Canada

HYGROTHERMAL EFFECTS IN CONTINUOUS FIBRE REINFORCED COMPOSITES

PART II: PHYSICAL PROPERTIES

by

J. P. Komorowski

National Aeronautical Establishment

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PART II: PHYSICAL PROPERTIES

EFFETS HYGROTHERMIQUES DANS LES COMPOSITES À RENFORT DE FIBRE CONTINU

PARTIE II: PROPRIÉTÉS PHYSIQUES

by/par

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National Aeronautical Establishment

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SUMMARY

This report is second in a series of literature reviews in which hygrothermal effects on aerospace composite materials (CM) with polymeric matrixes are examined. This report (Part II) deals primarily with the glass transition temperature and expansion properties due to temperature and moisture. The chapter on residual stresses is also included in this part as these stresses are a direct consequence of the expansion properties. Specific heat, thermal conductivity and emittance are briefly mentioned in Chapter 3.0, while properties connected with moisture absorption have been reviewed extensively in Part I of the series.

Other reports in this series deal with the following topics:

Part I:	Thermal and Moisture Diffusion
Part III:	Mechanical Properties 1
Part IV:	Mechanical Properties 2
Part V:	Composite Structures and Joints
Part VI:	Numerical and Analytical Solutions
Part VII:	Summary of Conclusions and Recommendations

A complete list of references is included in the Appendix and the numbers in the brackets appearing in the text refer to this list.

RÉSUMÉ

Le présent rapport est le deuxième d'une série de dépouillements bibliographiques concernant l'influence des effets hygrothermiques sur les matériaux composites utilisés en aérospatiale. Cette Partie II porte principalement sur la température de transformation vitreuse et la dilatation sous l'effet de la chaleur et de l'humidité. Le chapitre sur les constraintes résiduaires figure dans cette partie puisqu'elles résultent directement de la dilatation. La chaleur spécifique, la conductibilité thermique et le pouvoir émissif sont traités brièvement au chapitre 3.0, tandis que les propriétés découlant de l'absorption d'humidité avaient fait l'objet d'un examen détaillé dans la Partie I de la série.

Les autres rapports de la série portent sur les sujets suivants:

Partie I:	Diffusion de la chaleur et de l'humidité
Partie III:	Propriétés mécaniques 1
Partie IV:	Propriétés mécaniques 2
Partie V:	Structures et joints composites
Partie VI:	Solution numériques et analytiques
Partie VII:	Résumé des conclusions et recommandations

Une liste complète des références est incluse en annexe et les nombres entre parenthèses dans le texte se rapportent à cette liste.

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HYGROTHERMAL EFFECTS IN CONTINUOUS FIBRE REINFORCED COMPOSITES

PART II: PHYSICAL PROPERTIES

1.0 INTRODUCTION

The second part of the series of literature reviews* is concentrated on three properties: the glass transition temperature and expansions due to temperature and moisture. The properties connected with moisture absorption were dealt with extensively in Part I of the review.

Specific heat, thermal conductivity and emittance have not received very much attention from researchers in composites and therefore are only mentioned briefly.

Other properties may be affected by the absorption of moisture or heat but are considered of secondary importance or trivial (i.e. effect on specific weight) and are not therefore addressed in detail.

Material properties responsible for ultrasonic wave propagation were found to be affected by moisture and hygrothermal degradation. Those interested in Non Destructive Testing (NDT) of composites are referred to Kaelble and Dynes[153, 155, 95, 152], Ishai and Bar-Cohen[138, 139] and Kriz[180].

The changes in electrical properties may also be useful for NDT purposes as was shown by Cotinaud et all[68], Dewimille[87] (see Part I of review) and Kadotani[151].

The Appendix is a revised version of the bibliography for the whole series of reviews on Hygrothermal Effects on aerospace composites.

2.0 GLASS TRANSITION TEMPERATURE

At room temperature most polymer matrix materials are in a glassy state. On increasing the temperature, the elastic moduli and viscosity decrease slowly until a point is reached at which both these quantities drop drastically within a temperature range of 2° to 5°C. Discontinuity in the change of properties does not take place, however, the rates of change of various physical properties versus temperature undergo large increases. Similar effects were observed for crystals and denoted as second order transitions. However, in polymers the derivative properties do not appear to be discontinuous as in the case of crystals and to stress this difference, the use of the term glass transition temperature (Tg) is preferable to second order transition temperature[215].

The transition from a glassy to rubbery state is observed as a drastic drop in the mechanical properties of the matrix materials and is a natural upper temperature limit for structural applications of these materials. Glass transition temperature (Tg) is therefore one of the important composite material properties.

2.1 Methods of Measurements

Glass transition is manifested when a rapid rate of change of various physical and mechanical properties is observed with a slight increase in temperature. As a consequence, many methods have been used to measure the Tg. The mehods can be either static or dynamic.

---

* Only polymer matrix continuous fibre reinforced composites are considered (see Introduction to Part I).

Torsional braid analysis (TBA) is a commonly used dynamic method (Fig. 1) (ASTM2236-81). The frequency and the rate of decay of free vibrations of a pendulum are monitored with changing temperature. Transition temperature is recorded as a significant change in complex elastic shear modulus or more precisely as a maximum in the logarithmic decrement.

Static methods are more popular and generally easier. They include dilatometry, columnar loading (or linear thermal expansion method), differential thermal analysis and other methods. In dilatometry, the coefficient of cubical thermal expansion is monitored. A rather abrupt change in the value of the coefficient over a narrow temperature interval indicates the glass transition temperature.

The Tg values vary from test method to test method as the concept of second order transition is not precise. For this reason other tests were designed (i.e. Heat Distortion Temperature tests (HDT), Vicat softening temperature using a penetration probe) and are used to establish temperature envelope of polymers and for qualitative comparisons. What separates them from methods used for Tg measurement is that they do not measure any fundamental physical property. Data obtained from those tests is especially useful in applications where the factors of time, temperature, method of loading, and fiber stress are similar to those specified in that test [ASTM D648-72(78)].

Very popular tests, the heat distortion temperature (HDT) tests can have several forms (see ASTM D648-72(78) and ASTM D1637-61(76)). The HDT test, usually in the form of three point flexural displacement under constant loading, is an empirical method and does not measure any fundamental property. The temperature designated as HDT is arbitrarily chosen and therefore should not be referred to as glass transition temperature but simply as HDT. HDT tests may be useful in qualitative comparison of materials.

Tajima[28 3] compared results obtained using two different test methods. Materials tested were 5209 epoxy and T300/5209 composites. For dry resin, the HDT was 139°C while Tg from dilatometry was 154°C. Sykes et al[28 1] used TBA (Fig. 1) and HDT (Fig. 2) for the same T300/5209 composite. The difference between Tg from TBA and HDT was very pronounced for wet composites (Fig. 3).

Carter et al[5 2] suggested a practical method of defining a Tg value from a heat distortion experiment (flexural). Their method is demonstrated in Figure 4 and based on an equation derived from a viscoelastic model of cross-linked polymer. The curves shown represent probe displacement (δ) vs temperature (T). The point of maximum curvature (T_c, δ_c) is found by visual inspection or numerical analysis. The intersection between a line parellel to temperature axis at the distance of 3.60 δ_c and a tangent to the curve at (T_c, δ_c) gives Tg. This Tg value was in good agreement with results obtained from loaded columnar expansion (where a change in the first derivative of expansion curve is used as Tg). Carter et al designate the temperature of which this second order transition takes place as T_2 rather than Tg.

It should be mentioned here that the loads used in measuring the Tg or HDT usually have to be optimized for each material to increase sensitivity. The results of HDT or Tg measurement tests are generally repeatable to better than 2°C. Reproductivity is somewhat lower, but for worst conditions, should not exceed 10°C (ASTM D1637-61(76), D3418-82, D2236-81).

2.2 Glass Transition Temperature in Composites and Neat Resins

Browning et al[4 1] measured HDT of neat 3501-5 resin and AS/3501-5 composite. They do not make a distinction between HDT and Tg and refer to the measured softening point in deflection of their sample as Tg. The value of HDT for the dry resin was 177°C as opposed to 189°C for the composite. However, Tajima and Wanamaker[28 3] worked with 5209 resin and T300/5209 composite. For these materials, the result of HDT and Tg (dilatometry) tests were opposite to Browning's. Both the HDT and Tg of neat resin was higher then those for the composite in the dry state. These seemed to indicate that the effective cross-link density in the matrix is less than that in the neat resin. In the wet state the situation was reversed and the Tg and HDT values of wet composite were higher than those of wet resin (see Table 1).

2.3 Effect of Moisture on Glass Transition Temperature

The effect of moisture on Tg and HDT of epoxies and their composites has been studied extensively[18, 28, 41, 42, 211, 214, 220]. Typical results are shown in Figure 5. Even a small moisture content will lower the Tg of these materials considerably. Carter and Kibler[51] measured the effect of moisture on glass transition temperate for F178 polyimide resin. From Figure 6, it can be seen that the effect is similar to that observed in epoxies.

The lowering of Tg and HDT by moisture is observed regardless of the method of measurement. However, as McKague[214] pointed out, the column loading method is better suited for wet Tg measurement as the extension of the specimens core is measured. The surface is dried during the experiment and shrinks which must have an effect on bending tests.

Browning et all[41, 42] used Equation (1) suggested by Kelley and Bueche[165] to predict Tg of wet resin.

$$Tg = \frac{\alpha_p V_p Tg_p + \alpha_d (1 - V_p) Tg_d}{\alpha_p V_p + \alpha_p (1 - V_p)} \qquad (1)$$

where:

α	—	expansion coefficient
V	—	volume fraction
suf_p	—	denotes polymer
suf_d	—	denotes diluent

This equation is based on free volume theory. Browning used $\alpha = \alpha_i - \alpha_g$ where α_i and α_g are the linear expansion coefficients above and below Tg respectively. Browning et al had to assume the Tg of water as 4°C. Their results correlated well with measurements of Tg (or rather HDT) for 3501-5 resin (Fig. 7).

Delasi and Whiteside[81] modified Equation (1) by using specific volume of water values calculated from swelling measurements. This modification gave good correlation, especially for neat resins.

McKague[211, 214] observed that measured Tg temperatures from loaded column measurements are lower than those predicted by Equation (1). He pointed out that good correlation was obtained only for bending tests where drying of specimen surface affects the results. His modified equation introduces α_p as a volumetric expansion coefficient of a polymer in the glassy state. Swelling is also accounted for in his modified equation. The two models are compared in Figure 8.

Morgan and Mones[220] simplified Kelley and Bueche's equation. Since the expansion coefficient α_d 'amorphous water', was not known, it was assumed to be equal to α_p. The Tg of water was taken between 137°K and 182°K and the results compared with experimentally determined Tg for TGDDM-DDS epoxy-moisture system (see Fig. 9). The large discrepancy in results was attributed to the fact that in free volume theory, the hydrogen bonding interactions of active sites within epoxy are not accounted for. Morgan and Mones suggested that the Kelley-Bueche equation should not be used for predicting wet Tg in epoxies.

Carter and Kibler[51] proposed an entropy model for predicting glass transition temperatures in wet resins and composites. This model designates configurational entropy, rather then free volume, as the temperature dependent function that determines this transition. Arbitrary assignments for Tg and α of water are avoided and hydrogen bonding is accounted for. After some simplifying assumptions, the following Equation (2) is obtained:

$$Tg_f = Tg_o \left[1 - (R/M_s \Delta C_p)\, y(r)\right] \qquad (2)$$

where:

$$y(r) \equiv r \ell n \frac{1}{r} + (1 - r) \ell n \frac{1}{1 - r}$$

$$r \equiv (M_s/M_w) f$$

$Tg_f(^\circ K)$	—	glass transition temperature of material containing f grams of water per gram of dry resin
$Tg_0(^\circ K)$	—	Tg of dry resin
M_s(g/mole)	—	effective formula weight of hydrogen bond site
ΔC_p(cal/g°C)	—	jump in specific heat due to glass transition in dry resin
R	—	universal gas constant
M_w = 18 g/mole	—	formula weight of water

Carter and Kibler encountered difficulties in measuring ΔC_p so a final comparison of the two models was not possible at the time. For some materials, when parameters in Equation (1) are well chosen, equally good correlation with experimental values may be obtained with both models. However, as shown in Figure 6, for some resins Equation (2) gives much better correlation. The full potential of this model will be realized when problems with ΔC_p measurement are overcome.

When studying the relationships of Tg, peak thermal spike and moisture, McKague[211] pointed out the importance of moisture distribution. In Figure 10, the two different moisture distributions shown result in the same allover moisture content. However, wet Tg may be locally exceeded leading to accelerated moisture absorption and deterioration of material (see Part I and Part III of the review).

2.4 Conclusions

1) HDT is often referred to as Tg. This should be avoided as the two temperatures may be substantially different.

2) Moisture significantly lowers the Tg and HDT of matrix resins[41, 42, 81, 211, 214, 220, 281].

3) HDT assessments of wet materials should not be based on flexural type tests[214].

4) The loaded column expansion method seems to be better suited for wet Tg measurement[214].

5) A study comparing tests in which a fundamental property is being measured and from which Tg may be determined would be useful. At present it is difficult to relate results obtained in various laboratories using various methods.

6) Of all the models used for predicting wet Tg of composites reviewed here, the entropy model seems most promising. However, problems with some measurements, i.e. ΔC_p will have to be overcome before it becomes practical[51].

3.0 THERMAL PROPERTIES — COEFFICIENT OF THERMAL EXPANSION

When considering thermal effects in solids, specific heat, thermal conductivity, emittance and coefficient of thermal expansion (CTE) are the most often used properties. Recently, the first three mentioned properties have not received much attention from researchers in composite materials.

The methods of measuring of these properties are fairly well established and the ASTM standards are good references in this case. However, finding published values of these properties for specific composites is not usually easy. For graphite/polyimide, notably, Campbell and Burleigh[49] conducted an extensive study of these properties and some results are shown in Figures 11, 12 and 13. Christensen presented methods of predicting values of these properties for composite materials[61] Chapter IX].

The fourth of the above mentioned properties, namely the CTE, has been extensively measured by various researchers and some of their results will be discussed below. Matrix materials generally have very different CTE from the fibers. As the composites are cured at elevated temperature, there is on cooling to the normal usage temperature, a complex stress state created due to this CTE mismatch. These residual stresses may cause loss of dimensional stability or even failure of the interface or matrix material. Another reason for the interest in the CTE of composites, is that due to the negative CTE of the graphite fibers and the positive CTE of the resin matrices, laminates with practically zero CTE, within wide range of temperatures, may be made (e.g. graphite/epoxy antennae, telescopes). Hertz[130] in Figure 14 gave good illustration of the advantage of composites for applications where stiffness, dimensional stability and weight are of primary concern.

Rogers, Yates et al published a series of articles on the linear thermal expansion of composites[243, 324, 325, 326, 327, 242]. An interferometric (Fizeau) method was used to measure the changes of CTE within a temperature range of 90°K to 400°K (500°K). A large amount of data was produced using different graphite fibers, orientations, fiber volume fractions, resin types and lay-ups. The effects of matrix curing characteristics and fiber weave types on CTE were also investigated. Materials used in these studies included HTS and HMS graphite fibers, ERLA 4617/m PDA, DLS 351/ BF_3 400 and code 69 (Fathergill & Harvey Ltd) epoxy resins. CTE of neat resins, unidirectional and multidirectional lay-ups were measured.

The results provide useful data which can be immediately applied. When these data were compared with current predicting methods, generally good correlation were achieved. However, a major drawback to the application of these theories, is the lack of precise data on the CTE of fibers as well as their transverse elastic properties. When appropriate values are assigned to these thermoelastic constants, current techniques account well for fiber volumes (v_f) in the range of 0.5 to 0.8 at room temperature. Measurements have shown that the higher the fiber content v_f — the hig is the temperature at which resin softening effects on CTE are observed. Accuracy of predictive methods for CTE of composites was improved when detailed data on the temperature dependence of CTE of the neat resin had been used.

Experience gained from the response of simple lay-ups to temperature change has enabled the behavior of progressively more complex structures to be predicted with some degree of confidence according to Yates et al[326].

Recently, Parker et al[229] have expanded data on the CTE of graphite/epoxies by testing Fibredux 914C resin both neat and reinforced with HTS fibers. The scatter for this system was higher than for those previously tested by Rogers, Yates eta al. The averaged results are, however, fairly representative for the graphite/epoxy systems. Some of these data are shown in Figures 15, 16 and Table 2.

Wang et al[303] conducted a study of CTE of Modmor II graphite in an epoxy resin (unspecified). They used static and creep tests to obtain data on the mechanical properties of fibers and epoxy separately. This data was later used to calculate CTE of laminae and the results were compared with experimental data (Fig. 17). Wang et al also made comparison between direct measurement and co-ordinate transformation (Fig. 18). For a bidirectional laminate, a comparison was made between direct measurement and lamination theory (Fig. 19). All theories used were linear elastic and generally good correlation was obtained except for high temperatures where viscoelastic properties become more pronounced. The results agree well with conclusions reached by Rogers, Yates et al. Parker et al[229] also compared theory with experiment for multidirectional laminates (Fig. 20). According to Parker, the poor correlation for 0/±45° laminates was caused by the presence of moisture in the specimens.

Cairns and Adams[45] measured the thermal expansion for 3501-6 resin and its unidirectional composites made with AS graphite and S2 glass fibers. The data were compared with results obtained from a micromechanical analysis based on finite element methods. The correlation was poor. This was, according to Cairns and Adams, mainly caused by the fact that transverse CTE of fibers was not known (a sensitivity study of the model was undertaken, however, no synergistic effects were considered).

Kabelka[150] formulated a model for predicting the CTE of fabric reinforced composites. Comparison between the model and experimental results (Fig. 21) show poor correlation. Kabelka concluded that this should improve when the viscoelastic response of matrix material is included. In a previously mentioned study, Rogers et al[242] found that for fabric reinforced graphite/epoxies:

- fiber tow densities play a critical role in governing the average values of in plane CTE of laminates,
- the crimp in reinforcing fibers is a significant factor in controlling the temperature at which resin softening effects become apparent in the out of plane thermal expansion behavior,
- laminate stacking may change the thermal expansion by as much as 100%.

Camahort et al[46] thermally cycled near zero CTE laminates. A near zero CTE lay-up was designed from results obtained on unidirectional specimens and was found to be $[0°_4, \pm 40°, \pm 70°]_s$. Cycling was severe as samples were alternately immersed in liquid nitrogen and boiling water. Materials and corresponding results can be seen in Table 3. The CTE was measured over a range of temperatures from $-1°C$ to $38°C$. An increase of CTE was found to be caused by microcracking of the resin — the angle plies ceased to contribute and the laminate acted like a unidirectional one. The lower cure resin system marked 339 (121°C cure) performed better than the 177°C cure systems, as did the hybrid system where T300 plies made of woven graphite were added and these in effect acted as crack stoppers.

CTE of graphite/polyimide systems used by Campbell and Burleigh[48] showed scatter during temperature changes. According to these authors, this was also caused by microcracking of the resin.

Tennyson[286, 287] studied the effect of six months of temperature cycling from 24°C to 93°C in vacuum ($10^{-7} \sim 10^{-8}$ torr) on CTE. Over 30 cycles were applied during the whole test. Samples used were four ply $\pm\theta$ symmetrically balanced laminates of graphite, boron or Kevlar in an epoxy matrix. The results can be seen in Figures 22, 23 and 24. CTE predictions for laminates were calculated using unidirectional laminae properties in their respective environments. These are compared with data in Figures 25 and 26. Very good correlation was achieved. From these results Tennyson concluded that outgassing (mainly H_2O) and microcracking significantly affects CTE. Removal of moisture seems to increase CTE of $\pm\theta$ laminates (a similar observation was made by Parker[229]).

For 3501 epoxy, moisture seemed to have just the opposite effect (Adamson[4]). Dry epoxy samples had CTE equal to $8.0 \pm 0.5 \times 10^{-5}°C^{-1}$ while a sample saturated (7.3% wt gain) at 74°C with moisture displayed CTE equal to $1.9 \pm 0.5 \times 10^{-4}°C^{-1}$. (Adamson measured volumetric expansion.) Adamson described his observations of thermal expansion and swelling of epoxies in terms of free volume theory and postulated an equilibrium state existing between bound and unbound water in the resin. As free volume is inversely proportional to temperature, so is the volume of unbound water in the epoxy. As only bound water causes swelling it is important that CTE measurements for wet specimens allow for the time needed to reach equilibrium between bound and unbound water. Adamson found that one hour was sufficient time for this equilibrium to be reached at 25°C, however, at 1°C 24 hours were needed.

For applications where dimensional stability is of primary importance, two methods of sealing the composites from moisture were suggested at General Dynamics (Hertz[130]). Both the bonded aluminium foil and tin-indium eutectic over a thin coat of copper proved to be effective barriers up to 1500 hours of exposure. However, besides affecting the weight of the composite ($\sim$ 0.13-0.21 g/in^2) the coatings affected the CTE. For unsealed GY70 — X30 $[(0/45/90/-45)_s]_2$ the CTE was $-0.017 \times 10^{-6}\ ^{\circ}C^{-1}$ ($-15^{\circ} \div 24^{\circ}C$) and $+0.021 \times 10^{-6}\ ^{\circ}C^{-1}$ ($24^{\circ} \div 74^{\circ}C$). When sealed with 0.02 mm single layer aluminium, the CTE changed to $+0.058 \times 10^{-6}\ ^{\circ}C^{-1}$ and $+0.089 \times 10^{-6}\ ^{\circ}C^{-1}$ respectively.

Useful data for CTE of composites at cryogenic temperatures can be found in References [163 and 65].

4.0 MOISTURE EXPANSION OF COMPOSITES

The absorption of moisture into the composite poses a problem of dimensional stability very similar to the one caused by thermal expansion. Current polymer matrices absorb moisture and expand (swell) as a result. Most fibers (glass, graphite, boron) do not seem to absorb moisture and restrict the matrix expansion especially in the longitudinal direction of unidirectional lamina. An internal stress state is thus created along with dimensional changes. Yet another stress state is created when expansion of a lamina is restricted by adjacent plies in a multidirectional laminate. Since moisture distribution through the thickness of a composite is generally not uniform, this type of internal stress may be present even in unidirectional laminate [Part I of the review].

By analogy to thermal effects, most theoretical prediction techniques developed for thermal expansion are applicable. Work by Marom and Cohn[206] is a good example of the applicability using analogies. Schapery's theory was used there to predict coefficients of swelling of single lamina parallel and transverse to fibers (μ_L and μ_T). Swelling of unidirectional laminae (E glass/Araldite F/HT 972 or ERL 2256 epoxy) was measured in plane every 15° from 0° to 90°. The results were compared with two predictions, one based on Schapery's theory, and the other based on measured μ_L and μ_T. In Figure 27, comparison is made between the results. Schapery's equations should give better correlation if wet properties of constituent materials (resin) are used.

Menges and Gitschner[216] also used this analogy and applied Schneiders equations. The relations obtained between swelling strains and fiber volume fraction were used to produce the graph shown as Figure 28.

In moisture expansion of polymeric composites, the most important problem is the expansion of the matrix material. Shirrel and Halpin[262], in their review paper, compared experimental data from Hertz, Browning and McKague with the theory based on the assumption of additivity of volumes:

$$V_{\text{DRY LAMINATE}} + V_{H_2O} = \text{Swollen volume}$$

Within the restrictions that the moisture distribution is uniform and the resin material isotropic, the dilatational strain is:

$$e = \frac{1}{3}\ \frac{\Delta V}{V_o}$$

In Figure 29 the correlation seems to be good and differences with respect to expansion due to moisture among various epoxies are small.

However, results from more recently published experiments do not lend themselves to interpolation using assumptions based on additivity of volumes (see Figs. 30, 31 and 32). Hahn and Kim[118] developed a micromechanics model in which the expansion of the resin takes place after the voids are filled with absorbed moisture. For each sample, there is a threshold value of moisture

concentration below which no expansion takes place. Above the threshold the expansion is linear with moisture content. Hahn and Kim assumed that material behavior is elastic and that swelling strains are independent of temperature. Experiments did not quite agree with this model as some expansion could be seen below the threshold value (C_v) in Figure 31.

Adamson[4] used the concept of free volume to explain the thermal expansion and swelling of cured epoxy resins (see Review Part I, page 15). The free volume is the difference between the measured volume and the occupied volume. The occupied volume consists of mass volume plus the vibrational volume. In the first stage of moisture absorption only a fraction of absorbed water becomes bound to the epoxy network and causes swelling. The rest of the absorbed moisture occupies the free volume. The second stage of moisture absorption begins when the free volume is completely filled with water and all absorbed water becomes bound causing swelling. In this second stage, swelling is equal to the volume of absorbed water. In the third stage of swelling observed by Adamson water occupies free volume contained by micelles (highly cross-linked dense centers of generally less dense resin) and swelling again is less than the volume of absorbed water. As the equilibrium between bound and unbound water is inversely proportional to temperature (free volume changes with temperature, Fig. 33), swelling is also dependent on temperature. For a given amount of water in the sample, swelling will increase with an increase in temperature. With changes in temperature, it is very difficult to separate the effect of swelling from the pure thermal expansion in an experiment.

5.0 CONCLUSIONS (Chapter 3.0 and 4.0)

1) There is a lack of data on the transverse properties of fibers which in turn limits usefulness of theoretical predictions of CTE of composites.

2) Accuracy of predictive techniques for CTE of laminae are improved when the dependence on temperature of the fiber properties and even more so, the resin matrix are included in the analysis.

3) CTE of laminates can be predicted if physical properties of unidirectional laminae are known.

4) The hydrothermal history of the laminate may have an effect on its CTE, (i.e. thermal cycling which results in the microcracking of the resin matrix).

5) Moisture in the specimen complicates the measurement of CTE and in general, wet specimens require longer time at temperature before any change in dimension is measured. Wet composites have different CTE than the dry ones.

6) Even very thin layers of coating (aluminium or other metal coating which serves as moisture barrier) changes CTE of laminates significantly.

7) Swelling is significant in current polymeric composites It can be predicted with the same expressions used for predicting the CTE. These predictions are improved when the wet properties of resins are used.

8) Resin swelling seems to be a three stage process that can be best explained with a free volume concept.

6.0 RESIDUAL STRESSES

The thermal and moisture expansion properties of fibers and matrices are such that internal stress states are present in composites under general conditions. These residual stresses may be responsible for both defects and dimensional instabilities of cured composite materials before any external load is applied.

6.1 Micromechanics

As described in previous chapters, fibers and resins have greatly varying expansion coefficients. The cure temperature of resins which are of interest here, is typically between 120°C and 180°C. Immediately after cure and before cool down, the resin is in a leathery state and any stresses created at this stage will be relaxed almost instantly. During the cool down to room temperature, the resin becomes more elastic and, owing to the mismatch of expansion coefficients and restraints provided by the fibers, an internal stress state will result. This type of stress was studied in model materials made of thick glass filaments embedded in birefringent resins (epoxies typically are birefringent materials). Recently, Cunningham et al[175] used this method and obtained photoelastic data using a polarizing microscope. The principal stresses were obtained with an oblique incidence method. A plot of loop stress around the fiber is shown in Figure 34. The maximum loop stresses at the surface of the fiber were calculated to be approximately 100 MPa (tensile) while radial stresses were only 6MPa (compression).

Adams and Miller[2, 218] conducted finite element inelastic analyses of hygrothermal microstresses and their results generally agree well with Cunningham's photoelastic investigation. The magnitude of these microstresses was sufficient to cause yielding of the matrix. Hygrothermal cycling was shown to change the state of residual microstresses with subsequent dimensional instability of laminae.

Menges and Gitschner[216] demonstrated yet another mechanism for the rise of residual stresses in the transverse direction. In this direction, resin swelling is hardly restrained by the fibers, yet stresses still build up. Fiber distribution may be homogeneous or inhomogeneous (see Fig. 35). For both types of distributions zones of high and low fiber content may be identified and these will have different swelling strains. As a result, local residual stresses are present, and as Menges and Gitschner estimated, may lead to microcracking of the resin in a glass/resin composite.

6.2 Macromechanics

Residual stresses have been observed in composite materials not only at the microscopic level, but also at the macroscopic level in angle plied laminates or in unidirectional hybrids. These stresses have been studied experimentally and analytically by numerous authors.

Chamis[153] provides a good review of NASA Lewis Research Center activities and of NASA sponsored research in this field. He pointed to four factors from which lamination residual stresses (LRS) originate:

1) the differences in the ply CTE in the longitudinal (α_{11}) and in the transverse (α_{22}) direction. $\alpha_{22}/\alpha_{11} \cong 20$ for fiber/resin laminae;

2) the difference in ply orientation angle (θ) — there are no LRS in unidirectional laminates;

3) the difference between fabrication temperature and use temperature;

4) the ability of a ply to support stresses along its material axes.

Water is present in laminates under general usage conditions which implies, from the results of the previous chapter and from literature which will be reviewed below, that point one above should be broadened to include the difference in moisture expansion, as well as CTE. However, general points brought forward by Chamis are still true owing to the analogy between moisture and thermal effects.

The existence of LRS is evidenced by transply cracks and warpage of unsymmetric angle-plied laminates before any mechanical load was applied to them. The transply cracks are observed when LRS exceed the ply transverse strength (typically 28-63 MPa)[153]. Molcho and Ishai[219] observed these cracks in a graphite/epoxy T300/5208 skin for a control surface. The original lay-up

contained 0° and ±45° plies and after curing, not only transverse but also interlaminar cracks were observed. The latter originated from the tips of transverse cracks. It is worth noting that they found a uniform distribution of plies, as opposed to a lamped lay-up, to be preferable, as it resulted in less severe cracks.

Strain gauges have been employed in LRS measurements. Daniel, Liber and Chamis[78] embedded strain gauges during fabrication of laminates. Results for 0° plies of baron/epoxy $[0_2/\pm45°]_s$ laminate are shown in Figure 36.

Pagano and Hahn[228] used a simplier method of LRS measurement. They bonded gauges to laminates at RT and then heated them to cure temperature.

The most common method of measuring LRS is through deformation measurements of unsymmetric laminates. Unsymmetric laminates warp due to the existence of LRS. This method is however indirect as it is necessary to use lamination theory to obtain stress values corresponding to the measured warpage.

Chamis in his review reported on use of linear elastic laminate theory for ply thermal stresses (LRS caused by cure temperature being different then the use temperature). Effects of some material variables were analyzed with the aid of this model. In Figure 37(c) the effect of the lamping of plies in angle-plied laminate is shown and correlates well with the earlier mentioned findings of Molcho and Ishai. The effect of fiber volume ply angle, and matrix modulus is shown in Figures 37(a), (b) and 38.

Lee, Lewis and Sacher[188, 189] used [90°/0°/90°] glass/epoxy systems to study the effect of moisture on their mechanical properties. First ply failure, in the tension test, results in a change in slope of the stress-strain curve. Lee et al called this the yield point. They observed that yield strain was affected by residual strain (Fig. 39) and these in turn changed with the amount of moisture in the composite. They measured residual stresses in symmetric laminate by the deply technique. When one of the plies was removed, the laminate wareped and the stresses could be calculated.

Pagano and Hahn[228], Hahn[119] and Hahn and Kim[118] developed a linear elastic model to analyze curing stresses, however, they used a temperature dependent elastic moduli. Measurements of warpage in unsymmetric angle plied laminates were compared with predictions. The stress free temperature (T_o) was observed to be below the curing temperature. For T300/5208 and Scotchply 1002 (glass/epoxy) it was 121°C as opposed to a cure temperature of 177°C. In transverse direction it was found that the curing stresses may be more than 50% of UTS in this direction. For swelling, a moisture threshold model was used and it was found that moisture obsorption may result in a stress free laminate at room temperature (Fig. 40). Correlation of experimental data with calculated values was not alwasys satisfactory.

The elastic model does not account for significant stress relaxation, especially near the Tg of the resin. The lowering of the stress free temperature in a composite due to annealing, can readily be explained on the basis of a viscoelastic model. Crossman, Warren and Pinoli[73] studied the relations between residual stresses and annealing time and temperature (see Fig. 41). For Shell 1031 resin (190°C cure) the residual stresses at room temperature were lowered by 25% or ~ 7 MPa after 16 hours at 121°C. Moisture, it was concluded, by plasticizing the resin, further accelerates residual stress relaxation. Crossman and Flaggs[74, 101] compared results of a linear viscoelastic analysis of dimensional changes in laminates with experimental data and the results of elastic analysis. The correlation between viscoelastic analysis and experimental data (warping) was very good. The elastic model failed especially when used to analyze 121°C cure material (GY70/CE339). The viscoelastic model supported earlier observations (i.e. Crossman, Mauri and Warren[69]) that the viscoelastic stress relaxation during complete moisture absorption-desorption cycle at constant temperature can lead to unrecoverable dimensional changes and result in different residual stress state. Thus accelerated conditioning programs may result in a changed residual stress state. Crossman et al[69] found that hygrothermal cycling increased residual stresses in a T300/5209 unsymmetric laminate. Similar laminates made from T300/5208 showed a 5-10% loss of residual stress under the same thermal history.

Hedrick and Whiteside[128] demonstrated that choosing an appropriate cooling rate for graphite/epoxy laminates (based on 3501 epoxy), may also reduce the residual stresses through relaxation. Stress relaxation was studied (Fig. 42) and different cooling rates from 177°C to 121°C were investigated. In Table 4, a summary of photomicrographic examinations is given.

Harper and Weitsman[124] and Douglas and Weitsman[94] postulated that if residual stress relaxation is possible, than there should be an optimum cool down path for a laminate. They used a linear viscoelastic model to find this path. Experimental confirmation of their finding has not been very successful so far, as specimens used were relatively thick and contained many transverse cracks which obscureed the results (an AS-3502 system was used). Further experiments in this optimal time-temperature path are continuing.

6.3 Conclusions

1) The mismatch of thermal and moisture expansion of constituent materials or individual plies in a laminate is responsible for build up of residual stress states. Residual stresses are usually significant under normal usage conditions.

2) Residual stresses (or cure stresses) may cause transverse and interlaminar cracks in laminates before any external load has been applied. These stresses may be reduced by taking advantage of stress relaxation techniques.

3) Viscoelastic models seem to be better suited for studying residual stresses in composites.

4) When accelerated hygrothermal conditioning programs are used, care should be taken, as a residual stress state may result which would not be found under normal service conditions.

TABLE 1

GLASS TEMPERATURE[283]

Sample	M_s g/100g	HDT(°C) Penetration	Tg(°C) Dilatometry
5209	Dry	134	154
	3.730	95	90
6-Ply	Dry	109	131
	1.236	90	109
12-Ply	Dry	116	131
	1.329	96	109

TABLE 2

SMOOTHED VALUES OF THE LINEAR THERMAL EXPANSION COEFFICIENT α OF THE SPECIMENS AT THREE REPRESENTATIVE TEMPERATURES[229]

Fibre Lay-Up*	Fibre Volume Fraction (%)	Area of Plate Containing More Than 1% Voids (%)	Area of Plate Containing More Than 2% Voids (%)	$\alpha(^\circ C^{-1})$ at -150°C	$\alpha(^\circ C^{-1})$ at 0°C	$\alpha(^\circ C^{-1})$ at 150°C
100%/0°	67.1	0	0	-0.81×10^{-7}	-1.69×10^{-7}	-1.47×10^{-7}
75%/0°, 25%/±45°	65.8	0	0	-2.95×10^{-7}	-4.29×10^{-7}	-0.27×10^{-7}
50%/0°, 50%/±45°	68.6	5	0	1.40×10^{-7}	0.22×10^{-7}	4.72×10^{-7}
25%/0°, 75%/±45°	69.3	5	0	6.90×10^{-7}	7.85×10^{-7}	1.22×10^{-6}
50%/0°, 50%/90°	65.1	0	0	1.75×10^{-6}	1.88×10^{-6}	2.96×10^{-6}
25%/90°, 75%/±45°	69.3	5	0	3.65×10^{-6}	4.38×10^{-6}	5.15×10^{-6}
50%/90°, 50%/±45°	68.6	5	0	5.94×10^{-6}	7.98×10^{-6}	1.10×10^{-5}
75%/90°, 25%/±45°	65.8	0	0	8.55×10^{-6}	1.26×10^{-5}	1.75×10^{-5}
100%/90°	67.1	0	0	1.56×10^{-5}	2.41×10^{-5}	3.03×10^{-5}
No fibers				2.68×10^{-5}	4.45×10^{-5}	6.76×10^{-5}

* In relation to the direction of measurement

TABLE 3

THERMAL CYCLING EFFECTS ON LONGITUDINAL CTE[46]

Material System	Fiber Volume, %	Longitudinal CTE, μin./in.-°F	
		As-Cured	Thermally Cycled
HMS/934, U/D	65.6	-0.45	-0.35
HMS/3501, U/D	65.2	-0.35	-0.38
HMS/934, O/D	65.1	-0.10	-0.30
HMS/3501, O/D	69.5	-0.13	-0.26
HMS/339, O/D	60.6	-0.10	-0.12
Hybrid (HMS/3501 + T-300/934)	63.3	-0.13	-0.25

Note: U/D = unidirectional; O/D = oriented.

TABLE 4

SUMMARY OF PHOTOMICROGRAPHIC EXAMINATION OF Gr/Ep LAMINATES[128]

Cooling Rate (350°F to 250°F), °F/min.	No. Specimens Examined	Total Area* Examined, $in.^2$	Total No. of Cracks	Max. Crack Length, in.
5 to 6	3	3.24	47	0.012
2.5	2	1.89	3	0.005
1	9	7.21	0	—

* Microscopic examination of sectioned sine wave spars and travelers (300 X to 500 X)

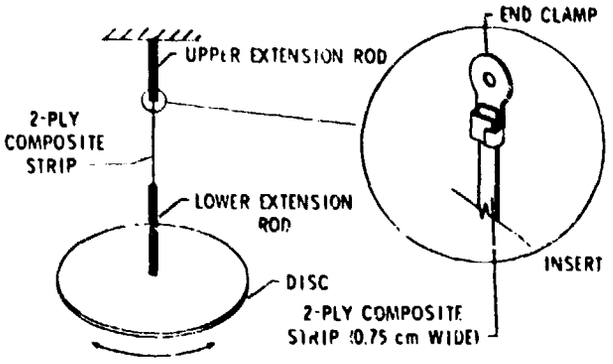


FIG. 1: SKETCH OF THE TBA PENDULUM. INSERT SHOWS METHOD USED TO ATTACH END CLAMPS TO COMPOSITE SPECIMEN[281]

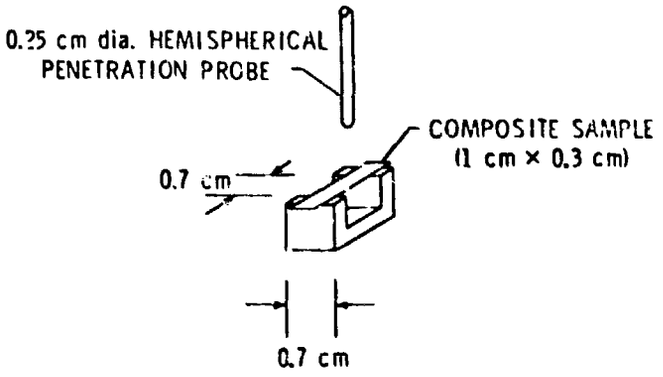


FIG. 2: SCHEMATIC OF THE TMA SAMPLE SUPPORT FIXTURE USED TO DETERMINE HEAT DISTORTION TEMPERATURES IN COMPOSITE MATERIALS[281]

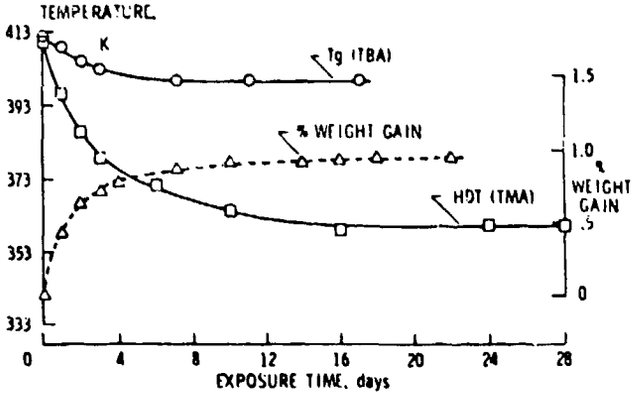


FIG. 3: EFFECT OF SOAK TIME ON THE HDT, Tg AND MOISTURE PICK UP OF A 2-PLY UNIDIRECTIONAL T-300/5209 COMPOSITE CURED AT 400 K[281]

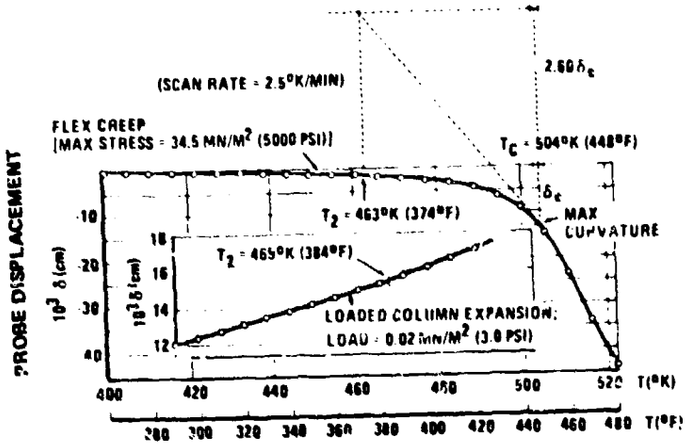


FIG. 4: TMA FLEXURE AND COLUMN LOADING RESULTS FOR DRY 5208 RESIN[82]

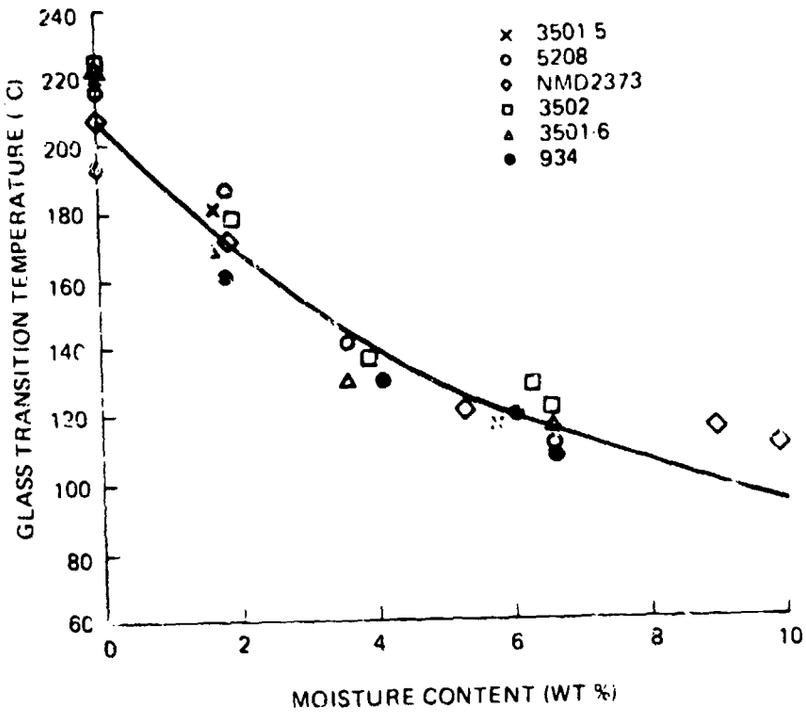


FIG. 5: RELATIONSHIP BETWEEN EQUILIBRIUM MOISTURE CONCENTRATION AND GLASS TRANSITION TEMPERATURE OF EPOXY RESINS[81]

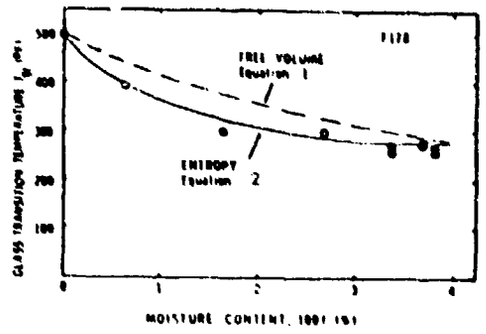


FIG. 6: VARIATION OF GLASS TRANSITION TEMPERATURE WITH MOISTURE CONTENT FOR CURED F178 POLYIMIDE RESIN. SOLID CURVE IS PREDICTION OF ENTROPY MODEL, EQUATION 2, USING $T_{go} = 533^{\circ}K$ AND ARBIRARY PARAMETERS $M_s = 270$ g/mole, $\Delta C_p = 0.022$ cal/g°C. DASHED CURVE IS PREDICTION OF FREE VOLUME THEORY, EQUATION 1, WITH $T_{gp} = 533^{\circ}K$, $\alpha_p = 1.98 \times 10^{-4\circ}C^{-1}$, $T_{gd} = 4^{\circ}C$, $\alpha_d = 3.66 \times 10^{-3\circ}C^{-1}$[51]

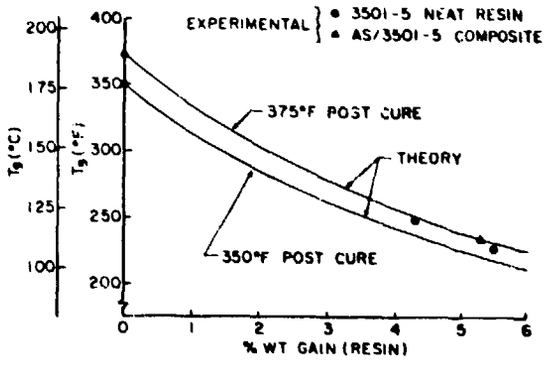


FIG. 7: GLASS TRANSITION TEMPERATURE AS A FUNCTION OF ABSORBED MOISTURE IN RESIN[41]

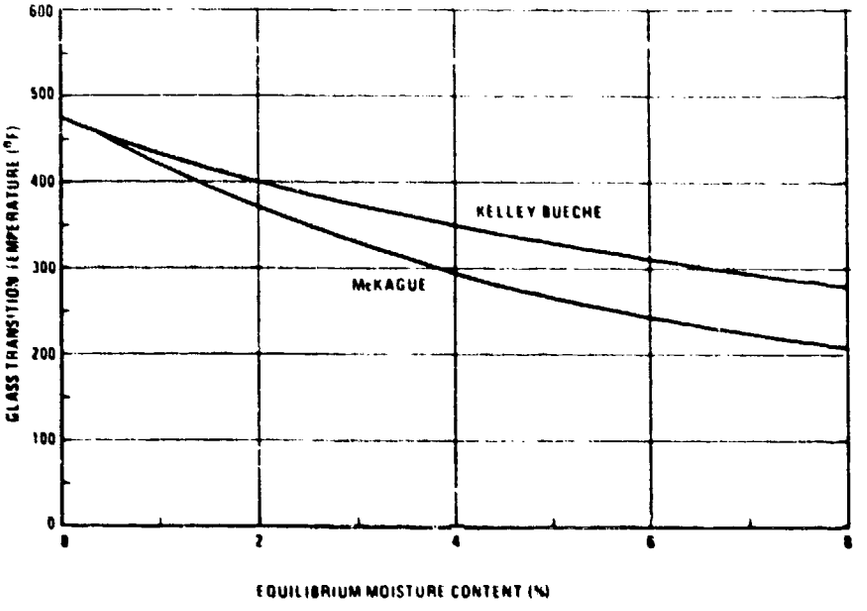


FIG. 8: COMPARISON OF GLASS TRANSITION MODELS[214]

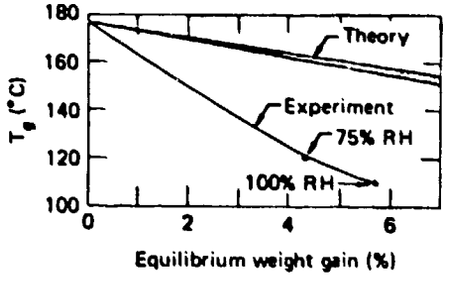


FIG. 9: THEORETICAL AND EXPERIMENTAL VALUES OF T_g AS A FUNCTION OF EQUILIBRIUM MOISTURE WEIGHT GAIN FOR A TGDDM-DDS EPOXY-MOISTURE SYSTEM[220]

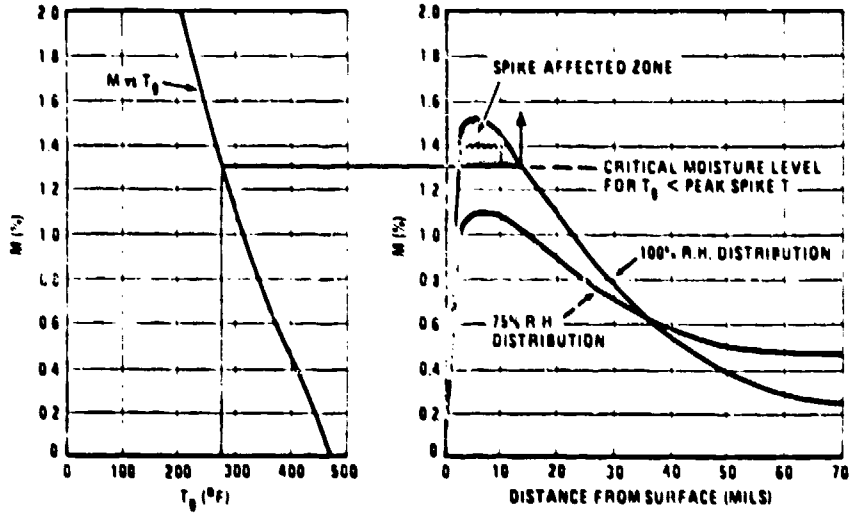


FIG. 10: RELATIONSHIP OF T_0, PEAK SPIKE TEMPERATURE AND MOISTURE DISTRIBUTION TO THE THERMAL SPIKE EFFECT[211]

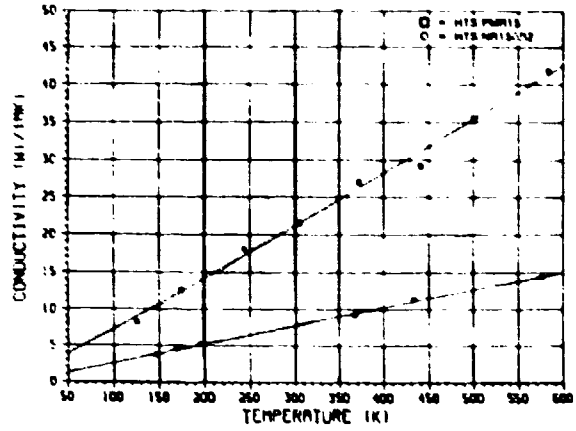


FIG. 11: THERMAL CONDUCTIVITY, $[0°]_n$ COMPARISON (CUT BAR)[48]

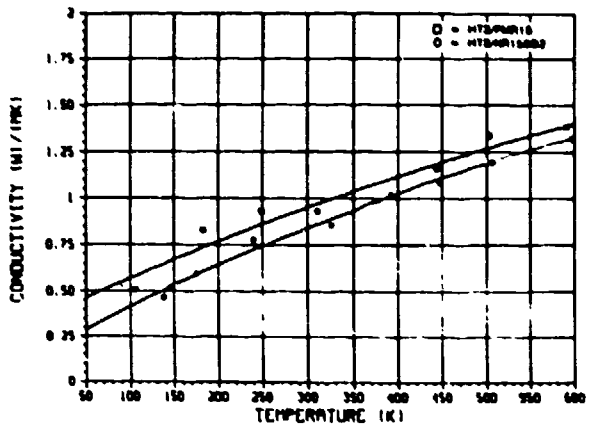


FIG. 12: THERMAL CONDUCTIVITY, $[90°]_n$ COMPARISON (HOT PLATE)[48]

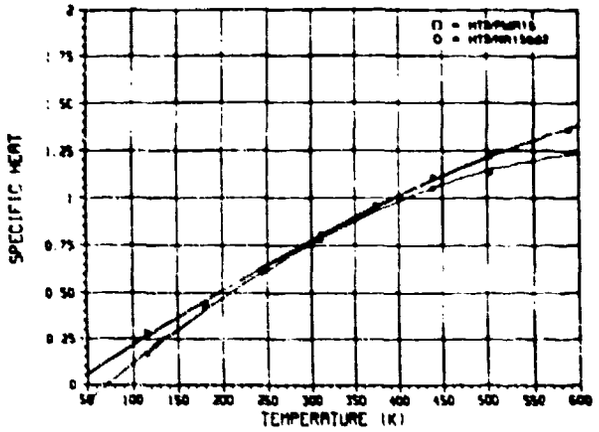


FIG. 13: SPECIFIC HEAT COMPARISON ISOTROPIC LAY-UP[48]

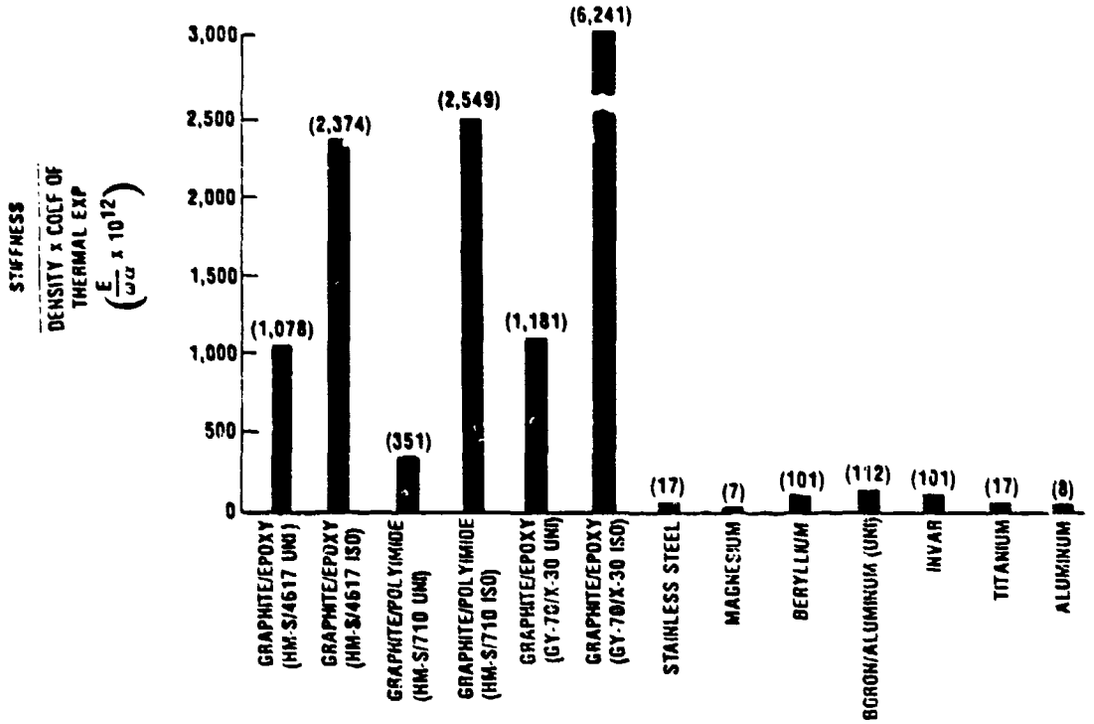
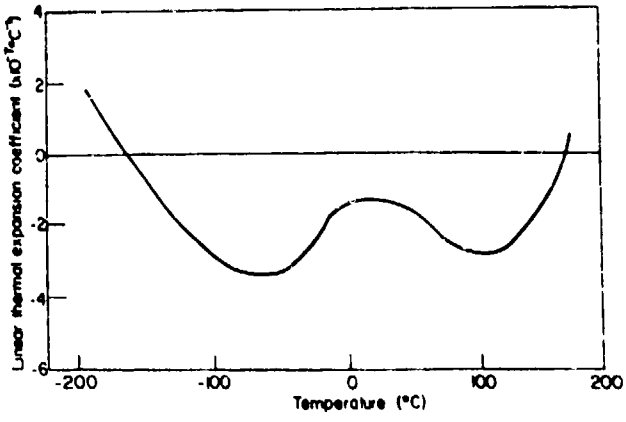
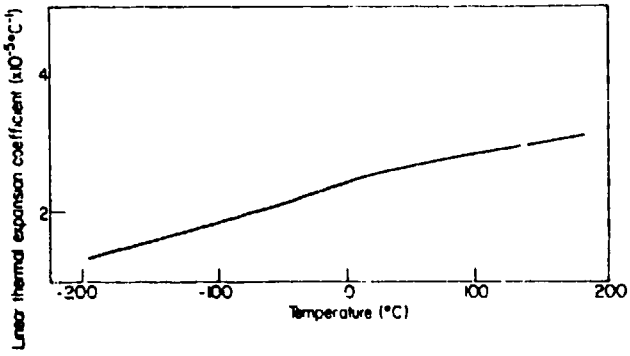


FIG. 14: RELATIVE MERITS OF CANDIDATE MATERIALS[130]

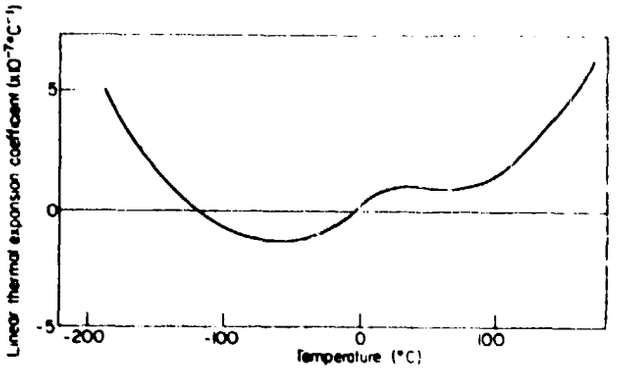


(a)

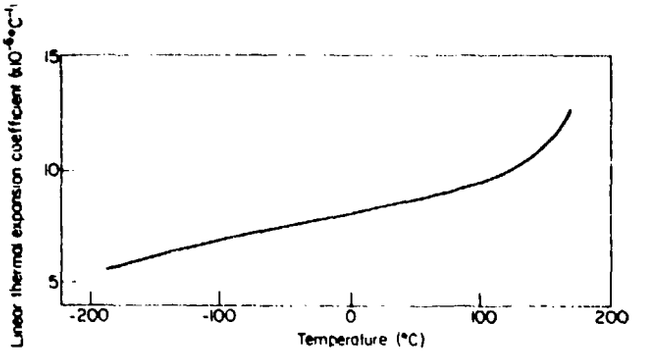


(b)

FIG. 15: THE LINEAR THERMAL EXPANSION COEFFICIENT OF $[0^\circ]_{16}$ LAMINATE IN (a) LONGITUDINAL AND (b) TRANSVERSE DIRECTION[229]



(a)



(b)

FIG. 16: THE LINEAR THERMAL EXPANSION OF $[+45^\circ, 0^\circ, -45^\circ, 0^\circ]_{2s}$ LAMINATE IN (a) LONGITUDINAL AND (b) TRANSVERSE DIRECTION[229]

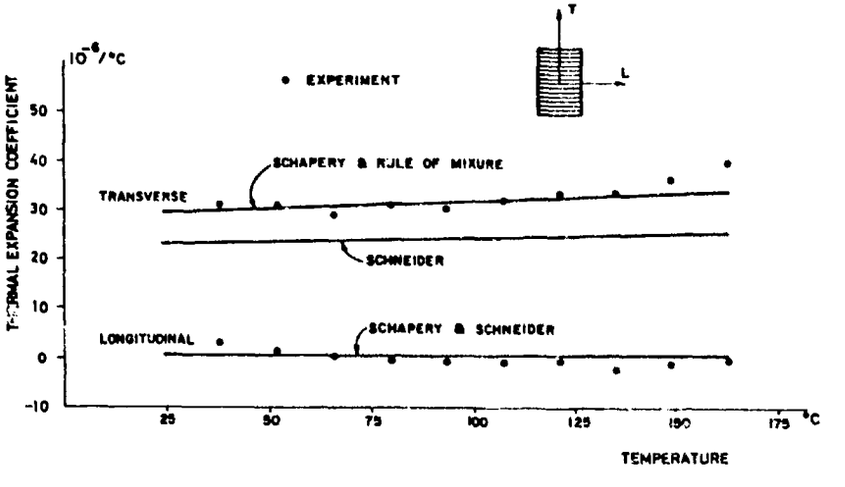


FIG. 17: COMPARISON OF THE CTE BETWEEN EXPERIMENT AND THEORY[303]

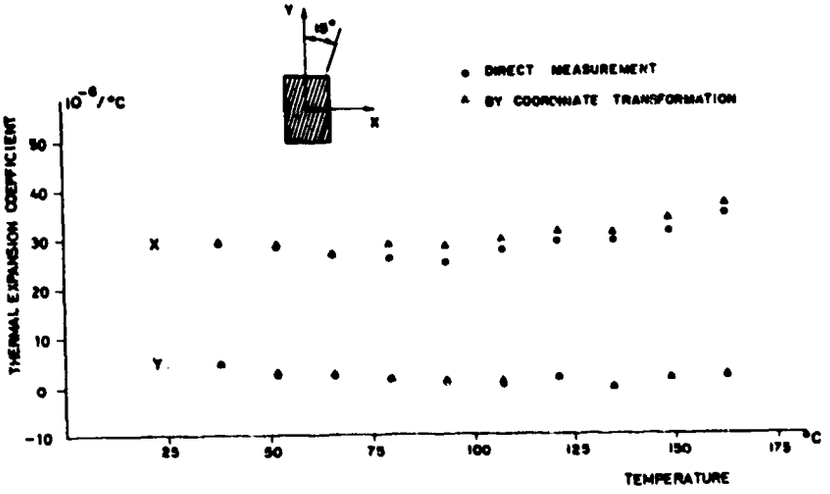


FIG. 18: COMPARISON OF THE CTE BETWEEN DIRECT MEASUREMENT AND COORDINATE TRANSFORMATION[303]

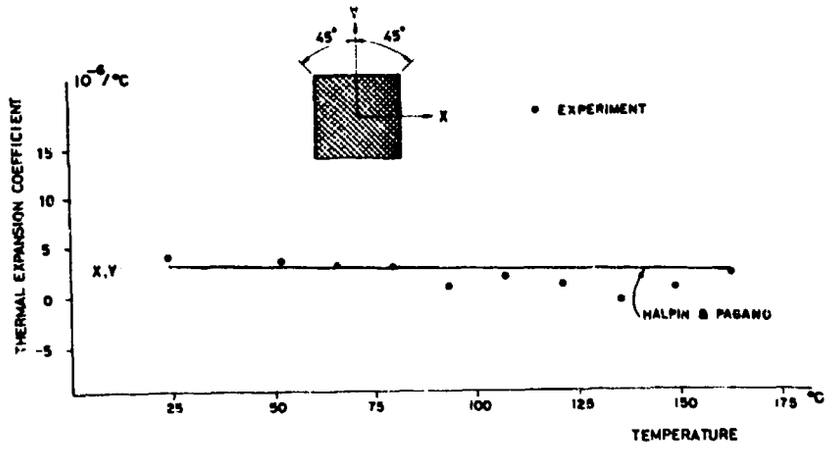
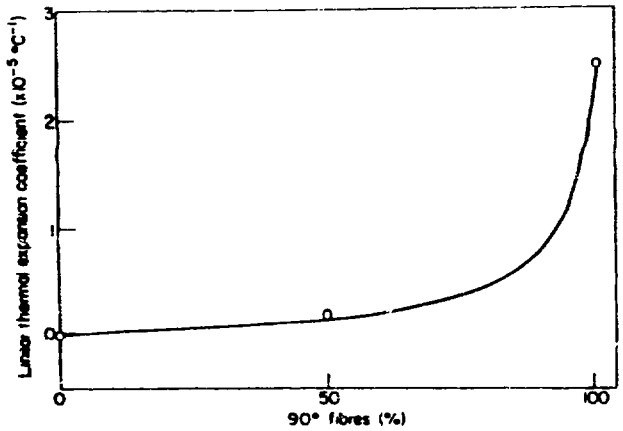
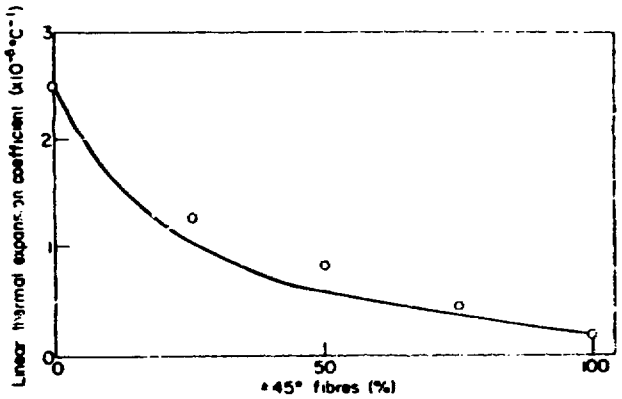


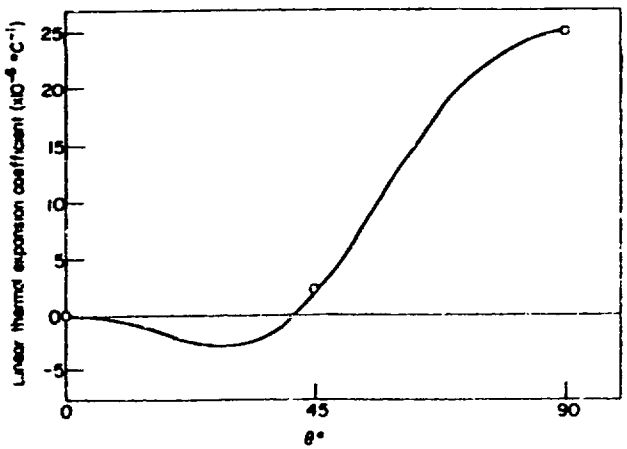
FIG. 19: COMPARISON OF THE CTE FOR A ±45-DEG LAMINATE BETWEEN EXPERIMENT AND THEORY[303]



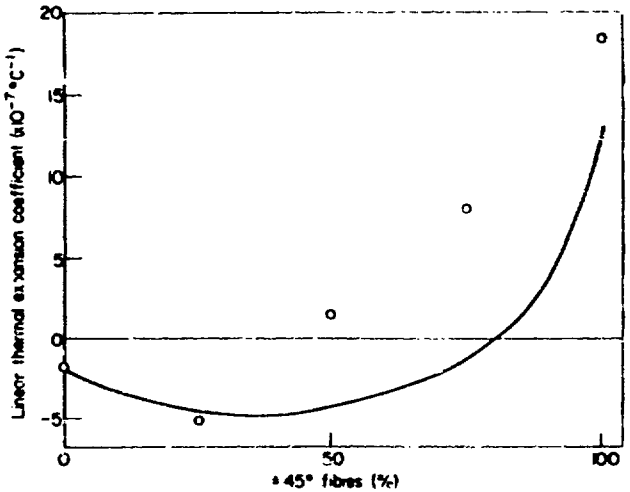
The room temperature linear thermal expansion coefficients of 0°, 90° laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated



The room temperature linear thermal expansion coefficients of 90°, ± 45° laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated



The room temperature linear thermal expansion coefficients of symmetrically balanced angle-ply (± θ) laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated



The room temperature linear thermal expansion coefficients of 0°, ± 45° laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated

FIG. 20: THE ROOM TEMPERATURE LINEAR CTE'S[229]

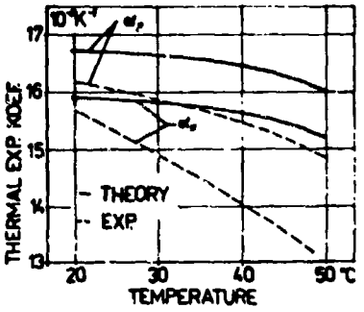


FIG. 21: COMPARISON OF THE THEORETICAL AND EXPERIMENTAL RESULTS[150]

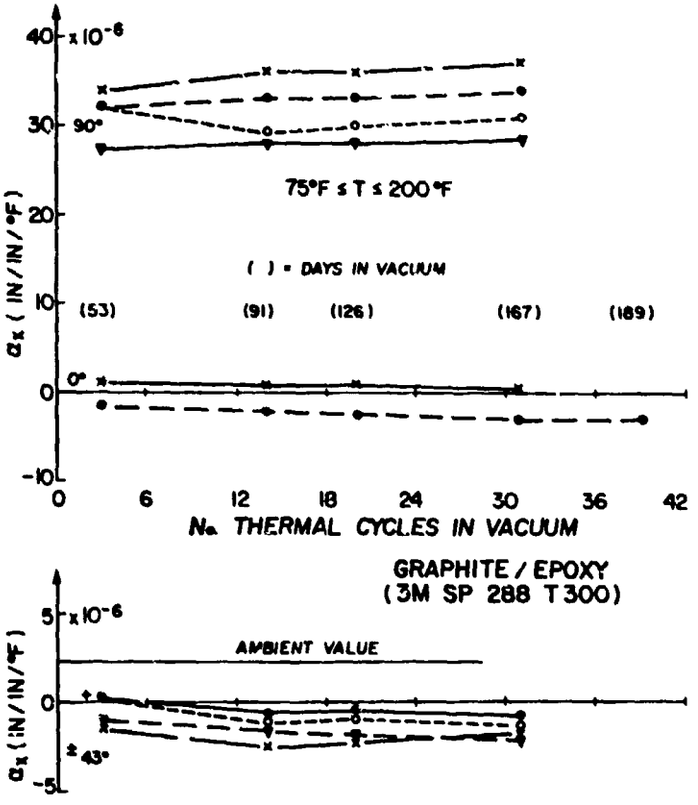


FIG. 22: THE EFFECT OF THERMAL CYCLING IN VACUUM ON CTE OF GRAPHITE/EPOXY[286]

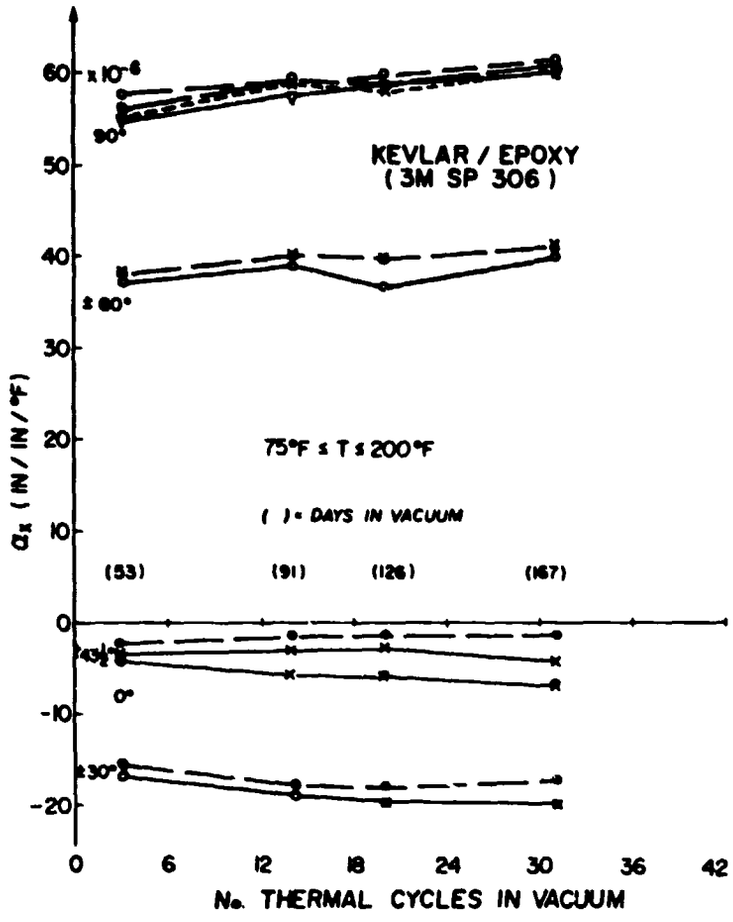


FIG. 23: THE EFFECT OF THERMAL CYCLING IN VACUUM ON CTE OF KEVLAR/EPOXY[286]

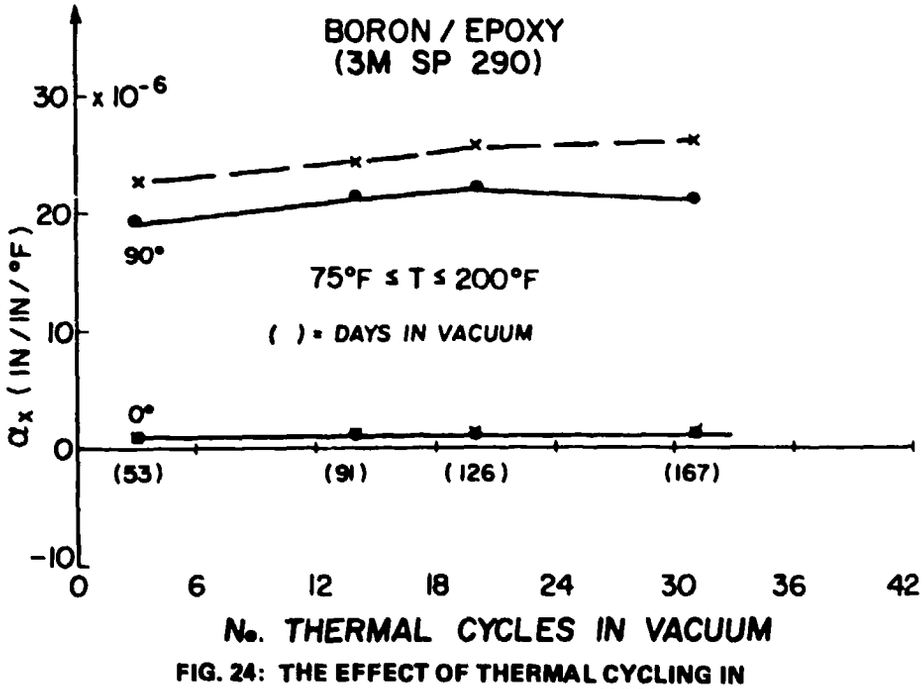


FIG. 24: THE EFFECT OF THERMAL CYCLING IN VACUUM ON BORON/EPOXY[286]

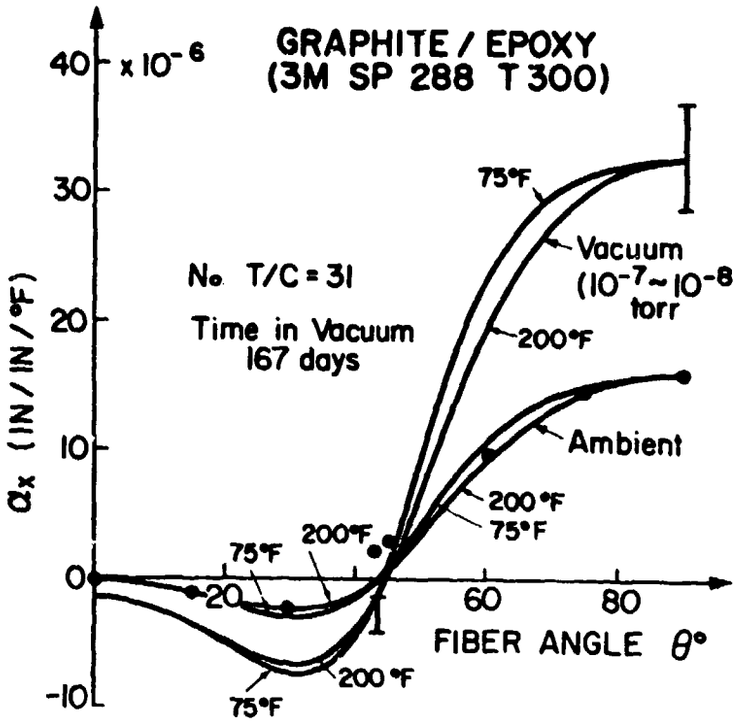


FIG. 25: COMPARISON OF CTE PREDICTED FOR VARIOUS θ WITH THE DATA[286]

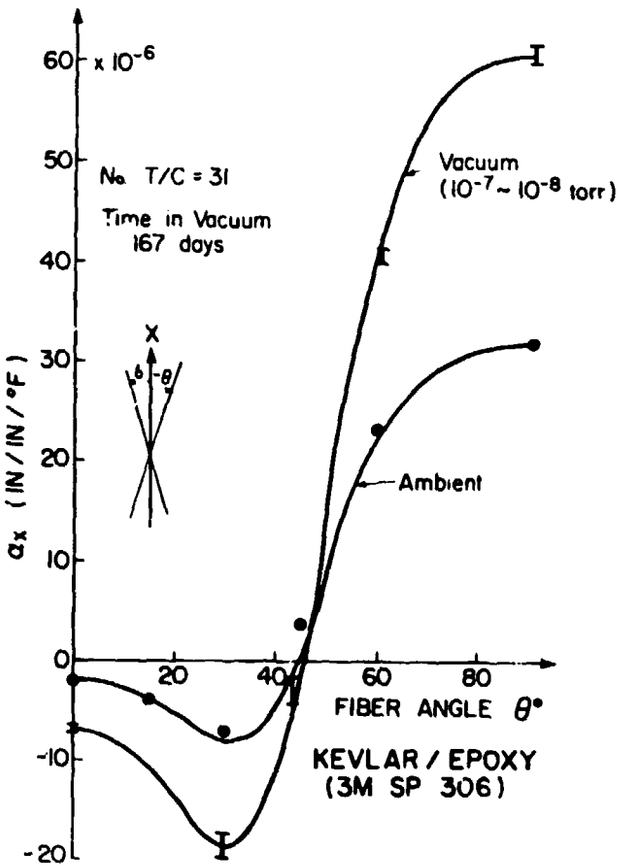


FIG. 26: COMPARISON OF CTE PREDICTED FOR VARIOUS θ WITH THE DATA[286]

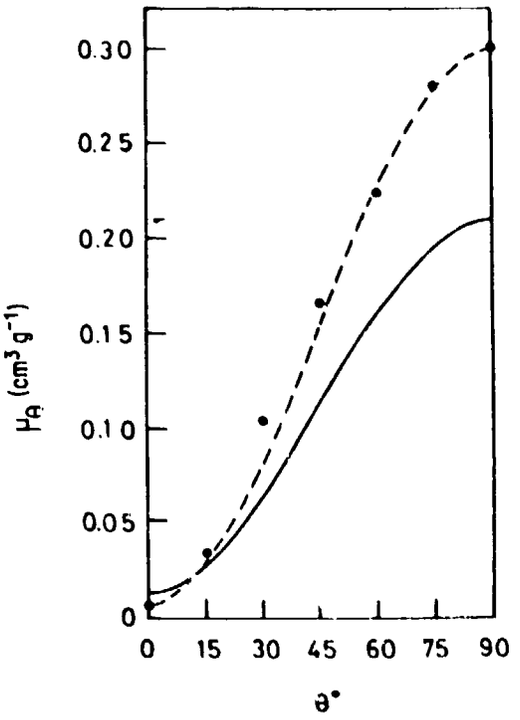


FIG. 27: COEFFICIENTS OF HYGROCLASTICITY AS FUNCTIONS OF θ, COMPARED WITH THE CALCULATION BASED ON EXPERIMENTAL μ_L AND μ_T (- - -), AND ON μ_L AND μ_T WORKED OUT BY SCHAPERY'S EQUATIONS TAKING THE CONSTITUENTS' ORIGINAL PROPERTIES (——).[206]

● MEASURED

$$\mu = \frac{\Delta L / L_o}{\Delta \omega / V_o}$$

L_o = length of specimen

$\Delta\omega$ = weight of water absorbed

V_o = original volume

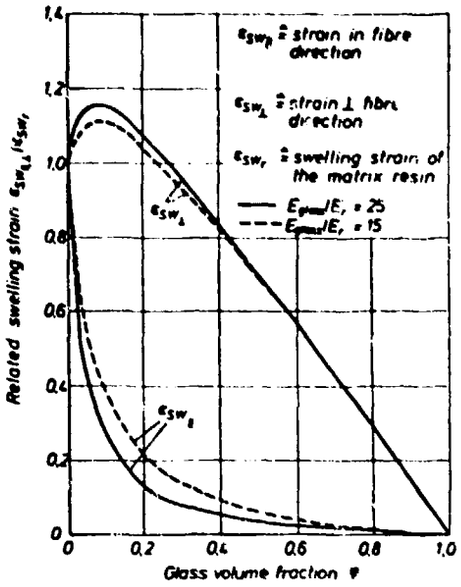


FIG. 28: SWELLING STRAIN BEHAVIOR OF ANISOTROPICALLY REINFORCED INDIVIDUAL LAYERS DUE TO MATRIX SWELLING[216]

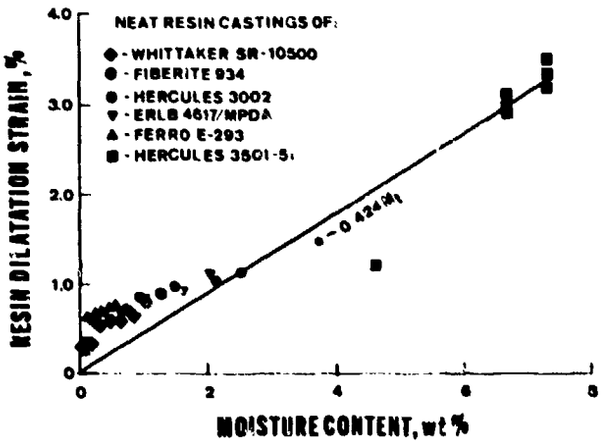


FIG. 29: SWELLING BEHAVIOR IS SIMILAR FOR SEVERAL EPOXIES[262]

RESIN	NO. DATA POINTS	LEAST SQUARES FIT	
		SLOPE	INTERCEPT
2373	51	0.840	−0.511
3501-5	42	0.977	−0.457
5208	34	0.765	−0.216

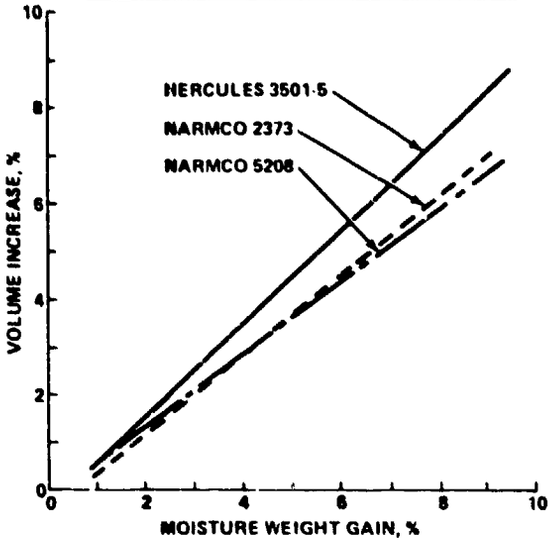


FIG. 30: RESIN SWELLING DUE TO ABSORBED MOISTURE[128]

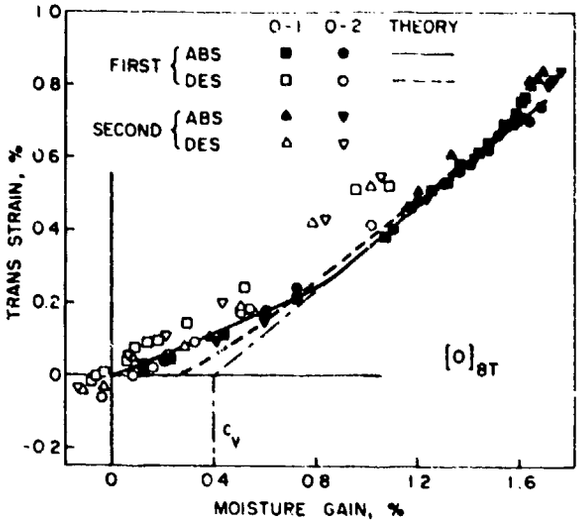


FIG. 31: TRANSVERSE SWELLING STRAIN OF $[0]_{8T}$ LAMINATE (AS/3501-5)[118]

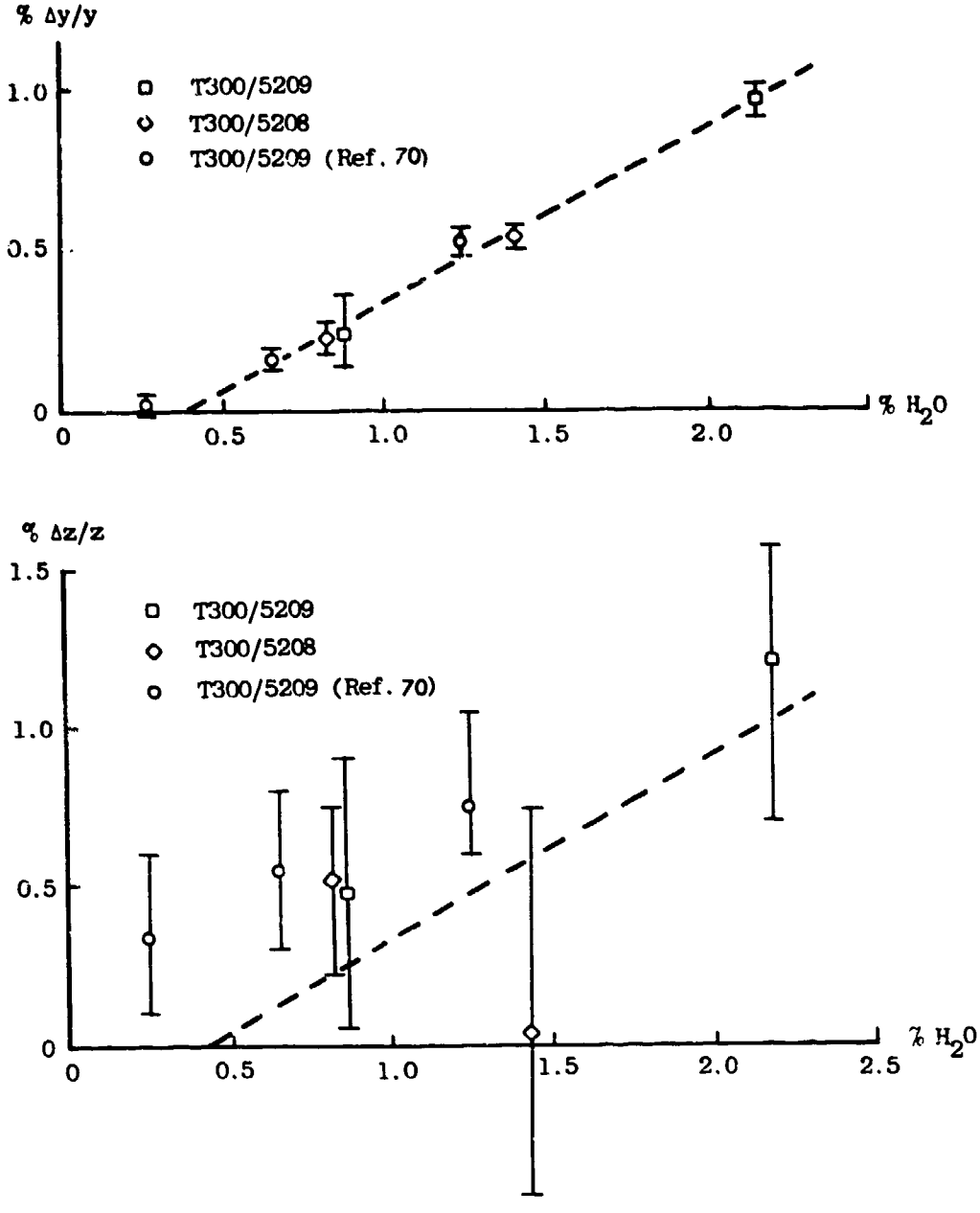


FIG. 32: DIMENSIONAL CHANGES IN TRANSVERSE (Δy/y) AND THROUGH THICKNESS (Δz/z) DIRECTIONS IN UNIDIRECTIONAL COMPOSITES vs EQUILIBRIUM MOISUTRE CONTENT[69]

The dotted line represents linear regression on Δy/y data for both graphs (Δz/z seems to be greater than Δy/y)

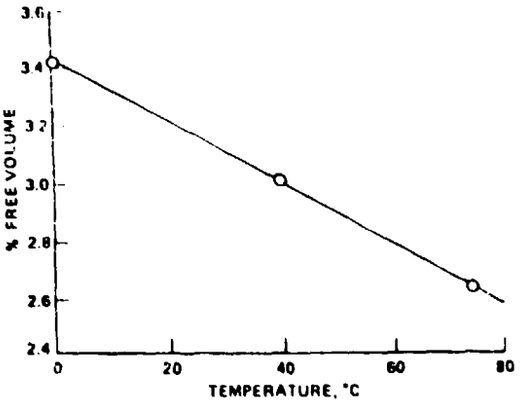


FIG. 33: PERCENT FREE VOLUME AS A FUNCTION OF TEMPERATURE, HERCULES 3501 RESIN. VALUES OF 74 AND 40°C DETERMINED BY SWELLING DATA DURING ABSORPTION. VALUE AT 1°C DETERMINED USING REVERSE THERMAL EFFECT FROM 74°C EQUILIBRIUM[4]

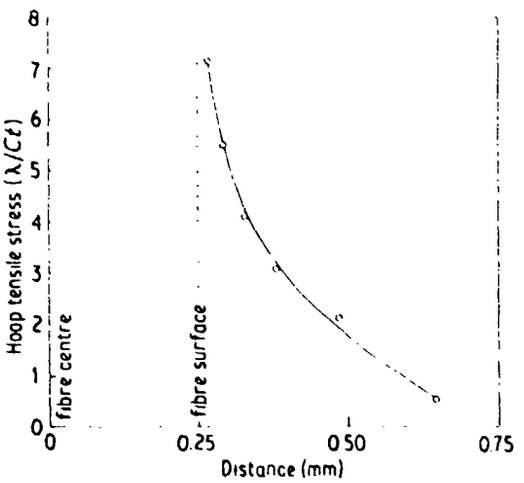


FIG. 34: PLOT OF THE HOOP TENSILE STRESS AGAINST RADIAL DISTANCE FROM THE FIBRE[75]

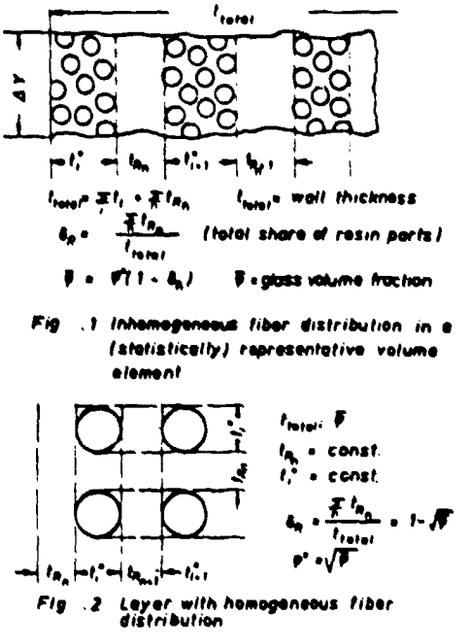


FIG. 35: SCHEMATICAL REPRESENTATION OF RESIN AND FIBRE DISTRIBUTION[216]

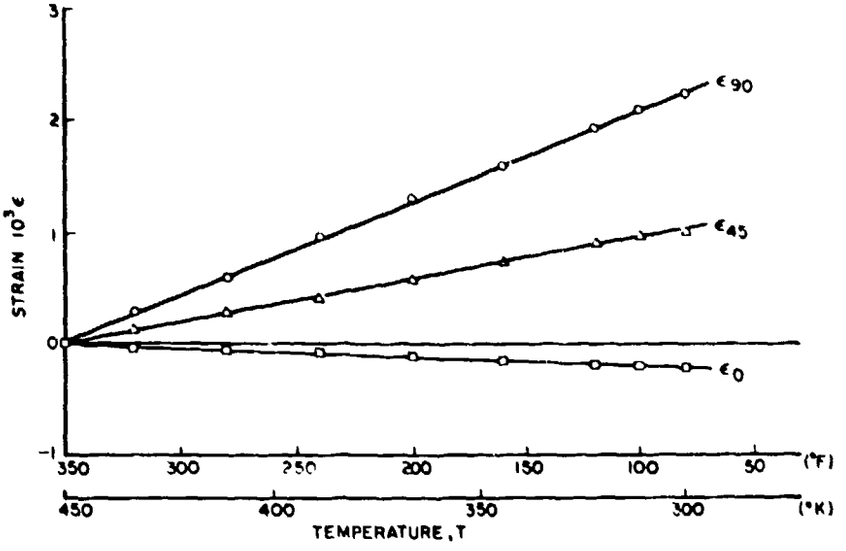


FIG. 36: RESIDUAL STRAINS IN 0-DEG PLIES OF $[0_2/\pm45]_s$ BORON-EPOXY SPECIMEN[78]

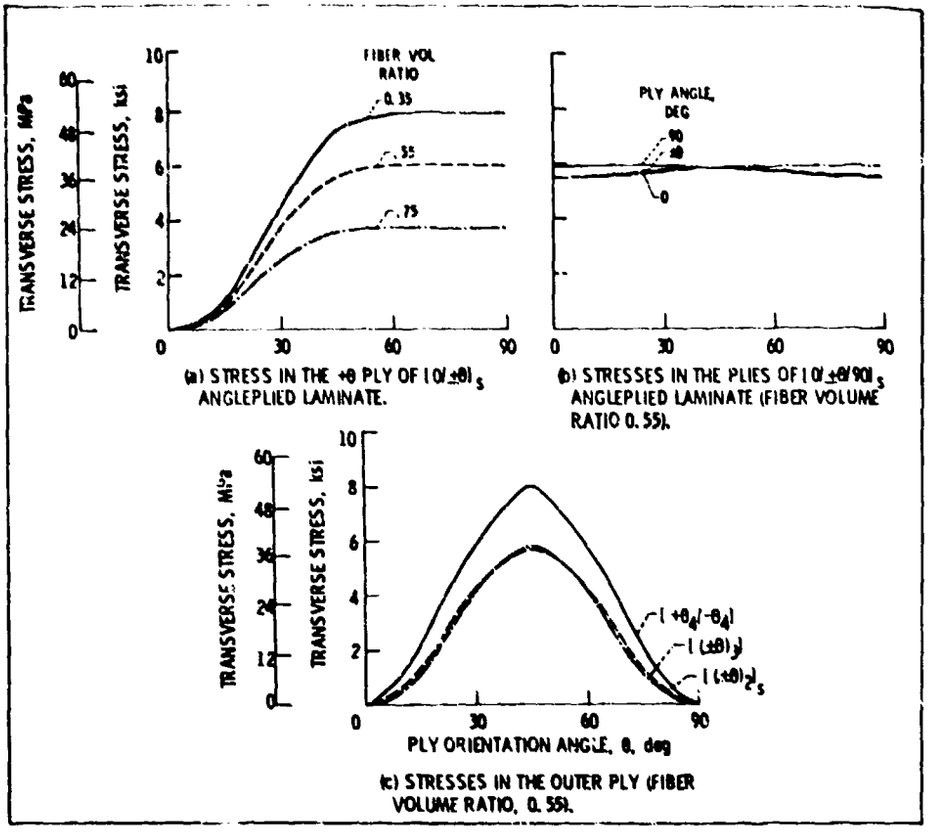


FIG. 37: PLY RESIDUAL TRANSVERSE STRESS FOR GRAPHITE THORNEL-50/EPOXY COMPOSITES. TEMPERATURE DIFFERENCE, 167 K (300°F)[63]

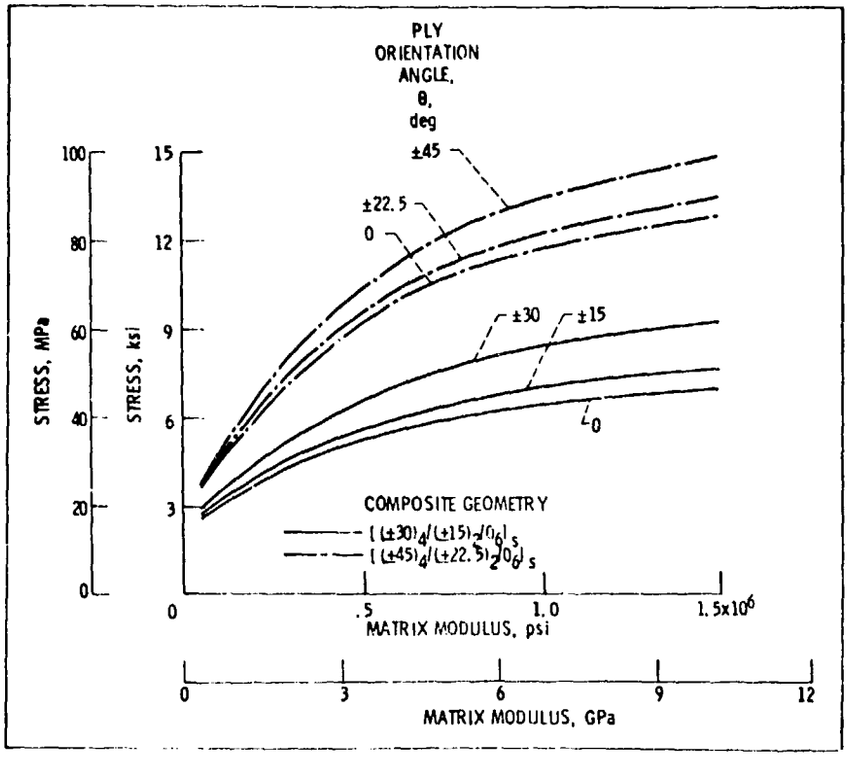


FIG. 38: EFFECT OF MATRIX MODULUS ON PLY RESIDUAL TRANSVERSE STRESS. MODMOR-I/ POLYIMIDE COMPOSITES; ZERO VOID CONTENT FIBER VOLUME RATIO, 0.50; TEMPERATURE DIFFERENCE, 333 K (600°F)[53]

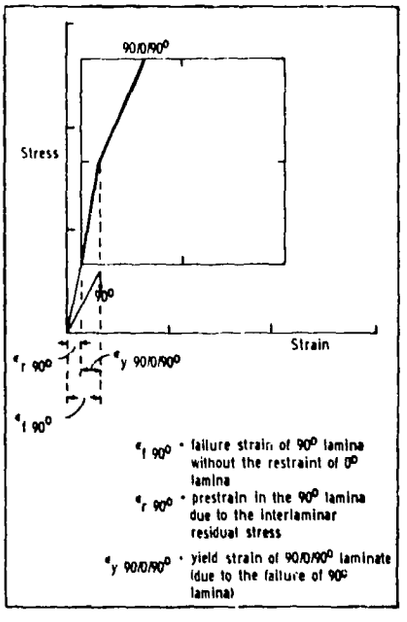


FIG. 39: APPROXIMATE RELATIONSHIP BETWEEN THE YIELD STRAIN OF A 90/0/90° LAMINATE AND THE FAILURE STRAIN OF A 90° LAMINA (WITHOUT THE RESTRAINT OF A 0° LAMINA)[188]

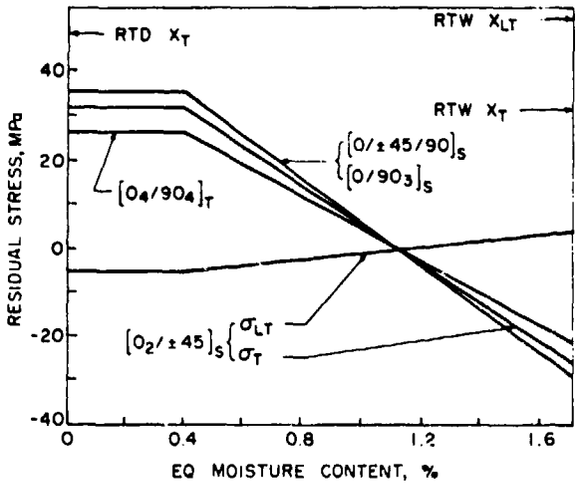


FIG. 40: RESIDUAL STRESSES VERSUS EQUILIBRIUM MOISTURE CONTENT FOR VARIOUS LAMINATES[118]

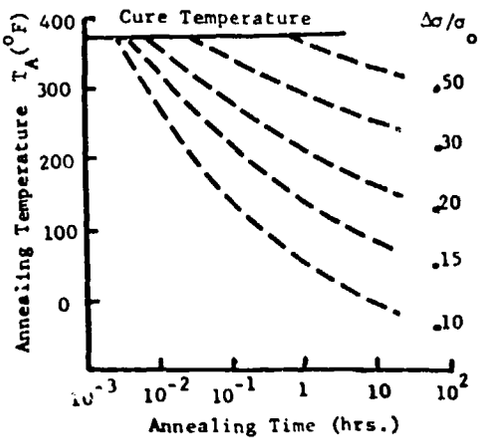


FIG. 41: KINETICS OF 1031 STRESS RELAXATION AS A FUNCTION OF ANNEALING TIME AND TEMPERATURE[73]

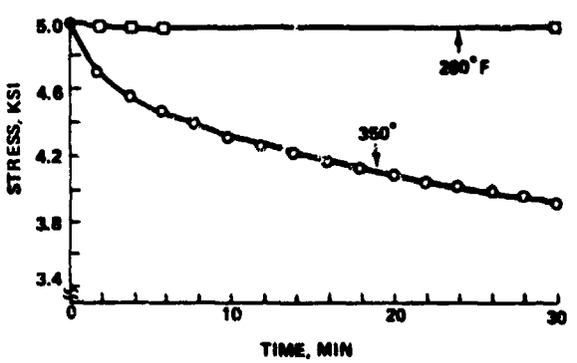


FIG. 42: STRESS RELAXATION OF HERCULES 3501-5A RESIN[128]

APPENDIX A — BIBLIOGRAPHY

ENVIRONMENTAL EFFECTS ON COMPOSITE MATERIALS

[1] Adams, D.F. "Influences of Environment on the Dimensional Stability of Fiber-Reinforced Composite Structures" - Environmental Degradation of Engineering Materials NSF 1977 pp 345-352.

[2] Adams, D.F., Miller, A.K. "Hygrothermal Microstresses in a Unidirectional Composite Exhibiting Inelastic Material Behavior", Journal of Composite Materials Vol 11 (1977) p 285.

[3] Adams, D.F. "Analysis of the Compression Fatigue Properties of a Graphite/Epoxy Composite", International Conference on Composite Materials 3 (1980).

[4] Adamson, M.J. "Thermal Expansion and Swelling of Cured Epoxy Resin Used in Graphite/Epoxy Composite Materials" Journal of Materials Science 15 (1980) pp 1736-1745.

[5] Adsit, N.R. "Elevated Temperature Testing of Graphite-Reinforced Materials", SAMPE Quarterly (July 1979) also 24th National SAMPE Symposium (1979).

[6] Alfrey, T., Gurnee, E.F., Lloyd, W.G. "Diffusion in Glassy Polymers", Journal of Polymer Science: Part C, No 12 249-261 (1966).

[7] Allen, R.C. "Corrosion Mechanisms in Attack of Resin and Resin-Glass Laminates", 33rd Annual Technical Conference (1978) SPI 6D, 1-7.

[8] Allen, R.C. "Effect of Moisture on Flexural Creep of Resins", SAMPE Quarterly April 1982.

[9] Allred, R.E., Lindrose, A.M. "The Room Temperature Moisture Kinetics of Kevlar 49 Fabric/Epoxy Laminates" ASTM STP 674 (1979).

[10] Allred, R.E. "The Effect of Temperature and Moisture Content on the Flexural Response of Kevlar/Epoxy Laminates: Part I and Part II", Journal of Composite Materials Vol 15 (March 1981) 100-116 and 117-132.

[11] Allred, R.E., Roylance, D.K. "The Influence of Moisture on Transverse Mechanical Behavior of Kevlar 49/Epoxy Composites at 25 C", Proceedings of the Critical Review Techniques for the Characterization of Composite Materials, May 1982 (AMMRC MS 82-3).

[12] Altman, J.H. "Advanced Composites Serviceability Program Status Review", Advanced Composites Special Topics (December 1979).

[13] Antoon, M.K., Starkey, K.M., Koenig, J.L. "Applications of Fourier Transform Infrared Spectroscopy to Quality Control of the Epoxy Matrix" ASTM STP 674 (1979).

[14] Antoon, M.K., Koenig, J.L. "Irreversible Effects of Moisture on the Epoxy Matrix in Glass-Reinforced Composites", Journal of Polymer Science: Physics Vol 19, 197-212 (1981).

[15] Antoon, M.K., Koenig, J.L., Serafini, T. "Fourier-Transform Infrared Study of the Reversible Interaction of Water and Crosslinked Epoxy Matrix", Journal of Polymer Science, Physics, Vol 19 (1981) pp 1567-1575.

[16] Apicella, A., Nicolais, L, "Environmental Aging of Epoxy Resins: Synengistic Effect of Sorbed Moisture, Temperature, and Applied Stress", Industrial Engineering Chemistry Production Research Development Vol 20 (1981) pp 138-144.

[17] Apicella, A., Nicolais, L., Astarita, G, Prioli, E. "Hygrothermal History Dependence of Moisture Sorption Kinetics in Epoxy Resins", Polymer Engineering and Science, June 1981 Vol 21 No 1.

[18] Apicella, A., Nicolais, L., Astarita, G., Prioli, E. "Effect of Thermal History on Water Sorption, Elastic Properties and the Glass Transition of Epoxy Resins", Polymer Vol 20 September 1979.

[19] Arrington, M., Harris, B. "Some Properties of Mixed Fibre CFRP", Composites, July 1978, 149-152.

[20] Atkins, A.G., Mai, Y.W. "Effect of Water and Ice on Strength and Fracture Toughness of Intermittently Bonded Boron-Epoxy Composites", Journal of Materials Science, 11, (1976), 2297-2306.

[21] Augl, J.M., Berger, A.E. "Moisture Effects on Carbon Fiber Epoxy Composites; II Prediction of Elastic Property Degradation", Naval Surface Weapons Center NSWC/WOL/TR - 61.

[22] Augl, J.M., Berger, A. "The Effect of Moisture on Carbon Fiber Reinforced Epoxy Composites I. Diffusion", NSWC/WOL/TR-76-7 (1976).

[23] Augl, J.M. "The Effect of Moisture on Carbon Fiber Reinforced Epoxy Composites II. Mechanical Property Changes", NSWC/WOL/TR-76-149 (1977).

[24] Augl, J.M., Berger, A.E. "The Effect of Moisture on Carbon Fiber Reinforced Composites. III. Prediction of Moisture Sorption in a Real Outdoor Environment", NSWC/WOL/TR-77-13 (1977).

[25] Augl, J.M. "Moisture Sorption and Diffusion in Kevlar 49 Aramid Fiber", NSWC/TR-79-51, March 1979.

[26] Aveston, J., Kelly, A., Sillwood, J.M. "Longterm Strength of Glass Reinforced Plastics in Wet Environments", International Conference on Composite Materials 3 (1980).

[27] Bailie, J.A., Duggan, M.F., Fisher, L.M., Dickson, J.N. "The Influence of Holes on the Compression Strength of Graphite Epoxy Cloth and Tape Laminate at Temperatures up to 430 K", International Conference on Composite Materials 3 (1980).

[28] Baker, A.A., Hawkes, G.A., Lumley, E.J. "Fiber-Composite Reinforcement of Cracked Aircraft Structures - Thermal-Stress and Thermal-Fatigue Studies", International Conference on Composite Materials 2 (1978).

[29] Baker, A.A., Rachinger, A.W., Williams, J.G. "Some Australian Exposure Trials on CFRP and GRP Materials", Australian Defence Scientific Service, Aeronautical Research Labs (1982).

[30] Baker, D.J., Gustafson, A. "Composite Flight Service Evaluation Program for Helicopters", Journal of American Helicopter Society, October 1981 p 70-74.

[31] Beaumont, P.W.R., Harris, B. "The Energy of Crack Propagation in Carbon Fibre-Reinforced Resin Systems", Journal of Materials Science, Vol 7, (1972), 1265-1279.
[32] Beck, C.E. "Advanced Composite Structure Repair Guide", Journal of Aircraft, Vol 18, No 9, (1981).
[33] Beckwith, S.W. "Creep Evaluation of a Glass/Epoxy Composite", SAMPE Quarterly, January 1980.
[34] Bergmann, H.W., Nitsch, P. "Predictability of Moisture Absorption in Graphite/Epoxy Sandwich Panels", AGARD-CP-288 (1980).
[35] Berman, L.D. "Reliability of Composite Zero-Expansion Structures for Use in Orbital Environment", ASTM STP 580 (1975).
[36] Bhatnagar, A., Lakkad, S.C. "Temperature and Orientation Dependance of the Strength and Moduli of Glass Reinforced Plastics", Fibre Science and Technology (1981) Vol 14 213-219.
[37] Blaga, A. "Water Sorption Characteristics of GRP Composite: Effect of Outdoor Weathering", Polymer Composites, January 1981, Vol 2, No 1.
[38] Bohlmann, R.E., Derby, E.A. "Moisture Diffusion in Graphite/Epoxy Laminates: Experimental and Predicted" 18th AIAA/ASME Structures, Structural Dyanmics & Materials Conference, 1977.
[39] Bonniau, P., Bunsell, A.R. "A Comparative Study of Water Absorption Theories Applied to Glass Epoxy Composites", Journal of Composite Materials, Vol 15 (May 1981) p 272.
[40] Bonniau, P., Bunsell, A.R. "Water Absorption by Glass Fiber Reinforced Epoxy Resin", International Conference on Composite Structures (1981).
[41] Browning, C.E., Husman, G.E., Whitney, J.M. "Moisture Effects in Epoxy Matrix Composites", ASTM STP 617 (1977).
[42] Browning, C.E. "The Mechanisms of Elevated Temperature Property Losses in High Performance Structural Epoxy-Resin Matrix Materials After Exposures to High Humidity Environments", International Conference on Composite Materials 2 (1978).
[43] Browning, C.E., Hartness, J.T. "Effects of Moisture on the Properties of High-Performance Structural Resins and Composites", ASTM STP 546 (1974).
[44] Browning, C.E. "The Mechanisms of Elevated Temperature Property Losses in High Performance Structural Epoxy Resin Matrix Materials After Exposures to High Humidity Environments", AFML-TR-76-153 March 1977.
[45] Cairns, D.S., Adams, D.F. "Moisture and Thermal Expansion of Composite Materials", AD-A109 131 November 1981
[46] Camahort, J.L., Rennhack, E.H., Coons, W.C. "Effects of Thermal Cycling Environment on Graphite/Epoxy Composites", ASTM STP 602 (1976).
[47] Camarda, L.J. "Application of the IITRI Compression Test Fixture at Elevated Temperature", Graphite/Polyimide Composites, NASA Conference Publication 2079, (1979).

[48] Campbell, M.D., Burleigh, D.D. "Thermophysical Properties Data on Graphite/Polyimide Composite Materials", ASTM STP 768 (1982).

[49] Carter, H.G., Kibler, K.G. "Lagumir-Type Model for Anomalous Moisture Diffusion in Composite Resins", Journal of Composite Materials, Vol 12 (April 1978) p 118.

[50] Carter, H.G., Kibler, K.G. "Rapid Moisture-Characterization of Composites and Possible Screening Applications", Journal of Composite Materials, Vol 10, (October 1976) p 355.

[51] Carter, H.G., Kibler, K.G. "Entropy Model for Glass Transition in Wet Resins and Composites", Journal of Composite Materials, Vol 11 (July 1977) p 265.

[52] Carter, H.G., Kibler, K.G., Reynolds, J.D. "Fundamental and Operational Glass Transition Temperatures of Composite Resins and Adhesives", ASTM STP 658 (1978).

[53] Chamis, C.C. "Residual Stresses in Angleplied Laminates and Their Effects on Laminate Behavior", International Conference on Composite Materials 2 (1978).

[54] Chamis, C.C., Lark, R.F., Sinclair, J.H. "Integrated Theory for Predicting the Hygrothermomechanical Response of Advanced Composite Structural Components", ASTM STP 658 (1978).

[55] Chamis, C.C., Smith, G.T. "Engine Environmental Effects on Composite Behavior", 21st AIAA/ASME Structures, Structural Dynamics & Materials Conference 1980.

[56] Chamis, C.C., Sinclair, J.M. "Prediction of Composite Hygral Behaviour Made Simple", NASA-TM-82780 (1982).

[57] Chapman, A.J., Hoffman, D.J., Hodges, W.T. "Effect of Commercial Aircraft Operating Environment on Composite Materials", 25th National SAMPE Symposium (1980).

[58] Chapman, A.J. "Graphite/Polyimide Tension Tests at Elevated and Cryogenic Temperatures", Graphite/Polyimide Composites, NASA Conference Publication 2079, (1979).

[59] Chen, J.S., Hunter, A.B. "Development of Quality Assurance Methods for Epoxy Graphite Prepreg", NASA-CR -3531 March (1982).

[60] Chiao, C.C., Sherry, R.J., Hetherington, N.W. "Experimental Verification of an Accelerated Test for Predicting the Lifetime of Organic Fiber Composites", Journal of Composite Materials, Vol 11 (January 1977), p 79.

[61] Christensen, R.M., "Mechanics of Composite Materials", John Wiley & Sons, (1979).

[62] Chung, T.J., Bradshaw, R.L. "Effects of Temperature and Moisture on Anisotropic Structures", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.

[63] Chung, T.J., Prater, J.L. "A Constructive Theory for Anisotropic Hygrothermoelasticity with Finite Element Applications", Journal of Thermal Stresses Vol 3 p 435-452 (1980).

[64] Chung, H.H., Crugnola, A. "Time-Temperature-Moisture Studies on Graphite Fiber Reinforced Epoxy Composites", 30th Annual Technical Conference (1975) SPI Sec 9A p 1-5.

[65] Clark, A.F., Fujii, G., Ranney, M.A. "The Thermal Expansion of Several Materials for Superconducting Magnets", IEEE Transactions on Magnetics Vol Mag 17 No 5 September 1981 pp 2316-2319.

[66] Clements, L.L., Lee, P.R. "Influence of Quality Control Variables on Failure of Graphite/Epoxy Under Extreme Moisture Conditions", ASTM STP 768 (1982).

[67] Coggeshall, R.L. "The 737 Graphite Composite Flight Spoiler Flight Service Evaluation", NASA-CR-165826 February (1982).

[68] Cotinaud, M., Bonniau, P., Bunsell, A.R. "The Effect of Water Absorption on the Electrical Properties of Glass-Fibre Reinforced Epoxy Composites", Journal of Materials Science 17, (1982), p 867-877.

[69] Crossman, F.W., Mauri, R.E., Warren, W.J. "Hygrothermal Damage Mechanisms in Graphite-Epoxy Composites" NASA Contractor Report 3189 (December 1979).

[70] Crossman, F.W., Mauri, R.E., Warren, W.J. "Moisture-Altered Viscoelastic Response of Graphite/Epoxy Composites", ASTM STP 658 (1978).

[71] Crossman, F.W., Flaggs, D.L. "Dimensional Stability of Composite Laminates During Environmental Exposure", 24th National SAMPE Symposium (1979).

[72] Crossman, F.W., Wang, A.S.D. "Stress Field Induced by Transient Moisture Sorption in Finite-W dth Composite Laminates", Journal of Composite Materials, Vol 12 (January 1978) p 2.

[73] Crossman, F.W., Warren, W.J., Pinoli, P.C. "Time and Temperature Dependant Dimensional Stability of Graphite -Epoxy Composites", 21st National SAMPE Symposium (1976).

[74] Crossman, F.W., Flaggs, D.L. "Dimensional Stability of Composite Laminates During Environmental Exposure", SAMPE Journal July/August 1979 p 15-20.

[75] Cunningham, B., Sargent, J.P., Ashbee, K.H.G. "Measurement of the Stress Field Created Within the Resin Between Fibers in a Composite Material During Cooling From the Cure Temperature", Journal of Materials Science Vol 16 (1981) pp 620-626.

[76] Curtis, P.T. "A BASIC Computer Program to Calculate Moisture Content in Resins and Fibre Reinforced Resin Composites", RAE-TM-375, June 1981.

[77] Daniel, I.M. "Effects of Material, Geometric and Loading Parameters on Behavior of Composites", 34th Annual Tech Conf (1979) SPI.

[78] Daniel, I.M., Liber, T., Chamis, C.C. "Measurement of Residual Strains in Boron-Epoxy and Glass-Epoxy Laminates", ASTM STP 580 (1975).

[79] Daniel, I.M., Schramm, S.W., Liber, T. "Fatigue Damage Monitoring in Composites by Ultrasonic Mapping", Materials Evaluation /39/ August 1981.

[80] Davis, A., Howes, B.V., Howes, E.A. "Weathering of Kevlar 49", Propellants, Explosives and Rocket Motor Establishment (1977), U.K., unpublished report.

[81] DeIasi, R., Whiteside, J.B. "Effect of Moisture on Epoxy Resins and Composites", ASTM STP 658 (1978).

[82] DeIasi, R.J., Schulte, R.L. "Moisture Detection in Composites Using Nuclear Reaction Analysis" Journal of Composite Materials, Vol 13 (October 1979) p 303.

[83] DeIasi, R. "Effect of Water on the Properties of a Glass-Polyimide Laminate", Journal of Materials Science 10, (1975), 1951-1958.

[84] Delmonte, J. "Technology of Carbon and Graphite Fiber Composites", Van Nostrand Reinhold Co. 1981 (Chapter 9 - Environmental Influences on Carbon/Graphite Fiber Composites).

[85] Deo, R.B. "Post First-Ply Failure Fatigue Behavior of Composites", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.

[86] Deteresa, S.J., Farris, R.I., Porter, R.S. "Fracture and Interface Studies of Aramid Reinforced Polyamide Composites: Compressive Effects and Critical Length Measurements", Interim Technical Report Ad-A109 506/6 (1981).

[87] Dewimille, B., Thoris, J., Mailfert, R., Bunsell, A.R. "Hydrothermal Aging of an Unidirectional Glass-Fibre Epoxy Composite During Water Immersion", International Conference on Composite Materials 3 (1980).

[88] Dexter, H.B., Chapman, A.J. "NASA Service Experience with Composite Components" 12th National SAMPE Technical Conference (1980).

[89] DiCarlo, J.A. "Time-Temperature-Stress Dependance of Boron Fiber Deformation", ASTM STP 617 (1977).

[90] Dijus, J.A.A.M. "Fatigue Test Results of Carbon Fibre Reinforced Plastic F28 Aircraft Component and its Structural Details", AGARD-CP-288 (1980).

[91] Dobyns, A.L., Porter, T.R. "A Study of the Structural Integrity of Graphite Composite Structure Subjected to Low Velocity Impact", Polymer Engineering and Science, Mid-June 1981 Vol 21 No 8.

[92] Docks, E.L., Buck, D.E. "Effect of Thermal Cycling on FRP Materials", 34th Annual Tech Conf (1979) SPI.

[93] Dorey, G. "Damage Tolerance in Advanced Composite Materials", RAE Technical Report 77172 (November 1977).

[94] Douglass, D.A., Weitsman, Y. "Stresses Due to Environmental Conditioning of Cross-Ply Graphite/Epoxy Laminates", International Conference on Composite Materials 3 (1980).

[95] Dynes, P.J., Kaelble, D.H. "Physiochemical Analysis of Graphite-Epoxy Composite Systems" ASTM STP 674 (1979).

[96] Eckstein, B.H. "Moisture Absorption by Epoxy Laminating Resins", UCC Paper Parma, Ohio (1977).

[97] Edge, E.C. "The Implications of Laboratory Accelerated Conditioning of Carbon Fiber Composites" AGARD-CP-288 (1980).

[98] Edge, E.C. "Effect on Moisture Absorption Experiments, of Failure to Dry Specimens Prior to Exposure", April 1980, Composites.

[99] Ekvall, J.C., Griffin, C.F. "Design Allowables for T300/5208 Graphite/Epoxy Composite Materials", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.

[100] Farley, G.L., Herakovich, C.T. "Influence of Two-Dimensional Hygrothermal Gradients on Interlaminar Stresses Near Free Edges", ASTM STP 658 (1978).

[101] Flaggs, D.L., Crossman, F.W. "Analysis of the Viscoelastic Response of Composite Laminates During Hygrothermal Exposure", Journal of Composite Materials, Vol 15 (January 1981) p 21.

[102] Flaggs, D.L., Vinson, J.R. "Hygrothermal Effects on the Buckling of Laminated Composite Plates", Fibre Science and Technology Vol 11 (1978) pp 353-365.

[103] Garber, D.P., Morris, D ..., Everett, R.A. "Elastic Properties and Fracture Behavior of Graphite/Polyimide Composites at Extreme Temperatures", ASTM STP 768 (1982).

[104] Garcia, R., McWithey, R.R. "Rail Shear Test Method", Graphite/Polyimide Composites, NASA Conference Publication 2079 (1979).

[105] Garrett, R.A., Bohlmann, R.E., Derby, E.A. "Analysis and Test of Graphite/Epoxy Sandwich Panels Subjected to Internal Pressures Resulting from Absorbed Moisture", ASTM STP 658 (1978).

[106] Gauchel, J.V., Steg, I., Cowling, J.E. "Reducing the Effect of Water on the Fatigue Properties of S-Glass Epoxy Composites", ASTM STP 569 (1975).

[107] Gazit, S., Ishai, O. "Hygroelastic Behavior of Glass-Reinforced Plastics Exposed to Different Relative Humidity Levels", Environmental Degradation of Engineering Materials, NSF 1977 pp 383-392.

[108] Gerharz, J.J., Schutz, D. "Fatigue Strength of CFRP Under Combined Flight-by-Flight Loading and Flight-by-Flight Temperature Changes", AGARD-CP-288 (1980).

[109] Gerharz, J.J., Schutz, D. "Literature Research on the Mechanical Properties of Fibre Composite Materials - Analysis of the State of the Art", RAE - Trans 2045 (1980).

[110] Gibbins, M.N., Hoffman, D.J. "Environmental Exposure Effects on Composite Materials for Commercial Aircraft" NASA-CR-3502 (1982).

[111] Gillat, O., Broutman, L.J. "Effect of an External Stress on Moisture Diffusion and Degradation in a Graphite-Reinforced Epoxy Laminate", ASTM STP 658 (1978).

[112] Givler, R.C., Gillespie, J.W., Pipes, R.B. "Environmental Exposure of Carbon/Epoxy Composite Material Systems", ASTM STP 768 (1982).

[113] Gourdin, C. "Kevlar and Kevlar Reinforced Composites Materials Aging Under Various Environments", International Conference on Composite Materials 3 (1980).

[114] Griffith, W.I., Morris, D.H., Brinson, H.F. "Accelerated Characterization of Graphite/Epoxy Composites", International Conference on Composite Materials 3 (1980).

[115] Grimes, G.C. "Experimental Study of Compression-Compression Fatigue of Graphite/Epoxy Composites", ASTM STP 734 (1981).

[116] Gruninger, G., Kochendorfer, R. "Fiber Reinforced Materials for Application in the Cold Part of Turbine Engines", AGARD-CP-112 (1972).

[117] Gurtin, M.E., Yatomi Chikayoshi "On a Model for Two Phase Diffusion in Composite Materials", Journal of Composite Materials, Vol 13 (April 1979) p 126.

[118] Hahn, H.T., Kim, R.Y. "Swelling of Composite Laminates" ASTM STP 658 (1978).

[119] Hahn, H.T. "Residual Stresses in Polymer Matrix Composite Laminates", Journal of Composite Materials, Vol 10 (October 1976) p 266.

[120] Hahn, H.T., Chiao, T.T. "Long-Term Behavior of Composite Materials", International Conference on Composite Materials 3 (1980).

[121] Halloff, E. "The Effect of Absorbed Moisture on Carbon-Fibre-Epoxy Composites", 25th National SAMPE Symposium (1980).

[122] Hancox, N.L. "The Influence of Voids on the Hydrothermal Response of Carbon Fibre Reinforced Plastics", Journal of Materials Science 16 (1981) p 627.

[123] Hancox, N.L. "Fibre Composite Hybrid Materials", Applied Science Publication, London 1981.

[124] Harper, B.D., Weitsman, Y. "Residual Thermal Stresses in an Unsymmetrical Cross-Ply Graphite/Epoxy Laminate", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.

[125] Haskins, J.F. "Recent Work on Techniques and Applications of Moisture Barriers to Graphite/Epoxy Composites", Advanced Composites Design and Applications - 29th Meeting of the Mechanical Failure Prevention Group 1979. NBS Spec. Publ. 563.

[126] Haskins, J.F., Wilkins, D.J., Stein,B.A. "Flight Simulation Testing Equipment for Composite Material Systems", ASTM STP 602 (1976).

[127] Haskins, J.F., Kerr, J.R., Stein, B.A. "Flight Simulation Testing of Advanced Composites for Supersonic Cruise Aircraft Applications", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference, 1977

[128] Hedrick, I.C., Whiteside, J.B. "Effects of Environment on Advanced Composite Structures", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference 1977 (Paper no. 77-463).

[129] Herakovich, C.T. "On the Relationship Between Engineering Properties and Delamination of Composite Materials", Journal of Composite Materials, Vol 15 (July 1981) p 336.

[130] Hertz, J. "Moisture Effects on Spacecraft Structures", 24th National SAMPE Symposium (1979).

[131] Hofer, K.E., Bennett, L.C., Stander, M. "Effects of Moisture and Fatigue on the Residual Mechanical Properties of S-Glass/Graphite/Epoxy Hybrid Composites", ASTM STP 636 (1977).

[132] Hofer, K.E., Porte, R. "Influence of Moisture on the Impact Behavior of Hybrid Glass/Graphite/Epoxy Composites", Journal of Elastomers & Plastics, Vol 10 (1978) July p 271.

[133] Hofer, K.E., Stander, M., Rao, P.N. "A Comparison of the Elevated Temperature Strength Loss in High Tensile Strength Graphite/Epoxy Composite Laminates Due to Ambient and Accelerated Aging", Journal of Testing and Evaluation, Vol 3 No 6 November 1975 pp 423-426.

[134] Hogg, P.J., Hull, D., Legg, M.J. "Failure of GRP in Corrosive Environments", International Conference on Composite Structures (1981).

[135] Hsu, A.C.T., Jemian, W.A., Wilcox, R.C. "Solvent Effect of Water on S-Glass", Journal of Materials Science Vol 11, (1976), 2099-2104.

[136] Humphrey, W.D., Liu, S.H., Plass, N.C., Timm, D.C. "Effects of Moisture Degradation: Molecular Structure of Composite Resin Systems", 13th National SAMPE Technical Conference (1981).

[137] Ishai, O, Arnon, U. "'Instantaneous' Effect of Internal Moisture Conditions on Strength of Glass-Fiber-Reinforced Plastics", ASTM STP 658 (1978).

[138] Ishai, O., Bar-Cohen, Y. "Hygrothermal Degradation of GFRP Laminates as Manifested in the Dispersion of Ultrasonic Data", 11th National SAMPE Technical Conference (1979).

[139] Ishai, O., Bar-Cohen, Y. "Dispersion of Ultrasonic Data as a Measure of Hygrothermal Effects on Fibre-Reinforced Plastic Laminates", Composites, (October 1980).

[140] Ishai, O. "Environmental Effects on Deformation, Strength, and Degradation of Unidirectional Glass-Fiber Reinforced Plastics. Part I Survey", Polymer Engineering and Science, July 1975 Vol 15 No 7 p 486-490 (see Part II [268]).

[141] Ishai, O. "Environmental Effects on Deformation, Strength, and Degradation of Unidirectioanl Glass-Fiber Reinforced Plastics. Part II Experimental Study", Polymer Engineering Science, July 1975 Vol 15 No 7 p 491-499 (see Part I [261]).

[142] Ishida, H., Koenig, J.L. "The Reinforcement Mechanism of Fiber-Glass Reinforced Plastics Under Wet Conditions: A Review", Polymer Engineering Science 1978, Vol 18, No 2, pp 128-145.

[143] Jackson, A.C. "Durability and Consistency of Composite Components", 21st AIAA/ASME Structures, Structural Dynamics & Materials Conference 1980.

[144] Jain, R.K., Asthana, K.K. "Effect of Natural Weathering on the Creep Behaviour of GRP Laminates in Tropical Climates", International Conference on Composite Materials 3 (1980).

[145] Jeans, L.L., Deo, R., Grimes, G.C., Whitehead, R.S. "Durability Certification of Fighter Aircraft Primary Composite Structure", Paper for presentation at 11th ICAF Symposium, Amsterdam (May 1981), Northrop Corp. Aircraft Division.

[146] Jeans, L.L., Grimes, G.C., Kan, H.P. "Fatigue Sensitivity of Composite Structure for Fighter Aircraft", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.

[147] Judd, N.C.W., Thomas, D.K. "The Effects of Outdoor Exposure on Non-Metallic Materials", (August 1974), RAE Technical Memo Mater. - 190.

[148] Judd, N.C.W. "The Water Resistance of Carbon Fibre Reinforced Plastics", RAE (1979). TR-78051, (BR64631).

[149] Judd, N.C.W. "The Effect of Water on Carbon Fibre Composites", 30th Annual Technical Conference (1975) SPI 18-A.

[150] Kabelka, J. "Thermal Expansion of Composites with Canvas-Type Reinforcement and Polymer Matrix", International Conference on Composite Materials 3 (1980).

[151] Kadotani, K. "Electrical Properties of the Glass/Epoxy Interface", Composites, October 1980 p 199-204.

[152] Kaelble, D.H., Dynes, P.J. "Moisture Diffusion Analysis for Composite Microdamage", 24th National SAMPE Symposium (1979).

[153] Kaelble, D.H., Dynes, P.J. "Nondestructive Tests for Shear Strength Degradation of a Graphite-Epoxy Composite", ASTM STP 617 (1977).

[154] Kaelble, D.H., Dynes, P.J., Crane, L.W., Maus, L. "Kinetics of Environmental Degradation in Graphite-Epoxy Laminates", ASTM STP 580 (1975).

[155] Kaelble, D.H., Dynes, P.J. "Methods for Detecting Moisture Degradation in Graphite-Epoxy Composites", Materials Evaluation April 1977 p 103-108.

[156] Kaelble, D.H., Dynes, P.J., Maus, L. "Hydrothermal Aging of Composite Materials, Part 1: Interfacial Aspects", Journal of Adhesion, 1976, Vol 8, pp 121-144.

[157] Kaelble, D.H. "Theory and Analysis of Fracture Energy in Fiber-Reinforced Composites", Journal of Adhesion, 1973, Vol 5, p 245-264.

[158] Kaelble, D.H., Dynes, P.J., Cirlin, E.H. "Interfacial Bonding and Environmental Stability of Polymer Matrix Composites", Journal of Adhesion, 1974, Vol 6, p 23-48.

[159] Kaelble, D.H., Dynes, P.J., Crane, L.W., Maus, L. "Interfacial Mechanisms of Moisture Degradation in Graphite-Epoxy Composites", Journal of Adhesion, 1974, Vol 7, p 25-54.

[160] Kaelble, D.H., Dynes, P.J., "Hydrothermal Aging of Composite Materials", Part 2 - Matrix Aspects. Journal of Adhesion, 1977 Vol 8 pp 195-212. (Part 1 - [222])

[161] Kan, H.P., Ratwani, M.M. "Compression Fatigue Behavior of Fiber Composites", SAMPE Quarterly, July 1980.

[162] Kasen, M.B., Schramm, R.E., Read, D.T. "Fatigue of Composites at Cryogenic Temperatures", ASTM STP 636 (1977).

[163] Kasen, M.B. "Properties of Filamentary-Reinforced Composites at Cryogenic Temperatures", ASTM STP 580 (1975)

[164] Keenan, J.D., Sefens, J.C., Quinlivan, J.T. "Effects of Moisture and Stoichiometry on Dynamic Mechanical Properties of Carbon Reinforced Composites", ACS Reprints, Organic Coatings and Plastics Chemistry Vol 40 p 700 (1979).

[165] Kelley, F.N., Bueche, F. "Viscosity and Class Temperature Relations for Polymer-Diluent Systems", Journal of Polymer Science, Vol 50, 549-556, (1961).

[166] Kerr, J.R., Haskins, J.F., Stein, B.A. "Program Definition and Preliminary Results of a Long-Term Evaluation Program of Advanced Composites for Supersonic Cruise Aircraft Applications", ASTM STP 602 (1976).

[167] Kibler, K.G., Carter, H.G. "Viscoelastic Parameters of Epoxy Resin from Thermomechanical and Electrical Conductivity Measurements", ASTM STP 674 (1979).

[168] Kibler, K.G. "Effects of Temperature and Moisture on the Creep Compliance of Graphite/Epoxy Composites", AGARD-CP-288 (1980).

[169] Kibler, K.G. "Time-Dependent Environmental Behaviour of Epoxy Composites", Proceedings of Annual Mechanics of Composites Review (5th) January 1980 AFWAL-TR-80-4020.

[170] Kim, R.H., Broutman, L.J. "Effects of Moisture and Stress on the Degradation of Graphite Fibre Reinforced Epoxies", - Deformation, Yield and Fracture of Polymers - 4th International Conference (April 1979).

[171] Kim, R.Y., Whitney, J.M. "Effect of Temperature and Moisture on Pin Bearing Strength of Composite Laminates", Journal of Composite Materials Vol 10 (1976) p 149.

[172] Koenig, J.L. "Improved Moisture Resistance of Fiber Reinforced Plastic", AD-A109 190/9 December 1981.

[173] Kong, S.I. "Bolt Bearing Strengths of Graphite/Epoxy Laminates", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.

[174] Kong, E.S., Lee, S.M., Nelson, H.G. "Physical Aging in Graphite/Epoxy Composites", Polymer Composites, January 1982 Vol 3 No 1.

[175] Kong, E.S.W. "Long Term Influence of Physical Aging Processes in Epoxy Matrix Composites", NASA-CR-166329 February (1981).

[176] Konishi, D.Y., Johnson, W.R. "Fatigue Effects on Delaminations and Strength Degradation in Graphite/Epoxy Laminates", ASTM STP 674 (1979).

[177] Konishi, D.Y., Lo, K.H. "Flow Criticality of Graphite/Epoxy Strucutres", ASTM STP 696 (1979).

[178] Kourtides, D.A. "Graphite Composites with Advanced Resin Matrices", 21st AIAA/ASME Structures, Structural Dynamics & Materials Conference 1980.

[179] Kreiner, J.H., Almon, M. "A Study of Environmental Effects on Aerospace Grade Composites", Advanced Composites Conference 1978.

[180] Kriz, R.D. "Absorbed Moisture and Stress-Wave Propagation in Graphite/Epoxy", Composites Technology Review (Winter 1981).

[181] Kunz, S.C. "Thermomechanical Characterization of Graphite/Polyimide Composites", ASTM STP 768 (1982).
[182] Labor, J.D., Verette, R.M. "Environmentally Controlled Fatigue Tests of Box Beams with Built-in Flaws", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference, 1977.
[183] Labor, J.D., Kiger, R.W., Scow, A.L., Myhre, S.H., Hall, A. "Repair Guide for Large Area Composite Structure Repair", AFFDL-TR-79-3039 (1979).
[184] Labor, J.D., Myhre, S.H. "Large Area Composite Structure Repair", AFFDL-TR-79-3040.
[185] Lamothe, R.M., Halpin, B.M., Neal, D. "Design Allowable Determination on a Fully Characterized Composite Material", 22nd AIAA/ASME Structures, Structural Dynamics & Materials Conference 1981.
[186] Lauraitis, K.N., Sandorff, P.E. "Experimental Investigation of the Interaction of Moisture, Low Temperature and Low Level Impact on Graphite/Epoxy Composites", Lockheed - Calif. Co., Burbank (Oct 1980) Report (Final) for Naval Air Development Center, Warminster, Penn, Contract No N62269-79-C-0276, Rept. LR-29655.
[187] Lauraitis, K.N., Sandorff, P.E. "The Effect of Environment on the Compressive Strengths of Laminated Epoxy Matrix Composites", AFML-TR-79-4179 (1979).
[188] Lee, B.L., Lewis, R.W., Sacher, R.E. "Environmental Effects on the Mechanical Properties of Glass Fiber/Epoxy Resin Composites", International Conference on Composite Materials 2 (1978).
[189] Lee, B.L., Lewis, R.W., Sacher, R.E. "Environmental Effects on the Mechanical Properties of Class Fiber/Epoxy Resin Composites", - AMMRC-TR-78-18 (June 1978).
[190] Leung, C.L., Kaelble, D.H. "Moisture Diffusion Analysis for Composite Microdamage", Advanced Composites, Design and Applications - Proceedings of 29th Meeting of the Mechanical Failure Prevention Group 1979. NBS Spec. Publ. 563.
[191] Leung, C.L., Dynes, P.J., Kaelble, D.H. "Moisture Diffusion Analysis of Microstructure Degradation in Graphite/Epoxy Composites", ASTM STP 696 (1979).
[192] Leung, C.L. "Space Environmental Effects on Graphite/Epoxy Composites", ASTM STP 768 (1982).
[193] Lifshitz, "Strain Rate, Temperature, and Humidity Influences on Strength and Moduli of a Graphite/Epoxy Composite", Composites Technical Review Vol 4 No 1 (1982) pp 14-19.
[194] Lisagor, W.B. "Mechanical Properties Degradation of Graphite/Polyimide Composites After Exposure to Moisture or Shuttle Orbiter Fluids", Graphite/Polyimide Composites, NASA Conference Publication 2079 (1979).
[195] Long, E.R. "Moisture Diffusion Parameter Characteristics for Epoxy Composites and Neat Resins", NASA Technical Paper 1474 (1979).
[196] Loos, A.C., Springer, G.S. "Moisture Absorption of Graphite-Epoxy Composites Immersed in Liquids and in Humid Air", Journal of Composite Materials, Vol 13 (April 1979) p 131.

[197] Loos, A.C., Springer, G.S., Sanders, B.A., Tung, R.W. "Moisture Absorption of Polyester-E Glass Composites", Journal of Composite Materials, Vol 14 (April 1980) p 142.

[198] Loos, A.C., Springer, G.S. "Effects of Thermal Spiking on Graphite-Epoxy Composites", Journal of Composite Materials, Vol 13 (January 1979), p 17.

[199] Lubin, C., Donohue, P. "Real Life Aging Properties of Composites", 35th Annual Tech Conf 1980 SPI.

[200] Lundemo, C.Y., Thor, S.E. "Influence of Environmental Cycling on the Mechanical Properties of Composite Materials", Journal of Composite Materials, Vol 11 (July 1977), p 276.

[201] Lundemo, C.Y. "Influence of Environmental Cycling on the Mechanical Properties of Composite Materials", Technical Note FFA HU-1853 - The Aeronautical Research Institute of Sweden (1977).

[202] Lyons, K.B., Phillips, M.G. "Creep-Rupture and Damage Mechanisms in Glass-Reinforced Plastics", Composites, (October 1981).

[203] Macander, A., Silvergleit, M. "Effect of Marine Environment on Stressed and Unstressed Graphite/Epoxy Composites", Naval Engineering Journal Vol 89 No 4 (1977) pp 65-72.

[204] Malter, V.L., Bolshakova, N.V., Andreev, A.V. "Method and Certain Results of a Semiempirical Description of the Heat Conductivity of Composite Materials", Journal of Engineering Physics, Vol 39 No 6 pp 1336-1342 (1980).

[205] Mandell, J.F. "Origin of Moisture Effects on Crack Propagation in Composites", Polymer Engineering and Science, April 1979, Vol 19, No 5, p 353-358.

[206] Marom, G., Cohn, D. "Angular Dependance of Hygroelasticity in Unidirectional Glass-Epoxy Composites", Journal of Materials Science Vol 15 (1980) 631-634.

[207] Marom, G., Broutman, L.J. "Moisture in Epoxy Resin Composites", Journal of Adhesion 1981 Vol 12 pp 153-164

[208] Maymon, G., Briley, R.P., Renfield, L.W. "Influence of Moisture Absorption and Elevated Temperature on the Dynamic Behavior of Resin Matrix Composites: Preliminary Results", ASTM STP 658 (1978).

[209] Mazzio, V.F., Mehan, R.L. "Effects of Thermal Cycling on the Properties of Graphite-Epoxy Composites", ASTM STP 617 (1977).

[210] McElroy, P., Allred, R., Roylance, D. "Effect of Weathering on the Mechanical Properties of Sheet Molding Compounds", 13th National SAMPE Technical Conference (1981).

[211] McKague, L. "The Thermal Spike Effect in "Wet" Composites", - Environmental Degradation of Engineering Materials NSF 1977 pp 353-362.

[212] McKague, L. "V378A Polyimide Resin - A New Composite Matrix for the 1980's", ASTM STP 768 (1982).

[213] McKague, E.L., Halkias, J.E., Reynolds, J.D. "Moisture in Composites: The Effect of Supersonic Service on Diffusion", Journal of Composite Materials, Vol 9 (January 1975) p 2.

[214] McKague, L. "Environmental Synergism and Simulation in Resin Matrix Composites", ASTM STP 658 (1978).
[215] Meares, P., "Polymers: Structure and Bulk Properties", Van Nostrand, (1965).
[216] Menges, G., Gitschner H.-W. "Sorption Behaviour of Glass-Fibre Reinforced Composites and the Influence of Diffusing Media on Deformation and Failure Behaviour", International Conference on Composite Materials 3 (1980).
[217] Miller, A.G., Wingert, A.L. "Fracture Surface Characterization of Commercial Graphite/Epoxy Systems", ASTM STP 696 (1979).
[218] Miller, A.K., Adams, D.F. "Inelastic Micromechanical Analysis of Graphite/Epoxy Composites Subjected to Hygrothermal Cycling", ASTM STP 658 (1978).
[219] Molcho, A., Ishai, O. "Thermal Cracking of CFRP Laminates", 10th National SAMPE Technical Conference (1976).
[220] Morgan, R.J., Mones, E.T. "The Effect of Thermal Environment and Sorbed Moisture on the Durability of Epoxies", 11th National SAMPE Technical Conference (1979).
[221] Morgan, R.J., O'Neal, J.E., Fanter, D.L. "The Effect Of Moisture on the Physical and Mechanical Integrity of Epoxies", Journal of Materials Science 15 (1980) p 751.
[222] Morley, J.M. "Role of the Matrix in the Preparation and the Properties of Carbon Fiber Composites", ACS Reprints, Organic Coatings and Plastics Chemistry Vol 38 p 666 (1978).
[223] Morris, E.E. "Filament Wound Composite Thermal Isolator Structures for Cryogenic Dewars and Instruments", ASTM STP 768 (1982).
[224] Murrin, L.I., Erbacher, H. "Composite Center Fuselage - Phase I", 35th Annual Tech Conf 1980, SPI.
[225] Myhre, S.E., Labor, J.D. "Repair of Advanced Composite Structures", Journal of Aircraft, Vol 18, No 7 (1981).
[226] Nicholas, J., Ashbee, K.H.G. "Further Destruction of Composite Materials by the Freezing or Boiling of Phase-Separated Water", Journal of Physics D: Applied Physics, Vol 11, 1978 pp 1015-1017.
[227] Nicolais, L., Apicella, A., Prioli, E. "Effect of Applied Stress, Thermal Environment and Water in Epoxy Resins", AFOSR-TR-82-0215 December 1980.
[228] Pagano, N.J., Hahn, H.T. "Evaluation of Composite Curing Stresses", ASTM STP 617 (1977).
[229] Parker, S.F.H., Chandra, M., Yates, B., Dootson, M., Walters, B.J. "The Influence of Distribution Between Fibre Orientations Upon the Thermal Expansion Characteristics of Carbon Fibre-Reinforced Plastics", Composites, (October 1981).
[230] Parmley, P.A., Konishi, D.Y., Hofer, K.E. "On the Accelerated Testing of Graphite/Epoxy Coupons", International Conference on Composite Materials 2 (1978).
[231] Pater, R.H. "Novel Improved PMR Polyimides", SAMPE Journal Nov/Dec 1981.
[232] Phelps, H.R., Long, E.R. "Property Changes of a Graphite/Epoxy Composite Exposed to Nonionizing Space Parameters", Journal of Composite Materials, Vol 14 (October 1980), p 334.

[233] Philips, D.C., Scott, J.M., Buckley, N. "The Effects of Moisture on the Shear Fatigue of Fiber Composites", International Conference on Composite Materials 2 (1978).

[234] Pipes, R.B., Vinson, J.R., Tsu-wei Chou "On the Hygrothermal Response of Laminated Composite Systems", Journal of Composite Materials, Vol 10 (April 1976) p 129.

[235] Porter, T.R. "Environmental Effects on Composite Fracture behaviour", ASTM STP 734 (1981).

[236] Porter, T.R. "Environmental Effects on Defect Growth in Composite Materials", NASA-CR-165213 January 1981.

[237] Pride, A. Richard, "Environmental Effects on Composites for Aircraft", NASA-TM-78716 (1978).

[238] Rao, R.M.V.G.K., Swaminadham, P., Rajanna, K. "Effect of Moisture and Class Contents on the Poisson's Ratio of FRP Plates as Determined by Laser Interferometry", Fibre Science and Technology Vol 15 (1951) pp 235-242.

[239] Rao, R.M.V.G.K., Balasubramanian, N., Chanda, M. "Moisture Absorption Phenomenon in Permeable Fiber Polymer Composites", Journal of Applied Polymer Science Vol 26 4069-4079 (1981).

[240] Renfield, L.W., Briley, R.P., Putter, S. "Dynamic Tests of Graphite/Epoxy Composites in Hygrothermal Environments", ASTM STP 768 (1982).

[241] Renieri, G.D., Coyle, J.M., Derby, E.A., Bohlmann, R.E. "Moisture Absorption Effects on the Strength of Composite Laminates", Environmental Degradation of Engineering Materials, NSF 1977 pp 363-372.

[242] Rogers, K.F., Kingston-Lee, D.M., Phillips, L.N., Yates, B., Chandra, M., Parker, S.F.M. "The Thermal Expansion of Carbon-Fibre Reinforced Plastics", Journal of Materials Science 16 (1981) p 2803 (Part 6).

[243] Rogers, K.F., Phillips, L.N et al "The Thermal Expansion of Carbon Fibre-Reinforced Plastics", Part 1, Journal of Materials Science, 12, (1977), 718-734.

[244] Rosen, B.W., Nagarkar, A.P., Hashin, Z. "Thermomechanical Response of GR/Pi Composites", NASA-CR-165753 (1981).

[245] Rotem, A., Nelson, H.G. "Fatigue Behavior of Graphite-Epoxy Laminates of Elevated Temperatures", ASTM STP 723 (1981).

[246] Rotem, A. "Fatigue Mechanism of Multidirectional Laminate Under Ambient and Elevated Temperature", International Conference on Composite Materials 3 (1980).

[247] Roylance, D., Roylance, M. "Influence of Outdoor Weathering on Dynamic Mechanical Properties of Glass/Epoxy Laminate", ASTM STP 602 (1976).

[248] Roylance, D., Roylance, M. "Degradation of Fiber-Reinforced Epoxy Composites by Outdoor Weathering", Environmental Degradation of Engineering Materials, NSF 1977, pp 393-402.

[249] Rubben, A., Domke, H. "A Method of Calculating Fatigue and Fracture of Glass Fiber Reinforced Materials Under Load and Temperature", International Conference on Composite Materials 3 (1980).

[250] Rummler, D.R., Clark, R.K. "Mechanical and Thermophysical Properties of Graphite/Polyimide Composite Materials", Graphite/Polyimide Composites, NASA Conference Publication 2079 (1979).

[251] Ryder, J.T., Walker, E.K. "The Effect of Compressive Loading on the Fatigue Lifetime of Graphite/Epoxy Laminates", AFWL-TR-79-4128 October 1979.

[252] Sandorff, P.E., Tajima, Y.A. "A Practical Method for Determining Moisture Distribution, Solubility and Diffusivity in Composite Laminates", SAMPE Quarterly (January 1979).

[253] Schramm, S.W., Daniel, I.M., Hamilton, W.G. "Nondestrucive Characterization of Flow Growth in Graphite/Epoxy Composites", 35th Annual Tech Conf 1980 SPI.

[254] Scola, D.A. "The Effects of Moisture on S-Class/Epoxy Resin Composite Shear Strength", 31st Annual Technical Conference (1976) SPI 14A, 1-12.

[255] Scola, D.A. "A Study to Determine the Mechanism of S-Glass/Epoxy Resin Composite Degradation Due to Moist and Solvent Environments", 30th Annual Technical Conference (1975) SPI 22-C

[256] Scola, D.A. "Thermoxidative Stability and Moisture Absorbtion Behavior of Glass- and Graphite Fiber-Reinforced PMR-Polyimide Composites", 22nd National SAMPE Symposium (1977).

[257] Scola, D.A., Pater, R.H. "The Properties of Novel Bisimide Amine Cured Epoxy/Celion 6000 Graphite Fiber Composites", SAMPE Journal Jan/Feb 1982 pp 16-23.

[258] Sendeckyj, G.P., Stalnaker, H.D., Kleismit, R.A. "Effect of Temperature on Fatigue Response of Surface-Notched [(0/ 45/0)] Graphite/Epoxy Laminate", ASTM STP 636 (1977).

[259] Serafini, T.T., Hanson, M.P. "Environmental Effects on Graphite Fiber Reinforced PMR-15 Polyimide", ASTM STP 768 (1982).

[260] Shen, C.-H., Springer, G.S. "Environmental Effects on the Elastic Moduli of Composite Materials", Journal of Composite Materials, Vol 11 (July 1977), p 250.

[261] Shen, C.-H., Springer, G.S. "Effects of Moisture and Temperature on the Tensile Strength of Composite Materials", Journal of Composite Materials, Vol 11 (January 1977), p 2.

[262] Shirrell, C.D., Halpin, J. "Moisture Absorption and Desorption in Epoxy Composite Laminates", ASTM STP 617 (1977).

[263] Shirrell, C.D. "Diffusion of Water Vapour in Graphite/Epoxy Composites", ASTM STP 658 (1978).

[264] Shirrell, C.D., Leisler, W.H., Sandow, F.A. "Moisture-Induced Surface Damage in T300/5208 Graphite/Epoxy Laminates", ASTM STP 696 (1979).

[265] Shirrell, C.D. "Moisture Sorption and Desorption in Epoxy Resin Matrix Composites", 23rd National SAMPE Symposium (1978).

[266] Shuart, M.J. "Sandwich Beam Compressive Test Method", Graphite/Polyimide Composites , NASA Conference Publication 2079, (1979).

[267] Shyprykevich P., Wolter, W. "Effect of Extreme Aircraft Storage and Flight Environments on Graphite/Epoxy", ASTM STP 768 (1982).
[268] Sih, C.C., Shih, M.T. "Hygrothermal Stress in a Plate Subjected to Antisymmetric Time-Dependent Moisture and Temperature Boundary Conditions", Journal Thermal Stresses Vol 3 p 321-340 (1980).
[269] Sih, G.C., Ogawa, A., Chou, S.C. "Two-Dimensional Transient Hygrothermal Stresses in Bodies with Circular Cavities: Moisture and Temperature Coupling Effects", Journal of Thermal Stresses Vol 4, p 193-222, 1981.
[270] Sih, G.C., Shih, M.T. "Transient Hydrothermal Stresses in Composites: Coupling of Moisture and Heat with Temperature Varying Diffusivity", AMMRC-TR-79-14, March 1979.
[271] Singh, J.J., Holt, W.H., Mock, W. "Moisture Determination in Composite Materials Using Positron Lifetime Technique", NASA Technical Paper 1681 (1980).
[272] Springer, G.S. "Environmental Effects on Composite Materials", Technomic, Westport, CT, 1981.
[273] Springer, G.S. "Environmental Effects on Epoxy Matrix Composites", ASTM STP 674 (1979).
[274] Springer, G.S. "Moisture Content of Composites Under Transient Conditions", Journal of Composite Materials, Vol 11, (January 1977) p 107.
[275] Sternstein, S.S., Ongchin, L., Silverman, A. "Inhomogeneous Deformation and Yielding of Glasslike High Polymers", Applied Polymer Symposia No 7 175-199 (1968)
[276] Stone, R.H. "Flight Service Evaluation of Kevlar-49 Epoxy Composite Panels in Wide-Bodied Commercial Transport Aircraft", NASA-CR-165841 (1982).
[277] Sumsion, H.T., Williams, D.P. "Effects of Environment on the Fatigue of Graphite-Epoxy Composites", ASTM STP 569 (1975).
[278] Sumsion, H.T. "Environmental Effects on Graphite-Epoxy Fatigue Properties", Journal of Spacecraft, Vol 13, No 3 (1976) p 150.
[279] Sun, C.T., Chim, E.S. "Fatigue Retardation Due to Creep in a Fibrous Composite", ASTM STP 723 (1981).
[280] Susman, S.E. "Graphite Epoxy Toughness Studies", 12th National SAMPE Technical Conference (1980).
[281] Sykes, G.F., Burks, H.D., Nelson, J.B. "The Effect of Moisture on the Dynamic Thermomechanical Properties of a Graphite/Epoxy Composite", 22nd National SAMPE Symposium (1977).
[282] Tajima, Y.A. "The Diffusion of Moisture in Graphite Fiber Reinforced Epoxy Laminates", SAMPE Quarterly, July 1980.
[283] Tajima, Y.A., Wanamaker, J.L. "Moisture Sorption Properties of T300/5209 Epoxy-Graphite Composites", Environmental Degradaton of Engieering Materials, NSF 1977 pp 373-382.
[284] Tanimoto, E.Y. "A Study of the Effects of Longterm Exposure to Fuels and Fluids on the Behavior of Advanced Composite Materials", NASA-CR-165763 August 1981.

[285] Teghtsoonian, E., Nadeau, J.S. "Effect of Environment on the Delayed Fracture of Fibre Reinforced Composites" Annual Report (1981) DND Contract 085B 329012, University of B.C.
[286] Tennyson, R.C. "Effect of Various Environmental Conditions on Polymer Matrix Composites", AGARD-CP-288 (1980).
[287] Tennyson, R.C. "Composite Materials in a Simulated Space Environment", 21st AIAA/ASME Structures, Structural Dynamics & Materials Conference 1980.
[288] Ting, R.Y., Keller, T.M. et al "Properties of Cured Diether-Linked Phthalonitrile Resins", SAMPE Quarterly, July 1981.
[289] Tompkins, S.S., Tenney, D.R., Unnam, J. "Prediction of Moisture Changes in Composites During Atmospheric Exposure", ASTM STP 674 (1979).
[290] Tompkins, S.S. "Influence of Surface and Environmental Thermal Properties on Moisture in Composites", Fibre Science and Technology Vol 11 (1978) pp 189-197.
[291] Trabocco, R.E., Stander, M. "Effect of Natural Weathering on the Mechanical Properties of Graphite/Epoxy Composite Materials", ASTM STP 602 (1976).
[292] Uemura, M., Iyama, H. Yamaguchi, Y. "Thermal Residual Stresses in Filament-Wound Carbon-Fiber-Reinforced Composites", Journal of Thermal Stresses Vol 2 p 393-412 (1979).
[293] Unnam, J., Tenney, D.R. "Analytical Prediction of Moisture Absorption/Desorption in Resin Matrix Composites Exposed to Aircraft Environments", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference, 1977.
[294] Vadala, E.T., Trabocco, R.E. "Effect of Exposure to Various Natural Environments on Organic Matrix Composites", 13th National SAMPE Technical Conference (1981).
[295] Waggoner, G., Erbacher, H. "Damage Tolerance Program for the B-1 Composite Stabilizer", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference 1977.
[296] Waggoner, G., Erbacher, H. "Evaluation of Manufacturing Defects Under Simulated Service Environments", 10th National Technical Conference (1976).
[297] Walrath, D.E., Adams, D.F. "Fatigue Behaviour of Hercules 3501-6 Epoxy Resin", Report NADC-78139-60 University of Wyoming, Laramie (1980).
[298] Wang, A.S.D., Crossman, F.W. "Some New Results on Edge Effect in Symmetric Composite Laminates", Journal of Composite Materials Vol 11 (January 1977) p 92.
[299] Wang, A.S.D., Crossman, F.W. "Edge Effects on Thermally Induced Stresses in Composite Laminates", Journal of Composite Materials, Vol 11 (July 1977) p 300.
[300] Wang, A.S.D., Crossman, F.W. "Calculation of Edge Stresses in Multi-Layer Laminates by Sub-Structuring", Journal of Composite Materials, Vol 12 (Jan 1978) p 76.
[301] Wang, C.S., Wang, A.S.D. "Creep Behavior of Glass-Epoxy Composite Laminates Under Hygrothermal Conditions", International Conference on Composite Materials 3 (1980).

[302] Wang, S.S., Choi, I. "Boundary-Layer Hygroscopic Stresses in Angle-Ply Composite Laminates", 21st AIAA/ASME Structures, Structural Dynamics & Materials Conference 1980.

[303] Wang, A.S.D., Pipes, R.B., Ahmadi, A. "Thermoelastic Expansion of Graphite-Epoxy Unidirectional and Angle-Ply Composites", ASTM STP 580 (1975).

[304] Wang, A.S.D., Liu, P.K. "Humidity Effects on the Creep Behavior of an Epoxy-Graphite Composite", Journal of Aircraft, Vol 14, No 4, (1977).

[305] Wanhill, R.J.H. "Environmental Fatigue Crack Propagation in Metal/Composite Laminates", National Aerospace Lab., Amsterdam, NLR MP 78027U (June 1978).

[306] Weinberger, R.A., Somoroff, A.R., Riley, E.L. "US Navy Certification of Composite Wings for the F-18 and Advanced Harrier Aircraft", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference, 1977.

[307] Weitsman, Y. "A Rapidly Convergent Scheme to Compute Moisture Profiles in Composite Materials Under Fluctuating Ambient Conditions" Journal of Composite Materials, Vol 15 (1981) p 349.

[308] Weitsman, Y. "Hygrothermal Viscoelastic Analysis of a Resin-Slab Under Time-Varying Moisture and Temperature" 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference, 1977.

[309] Weitsman, Y. "Diffusion with Time-Varying Diffusivity, with Application to Moisture-Sorption in Composites", Journal of Composite Materials Vol 10 (1976) p 193.

[310] Welhart, E.K. "Environmental Effects on Selected Resin Matrix Materials", NASA-CR-150938 (March 1976).

[311] Whitney, J.M., Browning, C.E. "Some Anomalies Associated with Moisture Diffusion in Epoxy Matrix Composite Materials", ASTM STP 658 (1978).

[312] Whitney, J.M. "Three Dimensional Moisture Diffusion in Laminated Composites", 18th AIAA/ASME Structures, Structural Dynamics & Materials Conference, 1977.

[313] Whitney, J.M. "Moisture Diffusion in Fiber Reinforced Composites", International Conference on Composite Materials 2, (1978).

[314] Whitney, J.M., Husman, G.E. "Use of the Flexure Test for Determining Environmental Behaviour of Fibrous Composites", Experimental Mechanics, Vol 18 (1978) No 5 p 185-190.

[315] Whitney, J.M., Kim, R.Y. "High Temperature Tensile Strength of Graphite/Epoxy Laminates Containing Circular Holes", Journal of Composite Materials Vol 10 October 1976 p 319-324.

[316] Wilkins, D.J. "Environmental Sensitivity Tests of Graphite-Epoxy Bolt Bearing Properties", ASTM STI 617 (1977).

[317] Wilkins, D.J., Wolff, R.V., Shinozuka, M., Cox, E.F. "Realism in Fatigue Testing: The Effect of Flight-by-Flight Thermal and Random Load Histories on Composite Bonded Joints", ASTM STP 569 (1975).

[318] Wolff, R.V. "Effects of Moisture Upon Mean Strength of Composite-to-Metal Adhesively Bonded Joint Elements", 22nd National SAMPE Symposium (1977).

[319] Wollner, B. "Temperature/Humidity Criteria for Advanced Composite Structures", 10th National SAMPE Technical Conference (1978).

[320] Wright, W.W. "The Effect of Diffusion of Water Into Epoxy Resins and Their Carbon Fiber Reinforced Composites", July 1981, Composites.

[321] Wright, W.W. "A Review of the Influence of Absorbed Moisture on the Properties of Composite Materials Based on Epoxy Resins", RAE Tech Memo Mat 324 (December 1979)

[322] Wu, E.M. "Strength Degradation of Aramid-Fiber/Epoxy Composites", AMMRC-TR-80-19 April 1980.

[323] Yamini, S., Young, R.J. "The Mechanical Properties of Epoxy Resins", (Part 1 & 2) Journal of Materials Science, 15 (1980) 1814-1831.

[324] Yates, B., Overy, M.J. et al "The Thermal Expansion of Carbon Fibre-Reinforced Plastics", Part 2, Journal of Materials Science, 13, (1978), 433-440.

[325] Yates, B., McCalla, A. et al "The Thermal Expansion of Carbon Fibre-Reinforced Plastics", Part 3, Journal of Materials Science, 13, (1978), 2217-2225.

[326] Yates, B., McCalla, A. et al "The Thermal Expansion of Carbon Fibre-Reinforced Plastics", Part 4, Journal of Materials Science, 13, (1978), 2226-2232.

[327] Yates, B., McCalla, A. et al "The Thermal Expansion of Carbon Fibre-Reinforced Plastics", Part 5, Journal of Materials Science, 14, (1979), 1207-1217.

[328] Yeow, Y.T., Morris, D.H., Brinson, H.F. "Time-Temperature Behavior of a Unidirectional Graphite/Epoxy Composite", ASTM STP 674 (1979).

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4

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DESCRIPTORS (KEY WORDS)/MOTS-CLÉS

1. Carbon fibre reinforced plastics
2. Composite materials

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SUMMARY/SOMMAIRE

This report is second in a series of literature reviews in which hygrothermal effects on aerospace composite materials (CM) with polymeric matrixes are examined. This report (Part II) deals primarily with the glass transition temperature and expansion properties due to temperature and moisture. The chapter on residual stresses is also included in this part as these stresses are a direct consequence of the expansion properties. Specific heat, thermal conductivity and emittance are briefly mentioned in Chapter 3.0, while properties connected with moisture absorption have been reviewed extensively in Part I of the series.

Other reports in this series deal with the following topics:

Part I: Thermal and Moisture Diffusion
Part III: Mechanical Properties 1
Part IV: Mechanical Properties 2
Part V: Composite Structures and Joints
Part VI: Numerical and Analytical Solutions
Part VII: Summary of Conclusions and Recommendations

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