro-cracks within the composite and lead to excessive weight gains (curve "C" in Figure 3).

Though difficult to quantify, the severity of the hydrolysis process increases with temperature and solvent content (Chateauminois et al., 1993) and depends on the material system (Bonniau and Bunsell, 1981; Fukuda, 1986). It seems that the onset of hydrolysis may require some "incubation time" (Maksimov and Urzhumstev, 1977), whose duration depends on temperature and solvent concentration as well. An important review regarding the effects of water on glass reinforced polymers, containing silane interfaces, accounted for atomic-level phenomena (Ishida and Koening, 1978).

It is interesting to note that once a weight-loss had occurred, the re-dried material absorbs ever increasing amounts of fluids upon repeated exposures to ambient environments (Lo et al., 1982). This observation suggests the presence of irreversible damage within the material.

When considering transport phenomena in composites it is important to realize that those materials consist not only of fibrous and polymeric phases but also of fiber/matrix interfaces and/or interphase regions.

It has been argued (Drzal et al., 1982, 1983, 1985; Gupta et al., 1985; Rich and Drzal, 1988; Hoh et al., 1990) that interphase regions may differ from bulk polymers in their chemical composition as well as in the amount of curing agent which they contain. These differences may lead to substantial discrepancies in the amounts of solvent which are absorbed by the polymer and interphase, with larger absorption within the latter – especially if it is undercured (Gupta et al., 1985; Jones et al., 1986; Hoh et al., 1990).

The above observations seem to confirm original, earlier interpretations that viewed the disparate concentrations of liquid in the bulk polymer and interphase matter as caused by an osmosis phenomenon, with

the polymer serving as a semi-permeable membrane (Ashbee et al., 1967; Ashbee and Wyatt, 1969; Walter and Ashbee, 1982, 1984).

The increased content of fluid in the vicinity of the fiber/matrix interface and the osmotic pressure combine to weaken the interfacial strength and bring about interfacial cracking (Ashbee et al., 1967; Ashbee and Wyatt, 1969; Walter and Ashbee, 1984) that has been observed by other investigators as well (Menges and Gitschner, 1980; Fang, 1986; Weitsman, 1991). These interfacial cracks are shown in Figure 9 below.

The effect of osmotic pressure may be compounded by the micro-level tensile stresses caused by the mismatch in mechanical and expansional properties of the resin and fiber materials (Tsotsis and Weitsman, 1990).

An alternate interpretation for the weakening of the interfacial bond between fibers and matrix due to the advent of fluids derives from consideration of chemical reactions that occur at the interfaces (Meyer et al., 1994). The progression of these rate-dependent reactions was correlated with observed degradation of the bond strength during single-fiber pull out tests.

The formation of interfacial cracks, as well as voids, may be the primary cause for an increase in the amount of solvent absorbed by the composites, resulting in a transition from weight-gain along curve "A" to weight-gain along curves "C" and "D" in Figure 3 (Menges and Gitschner, 1980; van den Emde and van den Dolder, 1991). It is also interesting to note that cyclic exposure to wet/dry environments increased the extent and amount of interfacial fiber/matrix cracks, with drying seemingly contributing more intensively to crack formation (Weitsman, 1991).

## 3. MOISTURE INDUCED SWELLING, TEMPERATURE DEPENDENCE, AND TIME SCALES

Upon absorption, liquids induce expansional strains into the polymer that are akin to thermal expansions. Typically, the coefficient of moisture expansion in polymers, $\beta$, ranges between $2 \times 10^{-3}$ and $5 \times 10^{-3}$ per 1% weight gain (Adamson, 1980; Cairns and Adams, 1984). When compared with the coefficient of thermal expansion, of typical value $\alpha \sim 2 \times 10^{-5}$ m/m/1°C, we arrive at the rough estimate that the expansional strain due to 1% moisture weight-gain is equivalent to the effect of about 100°C of thermal excursion.

In many circumstances fluids induce swelling only upon reaching some threshold value, say $m_1$. Thus, the expansional strain is given by $\varepsilon^H = \beta (m - m_1)$. Typically $m_1 \sim 0.1\%$.

The coefficient of moisture diffusion $D$ is extremely sensitive to temperature and may increase by two orders of magnitude with a temperature rise of 100°C (DeIasi and Whiteside, 1978; Shirrel, 1978; Loos and Springer, 1981; Grayson and Wolf, 1985; Harper and Weitsman, 1985). A typical value of $D$ at room temperature is $D = D_R \sim 10^{-7}$ mm$^2$/sec.

Temperature sensitivity can be expressed by an Arrhenius – type relation

$$D(T) = D_0 \exp (-A/T) \tag{20}$$

where $T$ denotes temperature.

The immediate consequence of the exceeding small values of $D$ is a very slow diffusion process. In fact it may require several months to saturate polymeric or polymeric composite plates even as thin as 1 mm. In accordance with equation (9) the time-to-saturation increases with the square of the thickness, $t_{saturation} \sim L^2$.

On the other hand, for polymeric materials the coefficient of thermal diffusion $k \sim 10^{-3} \, mm^2/sec$. Consequently, heat conduction may be uncoupled from moisture diffusion, but moisture diffusion cannot discard temporal fluctuations in temperature in view of the extreme sensitivity of D to T. Moisture saturation levels depend on the ambient level of solvent (e.g. the relative humidity of water vapor) and to a lesser degree on temperature and mechanical stress.

As will be discussed in more detail in the next section, the viscoelastic behavior of polymers depends on moisture content. Since typical time-spans for creep (which are also extremely sensitive to temperature) may extend up to several days, or even weeks and months, the viscoelastic response of polymers and polymeric composites is strongly coupled with the diffusion process (Weitsman, 1977, 1979, 1987, 1990, 1991; Douglas and Weitsman, 1980; Harper and Weitsman, 1985).

## 4. FLUID EFFECTS ON THE MECHANICAL RESPONSE AND MECHANICAL PROPERTIES OF POLYMERIC COMPOSITES

(a) Elastic Behavior.

The expansional strains, which accompany the sorption of fluids, induce residual stresses within composite materials, analogous to the thermal stresses that arise therein in the presence of geometrical constraints. Essentially, these residual stresses develop on the micro-scale, due to the mismatch between the properties of the fiber and the matrix, as well as on the ply/laminate level due to the discrepancies between longitudinal and transverse ply properties. The formulation and solution of these stress fields in composite laminates, for linear elastic behavior, are given in standard texts (Jones, 1975; Agarwal and Boutman, 1980; Hull, 1981; Vinson and Sierakowski, 1986; Gibson, 1994) and will not be reproduced here.

(b) Viscoelastic Response.

Fluids accelerate the time-dependent response of polymers and polymeric composites in a manner that is analogous to the influence of temperature. The effect of moisture can be related by a "time-moisture superposition" (Mochalov et al., 1972; Maksimov et al., 1975, 1976a, 1976b, 1972, 1976; Maksimov and Urzhumstev, 1977; Crossman et al., 1978; Renton and Ho, 1978; Ho and Schapery, 1981; Flaggs and Crossman, 1984; Harper and Weitsman, 1985) similar to the well known time-temperature superposition in thermoviscoelasticity. Accordingly, the effect of moisture can be formulated by means of a moisture dependent "shift factor" $a_H(m)$, which is coupled with the temperature-dependent shift $a_T(T)$. Though, in principle, the combined effects of moisture and temperature require a shift factor function of the for $a_{TH}(T,m)$, in many circumstances it was possible to coalesce creep data into a "master curve" by the more convenient product form $a_{TH}(T,m) = a_T(T) \cdot a_H(m)$ (Maksimov et al., 1972; Renton and Ho, 1978; Ho and Schapery, 1981; Harper and Weitsman ,1985).

Typical moisture and temperature affected creep data for $\left[\pm\ 45^{\circ}\right]_{2S}$ AS/3502 gr/ep composites are shown in Figure 10. These data may be represented by a family of surfaces such as sketched in Figure 11 and coalesced with the aid of shift-factors to form the master curves depicted in Figure 12.

For the data shown in Figure 10 and 12 the moisture and temperature shift factors are expressed by $a_T(T) = \exp(B - T/A)$ and $a_H(m) = \exp(-K_0 m + K_1)$ with B = 45.81, A=6.258, $K_0$ = 5.2 and $K_1$ = 0.26, where T is in °K and m in per-cent weight gain.

Several viscoelastic solutions that account for moisture and temperature effects (Weitsman, 1977, 1979; Douglas and Weitsman, 1980;

29

Flaggs and Crossman, 1984; Harper and Weitsman, 1985) demonstrate that viscoelastic relaxation accounts for a behavior which differs qualitatively from elastically predicted response. Specifically, upon subjecting a viscoelastic material to a humid environment, and subsequently to a dry ambient, the swelling strains introduced during moisture absorption, which tend to induce compression within the polymer, are followed by shrinkage caused by solvent withdrawal during the drying stage and a reversal in the stress amplitudes. However, since shrinkage is superimposed on the relaxed effect of the earlier swelling the resulting reversal in stresses will over compensate the relaxed levels of the previously imparted compression, yielding a net tensile outcome.

The foregoing viscoelastic formulations and solutions are useful for analyzing stresses and, particularly, for determining dimensional changes due to creep in polymeric composites. On the other hand it is important to recognize that the above methodology is restricted to linear viscoelastic response and applies to a limited range of stresses, temperatures and moisture content (Maksimov and Urzhumstev, 1977) and cannot account for such effects as damage. For instance, linear viscoelastic analysis may explain the emergence of tensile cracks upon drying of previously saturated resins (Browning, 1978) and composites (Jackson, 1984; Fang, 1986; Weitsman, 1991) and may account for the ever increasing departures between weight-gain data and prediction of classical diffusion theory shown in Figure 13. However, the proliferation of damage that ensues from the cycling of ambient moisture and which, in turn, amplifies the amount of sorbed fluid cannot be predicted by linear viscoelasticity. (Note that the synergism between moisture and damage is corroborated by the observation that, when coupled with an external load, exposure to cyclic ambient environment greatly accentuated the

creep of Kevlar fibers (Dillard et al., 1991)). Furthermore, linear hygrothermal viscoelasticity does not apply in circumstances that involve chemical reactions and does not account for the subsequent damage (Hull and Hogg, 1980). It would therefore be incorrect to utilize that theory in circumstances where solvent weight-gain data follows curves "C" or "D" in Figure 3, since the latter weight-gains are associated with excessive creep and early failures (Chateauminois et al., 1991). The presence or absence of satisfactory correlation between theory and experiment may also be inferred by comparing weight-gain data (Springer et al., 1981) and creep data (Springer, 1984a).

Another important observation concerns the long-term creep of polymeric composites. It has been noted on several occasions (Jain et al., 1979; Jain and Asthana, 1980; Menges and Gitschner, 1980) that the creep response of wet composites may accord with linear hygrothermal viscoelasticity for a limited duration to be followed by a noticeable upsurge in deformation as sketched in Figure 14. It seems that the increase in creep strains occurs after certain incubation-times required for the inception of additional mechanisms or reactions within the polymeric composite.

Viscoelastic behavior is associated with the damping capacity of the material and, in the absence of irreversible damage, may be correlated with the properties of the matrix (Coulter, 1981). Experimental data for gr/ep and gr/PEEK composites (Adams and Singh, 1991) exhibit a substantial increase in damping of gr/ep with exposure to hot/wet environment which could be correlated with reduced mechanical properties. It is inferred that in gr/ep (but not for glass fibers) those effects are recoverable upon re-drying.

(c) Strength and Durability.

It was already noted that fluids introduce residual stresses into polymeric composites and affect the mechanical fields by enhancing the creep and relaxation processes. In addition, it was remarked that fluids may degrade polymers and fiber/matrix interfaces by hydrolysis and chemical attack, induce osmotic pressure within interphase regions that contributes to the weakening of fiber/matrix bond, and chemically decompose the fibers themselves – especially glass fibers. Reductions of 30% to 50% in interfacial strength were reported for some graphite/epoxy systems (Kaelble et al., 1974).

The above effects are reflected in significant reductions in the strength of such polymers as epoxy and in the transverse and shear strengths of uni-directionally reinforced polymeric composites (Pomies et al., Hertz, 1973; Kaminski, 1973; Hofer et al., 1974, 1975; Verette, 1975; Browning et al., 1976; Husman, 1976; Dewimille et al., 1980; Shen and Springer, 1981a; Hamada et al., 1991; Juska, 1993).

Typically, one observes degradations of between 25% and 80% in the strength of epoxies and reductions between 50% and 80% in the transverse strength of fibrous composites attributable to the effects of solvents. The above range in the reduced values corresponds to an increasing amplitude of temperature. A decrease of strength with exposure time, ranging between 20% and 50%, was noted for glass/polyester composites immersed in water at 30°C (Norwood and Marchant, 1981).

Lesser reductions were observed in quasi-isotropic laminates and no diminutions occurred in the longitudinal properties of carbon fiber composites. Smaller reductions in transverse strength were also noted in several polymeric graphite and glass fiber composites immersed in sea water (Grant, 1991).

32

It is illuminating to remark that in some circumstances strength reductions in E-glass/polyester sheet moulding compounds (SMC-R50) correlated with moisture weight-losses that accord with curve "D" in Figure 3 (Springer et al., 1981).

Though no information is available about the detailed nature of degradation mechanisms in SMC-R50 caused by water, it is interesting to note that distinct degradation mechanisms were observed in E-glass/polyester SMC composites exposed to chemical solutions. Acids induced stress corrosion cracking within the fibers (Somiya and Morishita, 1993a), while alkalines degraded the fiber/resin interface (Somiya and Morishita, 1993b). The latter circumstance resulted in a more severe reduction in the fracture toughness of the composite.

While carbon fibers are largely immune to solvents, glass fibers are highly susceptible to chemical attack by water, acids and alkaline solutions (Thomas, 1960; Metcalfe et al., 1971; Metcalfe and Schmitz, 1972; Aveston et al., 1980; Bailey et al., 1980; Dewimille et al., 1980; Friedrich, 1981; Aveston and Sillwood, 1982; Jones et al., 1982; Hsu and Chou, 1985; Sheard and Jones, 1986; French and Pritchard, 1991). This susceptibility is noted by the formation of pits on the surface of glass-fibers immersed in water (Ashbee and Wyatt, 1969) and in sea water (White and Phillips, 1985) and by the progression of stress-corrosion cracking, leading to significant reductions in durability, as reflected by shorter times-to-failure in static fatigue under exposure to water and acids (Charles, 1958a, 1958b; Aveston et al., 1980, 1982; Bailey et al., 1980; Dewimille et al., 1980; Hogg et al., 1981; Kelly and McCartney, 1981; Hogg and Hull, 1982; Aveston and Sillwood, 1982; Jones et al., 1982; Hsu and Chou, 1985; Sheard and Jones, 1986; Castaing et al., 1993; Chateauminois et al., 1993). As remarked earlier, the corrosion of glass fibers

is delineated by a sharp front that separates the yet intact core from an outer, corroded, concentrically cylindrical region. Reductions in the strength of glass fibers and their composites can be correlated with the advance of the above corrosion process (Ehrenstein and Spaude, 1984).

It is worth noting that while data on times-to-failure under static fatigue are usually correlated by the expression

$$\sigma = A - B \log t_f \qquad (21)$$

(Zhurkov, 1965), plots of stress $\sigma$ vs. failure time $t_f$ in some composites, such as polyester/glass immersed in sea water, suggest the existence of two-stage mechanisms (White and Phillips, 1985) as depicted in Figure 15. This circumstance resembles the incubation times required for the stepping-up in creep response (Jain et al., 1979; Jain and Asthana, 1980; Menges and Gitschner, 1980; Bird and Allan, 1981). It may also be noted that data on the static fatigue of glass reinforced plastics immersed in sea water (Wyatt et al., 1981), seem to suggest the existence of a two stage mechanism, although they were fitted by the authors according to equation (21).

The foregoing two-stage mechanisms in the evolution of failure under static fatigue were observed also in R glass/epoxy specimens exposed to distilled water (Chateauminois et al., 1993). These mechanisms were interpreted in the context of Talreja's (1981) fatigue model shown in Figure 16. Accordingly, the shorter lives at elevated stress are due to the incidence of random fiber failures attributed to the statistical distribution of the initial flaw population. The subsequent gradual increase in times to failure under lower levels of external loads is deemed to reflect the progressive failure within the composite as broken fibers transfer their loads to intact neighboring fibers. This interpretation may differ from the aforementioned incubation-time suggestion.

For glass-fiber composites, static fatigue limits correspond to about 50% of their "instantaneous" static strength (Thomas, 1960; Metcalfe and Schmitz, 1972; Roberts, 1978; Aveston et al., 1980; Chateauminois et al., 1993). However, significantly larger reductions in both crack initiation times and failure times were noted in several glass/polymer systems immersed in a solution of sulfuric acid (van den Emde and van den Dolder, 1991). Obviously, the durability of polymeric composites exposed to solvents is affected by temperature (Charles, 1958b), since it is governed by thermally activated processes.

In the case of glass fiber cloth reinforced by vinyl ester resins that were immersed in hot water (Morii et al., 1991) it was possible to associate the degradation process with fiber/matrix interfacial failures. This was achieved by considering distinct fiber surface treatments and observing the existence of good correlations between the "knee-point" stress levels and water weight-gain data.

Swirl-mat and chopped mat glass fiber composites exhibit weight-losses when exposed to hot-water above 90°C. These weight losses correlate with reduction of up to 50% in strength and stiffness (Lou and Murtha, 1987).

Basic considerations of crack growth at various stages of the stress corrosion cracking process (Evans, 1972) suggest that chemical reactions control crack growth at low load levels while diffusion of corrosive substance governs the failure process under higher loads. At yet higher stress levels crack growth is dominated by stress assisted corrosion.

Upon drying composites regain a portion or the entire value of their original strength (Phillips et al., 1978; Dewimille et al., 1980; Springer et al., 1981; Manocha et al., 1982; Drzal et al., 1985). The amount of recovery

depends on the extent and kind of irreversible damage caused by the prior exposure to solvents.

Pre-stressing of composites prior to their exposure to fluids may accelerate the solvent-induced corrosion (Sandifer, 1982; Fujii et al., 1993). This enhancement is most likely due to mechanical damage caused by pre-stressing which facilitates the subsequent penetration of fluid through capillary action (Ehrenstein and Spaude, 1984).

Though generalizations are risky and unreliable, it seems that in many circumstances water (distilled or salty) causes more significant reductions in the strength of composites than fuels or motor oils (Sandifer, 1982; Blicblau et al., 1993). In some cases an increase in water salinity tends to intensify the losses in composites' properties (Nakanishi and Shindo, 1982).

(d) Fluid Effects on the Fracture Toughness, Fatigue Response and Impact Resistance of Polymeric Composites.

The fracture toughness of composite materials depends on the combined interplay of energy absorbing micro-mechanisms in the vicinity of a crack tip (Jordan, 1985). These mechanisms include the ductilities of the resin and the interphase material, as well as of the fiber/matrix interfacial bond. It is important to recognize that the capacity of the resin and the interphase matter to undergo ductile deformation is restricted by the confining effects of the stiffer and more brittle fibers.

Liquids enhance the ductility of polymers through plasticization, which should increase the toughness of composites. However, liquids tend to weaken the fiber/matrix interfacial bond and induce osmotic pressures which may assist in the activation of crack growth, thereby diminishing the toughness of composites. The interplay among the foregoing competing effects is difficult to quantify. These contradictory effects may cancel each

36

other, as evidenced by the insensitivity of the extent of edge delaminations in cross-ply glass/epoxy laminates to the presence or absence of water (Yang et al., 1992). Similar insensitivity was observed in the growth of edge delamination in cross-ply gr/ep laminates immersed in sea water, inspite of some differences in detail when compared to dry circumstances (Chiou and Bradley, 1993). On the other hand, it was demonstrated that in gr/ep laminates the ingress of fluids results in a monotonic reduction in the available energy for delamination with the amount of absorbed fluid (Hooper et al., 1991a). Furthermore, the critical energy, which is required to initiate delamination, increased with the amount of absorbed fluid (Hooper et al., 1991b).

Exposure of unidirectionally reinforced E glass plastics to the combined effects of environment and stress may lead to their dramatic embrittlement (Price, 1989). On the other hand, the presence of liquids may greatly enhance the fracture toughness of other composites in certain circumstances, as occurs for mode I delamination of uni-directionally reinforced gr/ep double-cantilever beam specimens immersed in sea water (Sloan and Seymour, 1992). The reason for the latter, seemingly surprising, result is that the extended weakening of the fiber/matrix interfaces caused by sea water gives rise to fiber bridging across the crack surfaces.

Fatigue of composite materials is the subject of much ongoing research (Sendeckyj, 1990). The fatigue response is characterized by crack velocity (da/dt) vs. stress intensity ($K_I$) plots (Friedrich and Karger-Kocsis, 1990) or by the familiar S-N diagrams, except that composites exhibit larger data scatter than metals. The S-N data are described by empirical expressions, with attempted predictions and reliability assessments based upon statistical consideration (Sendeckyj, 1990; Talreja, 1990).

37

A rational, though still qualitative, approach to fatigue in composites was proposed by Talreja (1981), where S-N data were converted from stress space to strain space, namely into $\varepsilon$ vs. N diagrams as shown in Figure 16. The selection of $\varepsilon$ ranging over $\varepsilon_m < \varepsilon < \varepsilon_c$ (where $\varepsilon_m$ and $\varepsilon_c$ denote the fatigue limit strain and static failure strain of the composite, respectively) was motivated by the fact that during fatigue the various phases (and plies) within a composite are subjected to common strains, but to disparate stresses. If failure of a composite can be prescribed by means of a strain criterion then $\varepsilon$ - N diagrams would account more closely for its fatigue response. The foregoing selection seems natural in accounting for environmental effects in cases where the major role of the liquid is confined to enhancing the resin's ductility by plasticization. In addition, it is reasonable to expect that, in the least, the fatigue limit corresponds to a physically meaningful value of $\varepsilon_m$.

The horizontal band about $\varepsilon_c$ in Figure 16 represents failure strains that are independent of the number of fatigue cycles N. These failures are attributable to the random distribution of initial flaw sizes within the composite. At lower strain levels, the sloping band of failure strains $\varepsilon$ vs. N corresponds to a progressive failure process within the composite where the weakening caused by localized failures is taken up by intact regions until the interaction and coalescence of growing cracks reach critical levels that result in failure after N fatigue cycles. The lower horizontal band about $\varepsilon = \varepsilon_m$ in Figure 16 corresponds to a sufficiently low strain level, possibly a matrix property, which is commensurate with the fatigue limit.

In a variety of circumstances it was observed that fluids accelerate the fatigue failure process and shorten the fatigue life of glass fiber composites (Boller, 1964; Phillips et al., 1978; Mandell, 1979; Aveston et al., 1980; Dewimille et al., 1980; Lou and Murtha, 1987; Friedrich and Karger-Kocsis,

1990; Yang et al., 1992) and carbon fiber composites (Sumison, 1976; Morton et al., 1988). The extent of these effects depends on both fluid type and material system (Sandifer, 1982). In addition, the presence of water may affect the failure mechanisms that evolve during the fatigue process (Morton et al., 1988).

It is reasonable to assume that all the aforementioned fluid induced mechanisms, which degrade the strength of composites, operate also to shorten the fatigue life of those materials. Nevertheless, there exist two additional degradation mechanisms that are specific to fatigue. The first involves the synergistic interaction between the solvent sorption process and fatigue induced damage, namely a profusion of microcracks that opens capillary paths for solvent ingress (Jones et al., 1984). This mode of solvent penetration is orders of magnitudes faster than the diffusion process and subjects the composite to accelerated degradation (Kosuri and Weitsman, 1995). The second mechanism involves the synergistic destruction of interfacial fiber/matrix bonds caused by their cyclic rubbing under fatigue loading. The introduction of liquids into the composite enhances the above phenomenon, since liquids act as lubricants (Jones et al., 1984). Evidence for the smoothening and polishing of fiber/matrix interfaces due to moisture abound in the literature, but only circumstantial evidence exists at the present time to imply that the same effect occurs during fatigue (Aveston and Sillwood, 1982; Galea and Saunders, 1993).

All the "wet fatigue" data noted thus far were obtained for specimens with prior, but not concurrent, exposure to fluids. A recent study (Kosuri and Weitsman, 1995) on the effects of sea water on the fatigue of cross-ply gr/ep composites indicates that significant reductions in fatigue life occur especially under immersed conditions, when capillary action is highly accentuated. The

resulting S-N curves are shown in Figure 17. The reduced fatigue life under immersed conditions is observed to occur in association with profound inter-ply delaminations. An analytical model, which explains this phenomenon, was derived recently (Smith and Weitsman, 1995).

The effects of fluids on the impact resistance of composites contain the same contradictory aspects that hold for fracture toughness. In view of the solvent-induced weakening of the fiber/matrix interfacial strength the impacting object may engage a larger volume of fibers in the absorption of the impact energy, thus resulting in improved impact resistance (Strait et al., 1992; Lin, 1993). In addition, the plasticization and enhanced ductility of the wet polymer may explain the observed reduction in the peak amplitudes of the contact pressures during impact (Strait et al., 1992; Lin, 1993). On the other hand, impact induced damage may enhance the amounts of absorbed fluids within the composite under subsequent exposures and lead to long term degradations in residual mechanical properties (Ma et al., 1991).

## 5. CONCLUDING REMARKS

Good basic understandings, accompanied by adequate predictive methodologies, are available to account for sorption mechanisms that are akin to linear Fickian diffusion and for the incorporation of solvent effects within the scope of elastic and linearly viscoelastic material response.

Unfortunately, the above understandings are inadequate for predicting the more intricate, yet crucially important, matters of durability and strength of composites, since no comprehensive formalism is available to account quantitatively for the multitude of materials and circumstances in a manner that may apply to a specific case of interest.

What emerges from this review is the realization that practical design considerations must derive from an adequate data base, specific to each

composite material system. An assessment of the significance of fluid effects can be obtained by recording their weight-gain within the composites. Substantial departures from linear Fickian predictions portend serious degradation in mechanical properties, and should be followed by detailed study and microscopic examination. In addition, careful consideration should be given to circumstances when mechanical loads, temperature and solvents interact synergistically to degrade properties of the composites. To some extent, such considerations may be guided by fundamental concepts of polymer science and applied mechanics. They may also benefit from familiarity with existing knowledge that, at least to a limited extent, may provide general guidance.

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47

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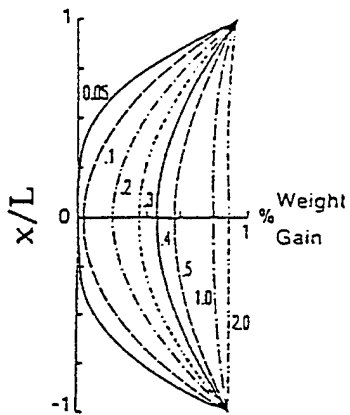
Fig. 1 Moisture distribution
profiles predicted by Fick's
law at various values of
non-dimensional time t*.
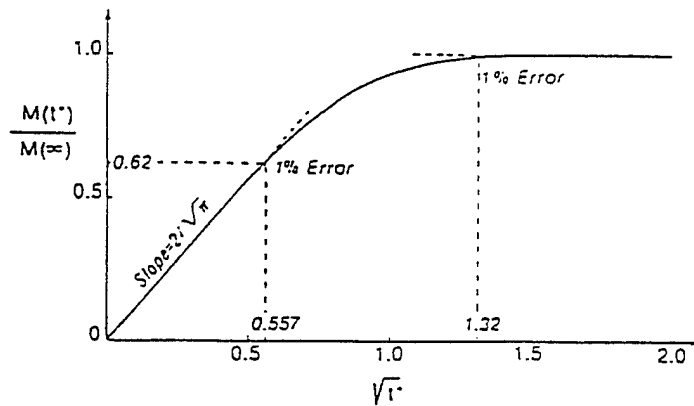


Fig. 2 The total weight gain $M(t^*)/M(\infty)$
vs. $\sqrt{t^*}$ according to Fick's law, with
locations where departures from
straight lines exceed 1%.
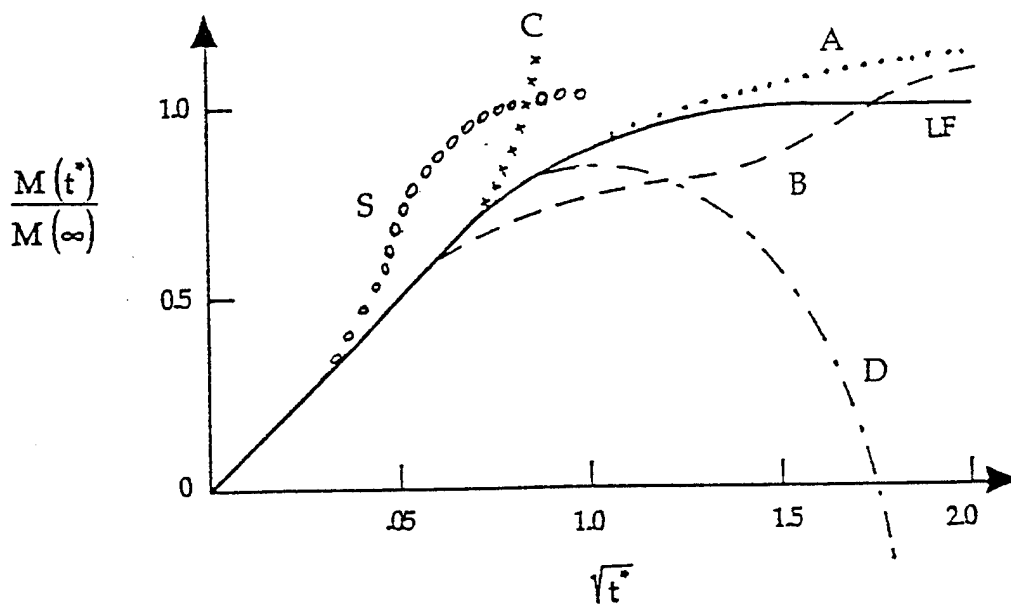


Fig. 3 Schematic curves representing four categories of recorded non-Fickian
weight-gain sorption data in polymers and polymeric composites. The solid
line, designated by LF, corresponds to linear Fickian diffusion.
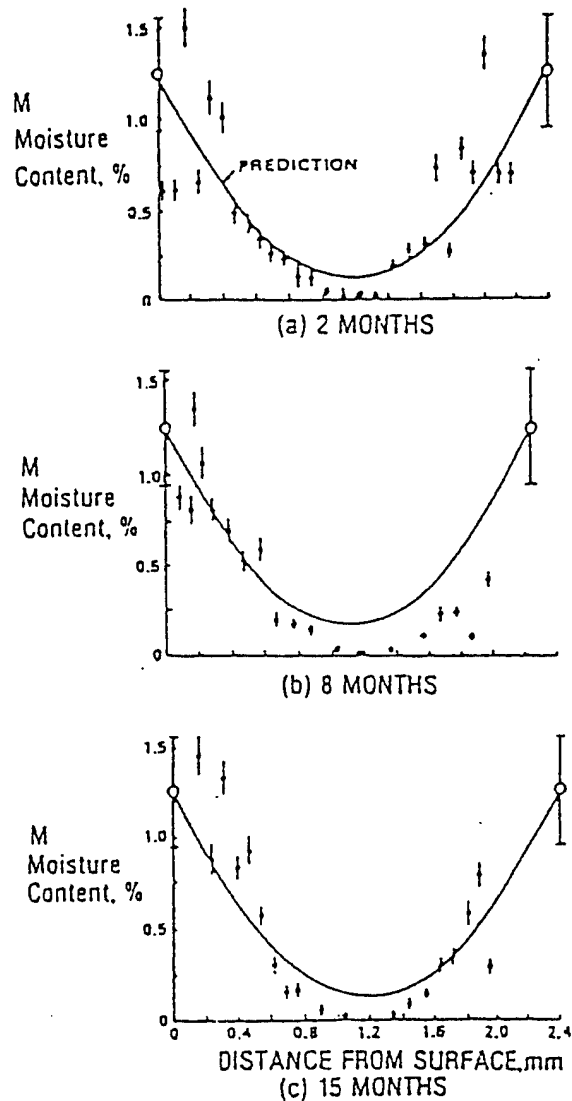
Fig. 4 Recorded concentration values with distribution profiles predicted
by Fick's law (Whiteside et al., 1984). Dots show average recorded
concentrations of heavy water ($D_2O$) after 56 days of exposure to a 70% relative
humidity of $D_2O$ at 305 K (90°F), with vertical lines indicating statistical error.
Cases (a), (b) and (c) refer to pre-exposure to hygrothermal cycles,
after which all specimens were completely redried.
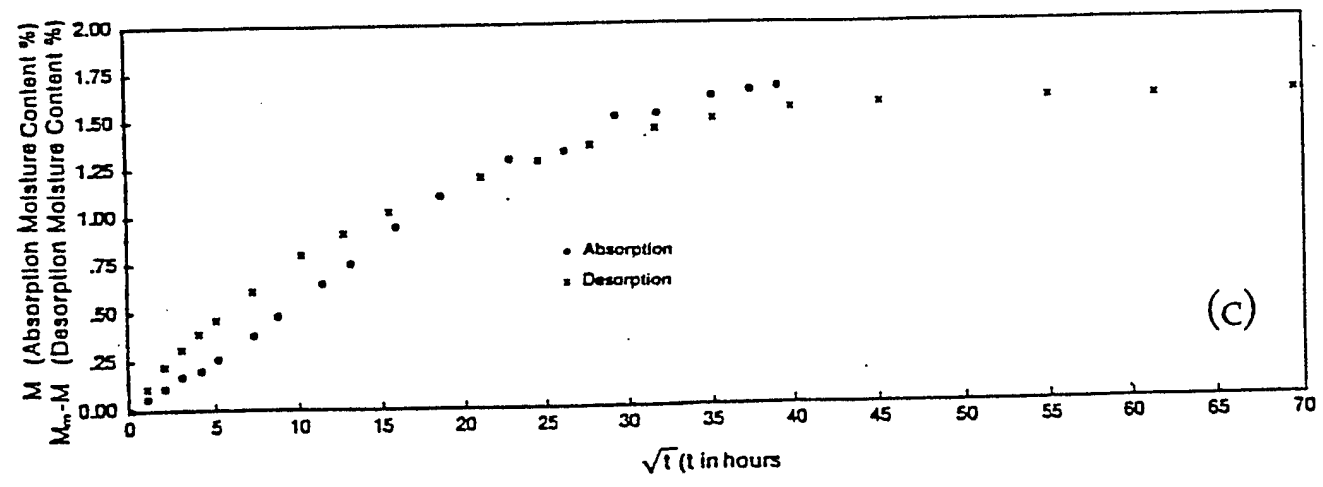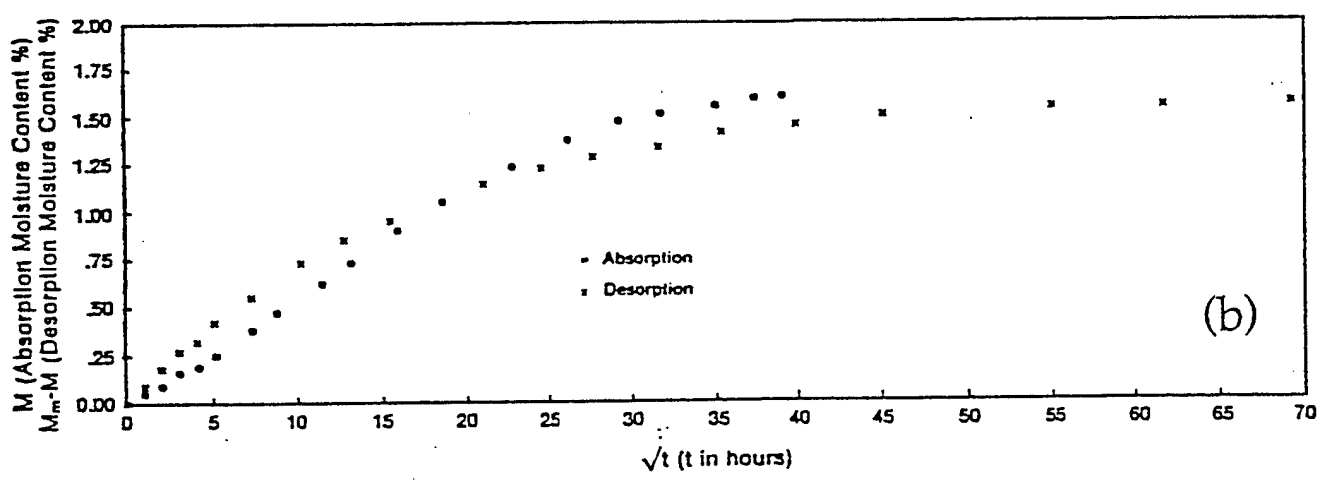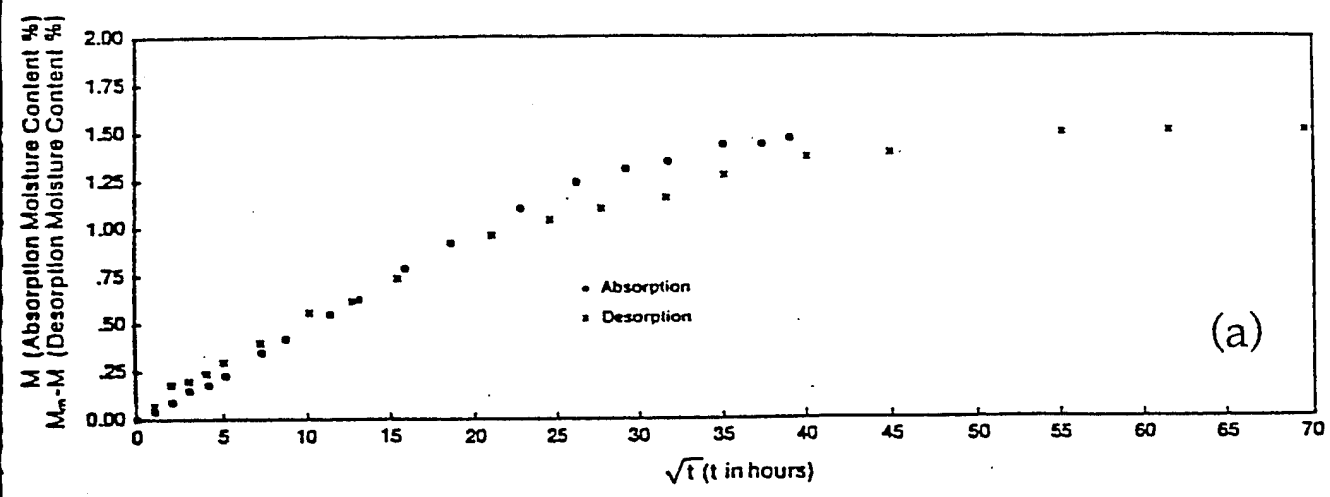
Fig. 5  Hysteresis loops at various stress levels.
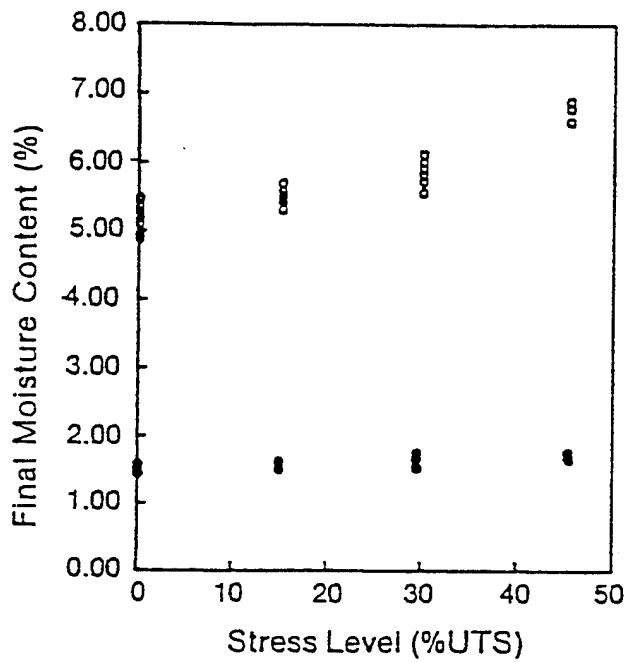
Fig. 6 Maximal moisture content attained in absorption tests vs. stress level under exposure at 97% RH and 40°C. 3502 epoxy after 35 days (open circles) and AS4/3502 composite after 63 days (solid circles).
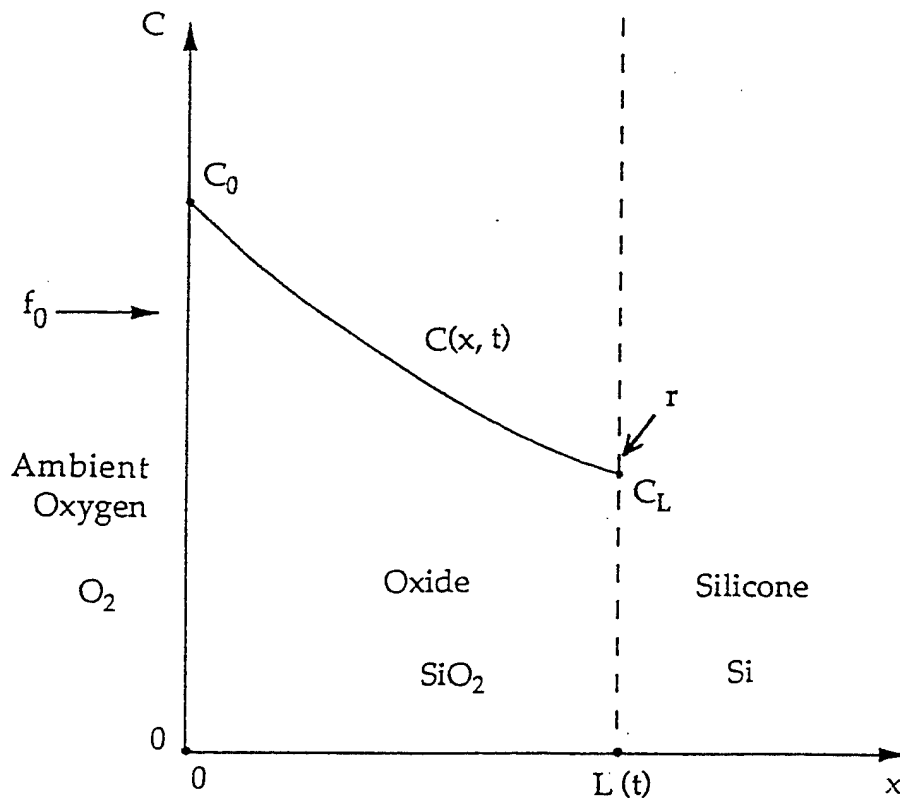


Fig. 7 Three-phase oxidation system and excess $O_2$ distribution in the oxide. (Adapted from Ghez, 1988).
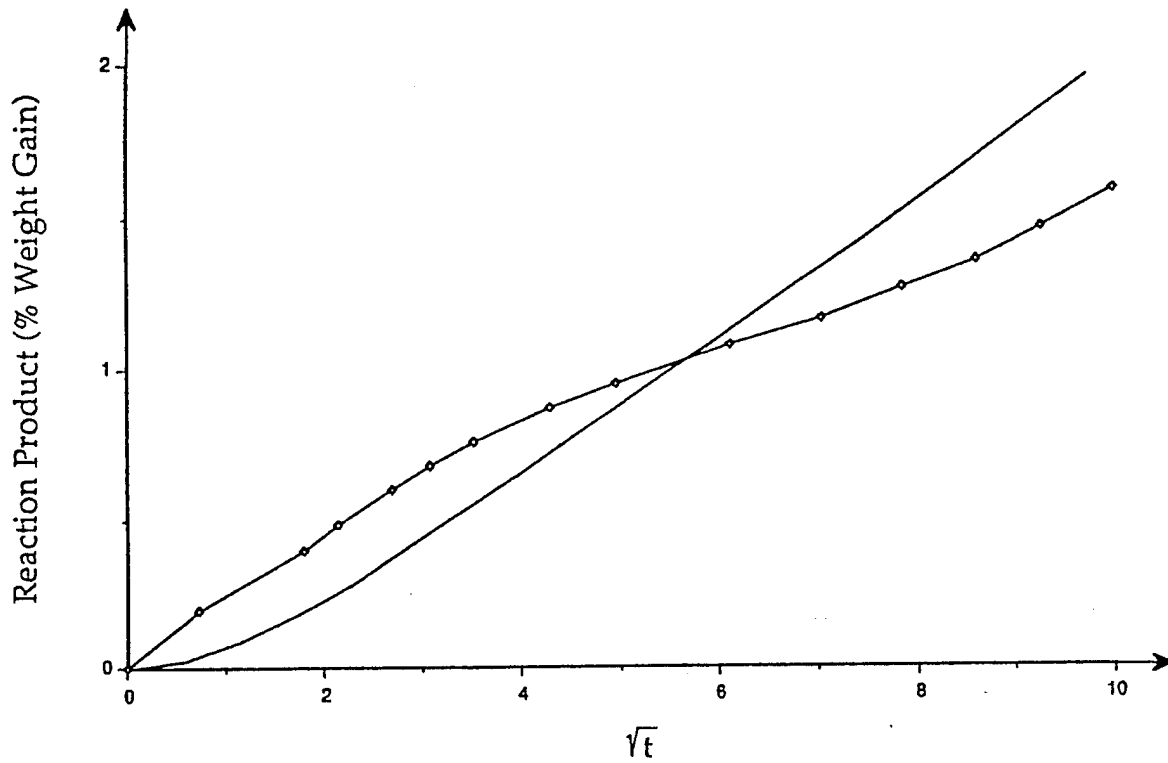
Fig. 8  Reaction product weight gain vs. $\sqrt{\text{time}}$ .  (Time in hours).

———— Predicted by equation (19).  (Schematic)

——◇——◇—— Data reduced from Bhatt (1992).
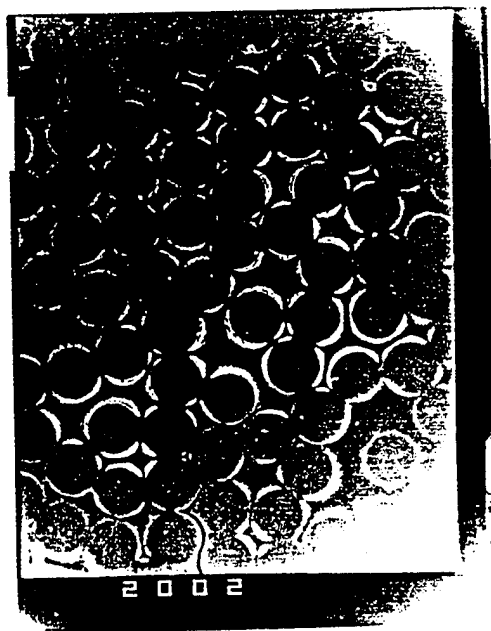


Fig. 9  A micrograph of moisture induced fiber/matrix interfacial cracks.
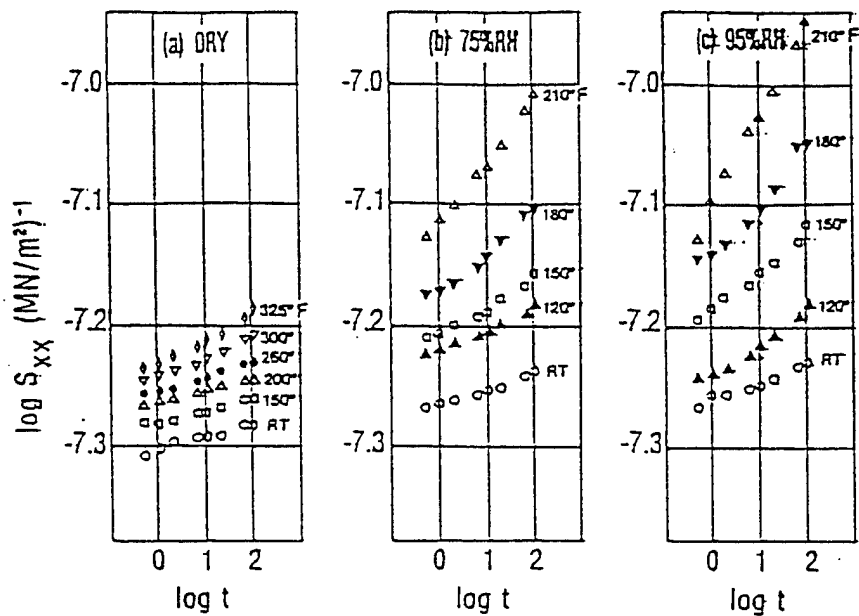
Fig. 10 The creep compliance $S_{xx}$, as recorded at various temperatures and relative humidities, for $[\pm 45]_{2s}$ AS/3502 composite specimens with (a) $R_h = 0\%$, (b) $R_h = 75\%$ and (c) $R_h = 95\%$. (Kibler, 1980).
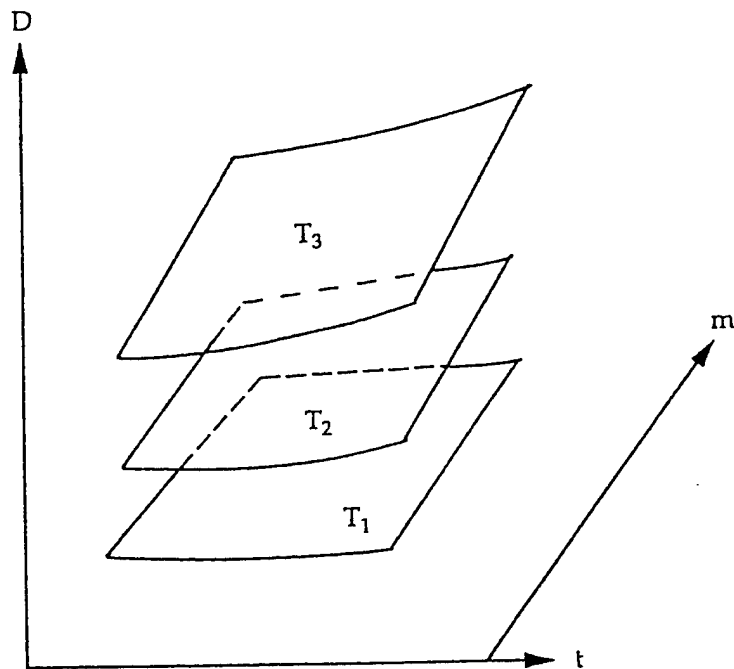


Fig. 11 A schematic drawing of the time-temperature-moisture dependence of the the creep compliance D. $(T_3 > T_2 > T_1)$.

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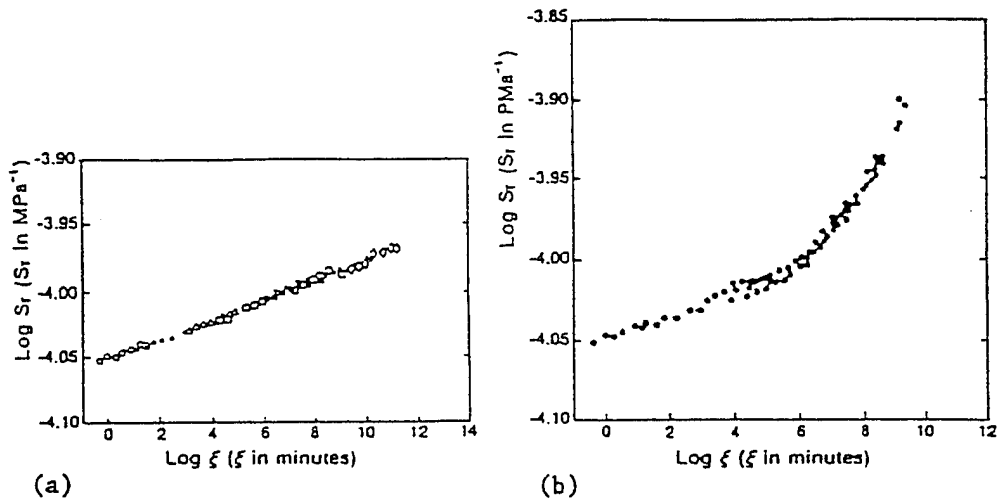
Fig. 12 "Master curves" for the transverse compliance $S_T$, as inferred from data for $S_{xx}$ shown in Figure 10, AS/3502 composite. Curves obtained by horizontal shifts (parallel to the log t axis) of isothermal data. For (a) dry (b) "wet" cases. (Harper, 1983).
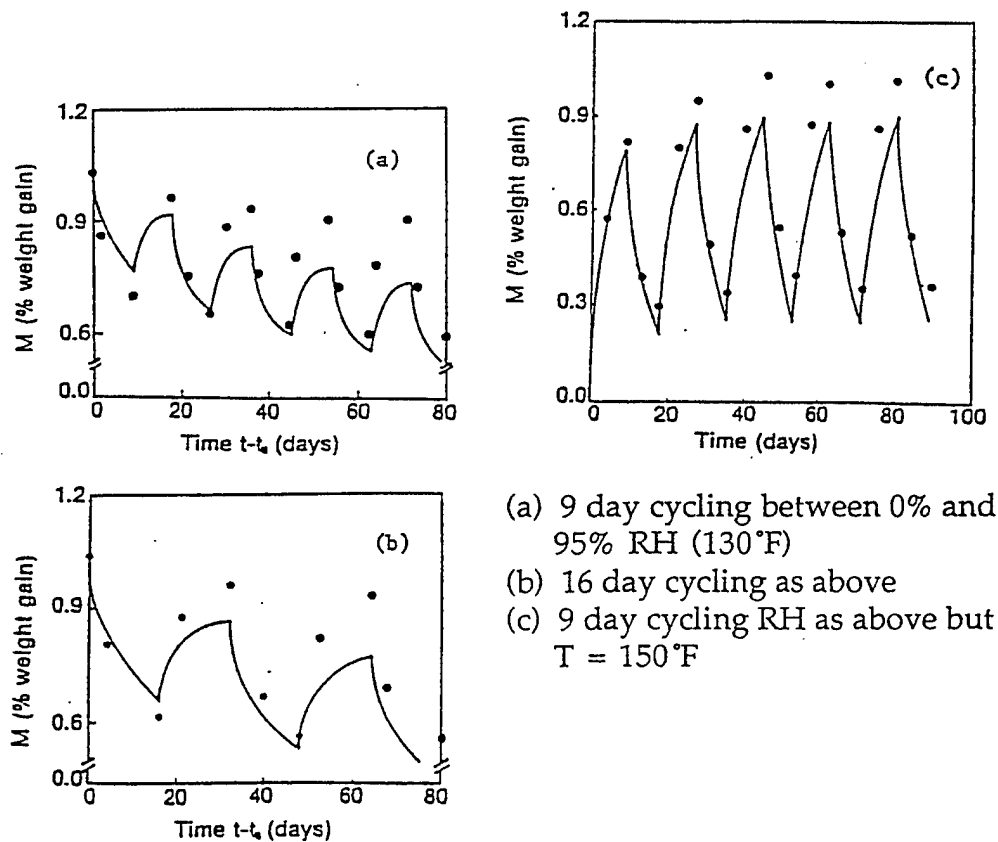


(a) 9 day cycling between 0% and 95% RH (130°F)
(b) 16 day cycling as above
(c) 9 day cycling RH as above but T = 150°F

Fig. 13 Weight gain in $[0/90/0_4/90_4/0/90]_T$ AS/3502 gr/ep samples under cyclic exposure.

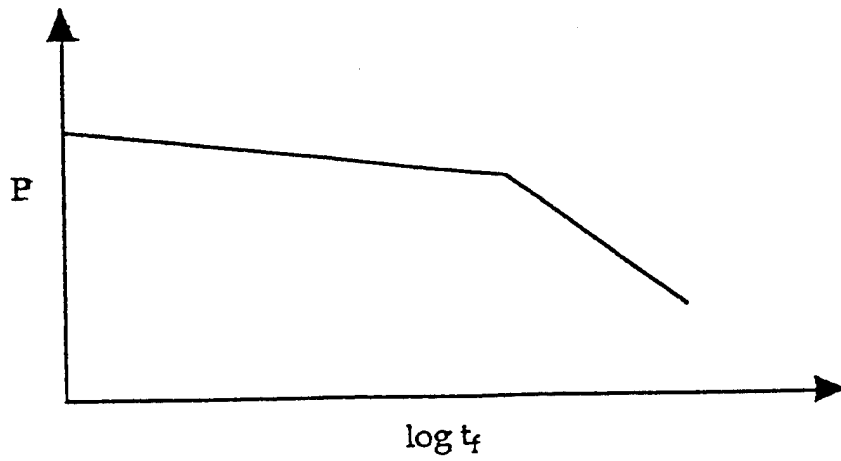Fig. 14 "Two-stage" creep under extended exposure to environment.



Fig. 15 A semi-logarithmic plot of load P vs. failure time $t_f$ in static fatigue
tests of glass/polyester composites in sea water.
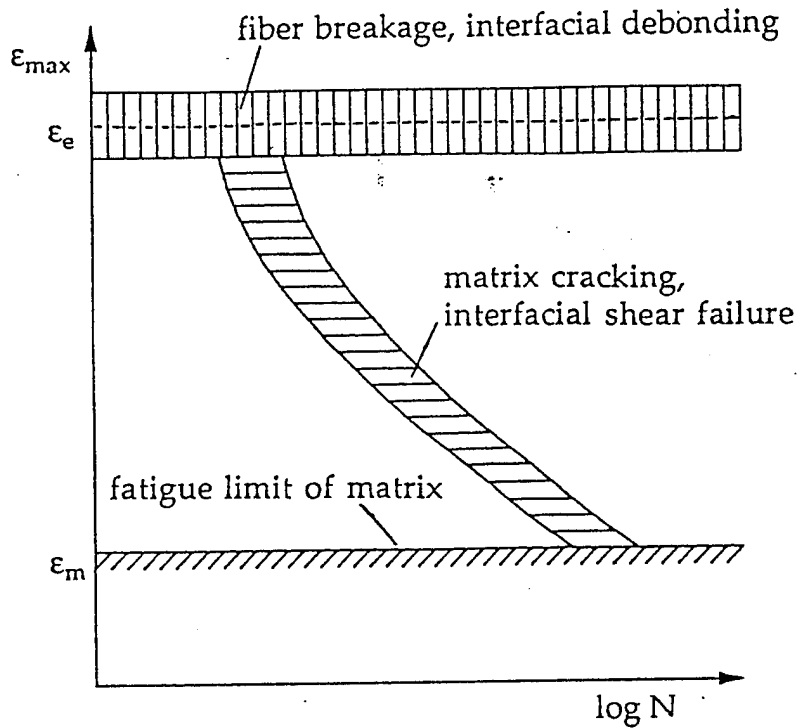(Adapted from White and Phillips, 1985).

Fig. 16 Fatigue-life diagram for unidirectional composites under loading parallel to fibers. (Adapted from Talreja, 1981).
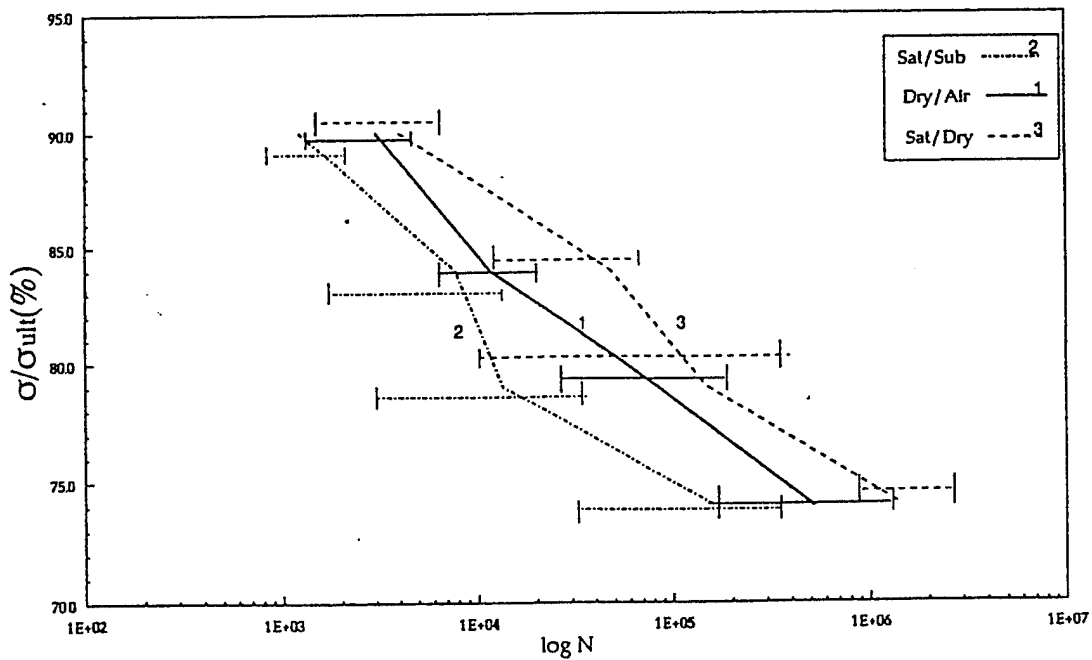


Fig. 17 Fatigue life data for $\left[0°/90°_3\right]_s$ gr/ep laminates under distinct exposure conditions.