Accelerated Environmental Testing of Composite Materials

Roger Vodicka

Airframes and Engines Division
Aeronautical and Maritime Research Laboratory

DSTO-TR-0657

ABSTRACT

Composite materials are found to lose mechanical on exposure to aircraft operating environments. This is mainly due to absorption of moisture from humid air by the matrix material. Composite materials are extensively used by the RAAF for both major structural components on the F/A-18 and for bonded repairs and doublers. The performance of these materials under long-term environmental exposure is an important aspect of both aircraft certification and in the understanding of how the components will age. This report provides a broad overview of environmental effects on composite materials and methods which may be used to predict their long-term behaviour. The use of accelerated testing environments in the laboratory is an attractive proposition as it enables tests to be carried out in reduced time frames. A number of accelerated testing methodologies and their implications are outlined here. Accelerated testing can be carried out with confidence if the exposure conditions are representative and the failure modes of the material during mechanical tests reflect those seen in service.

RELEASE LIMITATION

Approved for Public Release

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

Published by

DSTO Aeronautical and Maritime Research Laboratory
PO Box 4331
Melbourne Victoria 3001

Telephone: (03) 9626 7000
Fax: (03) 9626 7999

AR-010-516
April 1998

Approved for Public Release

Accelerated Environmental Testing of Composite Materials

Executive Summary

This document covers most of the important aspects of environmental exposure for composite materials used by RAAF aircraft. These materials are subject to environmental degradation under aircraft operating conditions over long periods of time. Temperature, humidity, erosion and UV radiation all play a part in reducing the integrity of composites. Composite materials absorb moisture from humid air. Combined with elevated temperature this is known as a hot/wet condition. Hot/wet conditions are known to significantly reduce composite mechanical properties. The extent of this reduction is critical in aircraft design, certification and operation.

Hot/wet testing of composites involves conditioning the component under humid conditions to allow the composite to absorb moisture. Mechanical tests are then performed at elevated temperatures. The conditioning of thick composite sections can take many years under normal operating environments. This is impractical for the laboratory evaluation of materials.

There is a need to develop accelerated testing techniques which can faithfully replicate the effects of long-term operating conditions in a shorter time-frame. Careful choices must be made to ensure that the accelerated test is fully representative of aircraft flight and ground storage climates.

This document covers many aspects of accelerated testing as well as the effects of temperature and moisture. Combined fatigue and environmental spectrum testing (known as ENSTAFF) is also addressed. Candidate techniques are identified and examples of their use given.

Authors

Roger Vodicka
Airframes and Engines Division

Roger Vodicka graduated BSc. (Hons.) from Monash University and joined AMRL in 1990. He currently works in the area of composite materials and crack-patching repair technology. Current working projects include moisture diffusion properties of epoxies, battle damage repair, environmental certification of composite materials and composite manufacturing methods.

Contents

1. Introduction

This report addresses material durability and strength issues for composite materials in RAAF aircraft operating under Australian climatic conditions. The effects of the natural environment during both flight and ground storage are assessed. Methods which may be used to simulate these effects in the laboratory in shorter time frames are outlined. Such information may be vital in formulating life-extension strategies and anticipating material problems well in advance. This report does not address issues related to corrosion or the effects of chemical action on materials such as fuels or hydraulic fluids.

The environmental conditioning of composite materials is an important aspect of their certification for use in aircraft structures. The mechanical properties of composite materials such as boron/epoxy and graphite/epoxy degrade in the natural environment and particularly under hot/wet conditions. It is important to understand these effects in order to design confidently and certify composite structures. There are numerous mechanisms which act to degrade the matrix and in some cases, the fibre itself. Changes in material properties over time may also need to be quantified. This can be difficult since real-time environmental testing of a composite in a natural environment may take many years to complete.

Both graphite/epoxy and boron/epoxy materials are currently used by the RAAF on a number of aircraft. Boron/epoxy material is primarily used in adhesively bonded repairs or reinforcements such as on the F-111 upper wing-pivot fitting. Large boron/epoxy doublers were also fitted to the lower wing pivot fitting during original manufacture. Graphite/epoxy material is used extensively on the surfaces of the F/A-18 aircraft such as the main wing skins, horizontal stabilator and vertical fins. Understanding the way in which these materials will perform in the future is vital knowledge for the supportability of the RAAF fleet.

Creating accelerated testing environments which replicate the effects of long-term natural environmental exposure and flight mission profiles can significantly reduce testing time and give advance warning of material problems which may arise in the future. It must be stressed that such tests must be carried out carefully to avoid exposing the material to conditions it may never see in service. It is therefore important to accurately define the conditions the material will be exposed to in the first place.

The accelerated conditioning of a material is not a trivial exercise if the results are to faithfully represent real-time exposure. Many factors must be taken into account before results can be considered conclusive. Validation of accelerated tests by comparison to long-term exposure is desirable but may be impractical in many situations.

The certification of composite materials and structures is also an important issue. Accelerated testing is very desirable as decisions on materials to be used in structures cannot wait for long-term trials to complete. Rapid, accurate and low-cost methods of assessing materials are often desired.

There have been a number of reviews and publications on environmental effects on composite materials. These are addressed throughout this paper and serve as a good basis for understanding environmental effects, accelerated testing procedures and certification methods.

This report details the main types of composite materials used by the RAAF.

2. Material Operating Environment

The natural environmental conditions which act upon a material in service can change it's mechanical properties. Although composites do not suffer from corrosion they may degrade in the environment in other more subtle ways. It is important to understand the material and the environment under which it will operate. Carefully chosen composite materials have shown very good environmental durability in aircraft components.

There are many environmental factors which can create changes in the properties of a composite material which in turn affect the ultimate mechanical performance. These need to be carefully identified and related to the type of service the material will see. For example, the combination of humidity and temperature creates what is often termed a hot/wet environment. This environment causes the composite matrix to absorb moisture from humid air which combined with elevated temperature reduces mechanical properties.

The definition of an environment must be carefully established before any test program commences. For aircraft components this must include full details of the conditions experienced both during flight and ground storage. The details which may be required for ground storage include:

- Humidity
- Temperature (of air and material surface)
- Ultraviolet and Infrared radiation levels
- Wind conditions
- Rainfall
- Thermal Shock

The different mission profiles that the aircraft experiences will affect the severity and frequency of these conditions. The accurate simulation of the conditions the material will experience on the aircraft is most important. The combination of these effects may also prove to be important as shown in the hot/wet exposure case. Specific details which may need to be defined for flight conditions include:

- Temperature at altitude
- Humidity at altitude
- Solar radiation at altitude
- Temperature the material sees during
    - cruising, supersonic dash, acceleration, climb and descent
- Rates of heating and cooling during flight manoeuvres
- Frequency and duration of each exposure

Materials on different parts of the aircraft will experience different environmental conditions. A set of conditions or flight profiles must then be defined for each specific part of the aircraft.

3. The Composite Material

The composite material used in a particular aircraft structure must be carefully quantified before testing and environmental exposure. This includes determining the location and type of material used, it's layup configuration, thickness and physical properties such as thermal conductivity, density and moisture diffusion characteristics. Composite specimens for testing should also be manufactured as per the original specification used for the aircraft manufacture.

Material type and the manufacturing method affect mechanical properties as well as durability. Material thickness is important since thick composites may develop temperature and moisture gradients. Thermal conductivity and density define the flow of thermal energy through the material. Diffusion characteristics define the way in which the matrix of a composite material will absorb moisture from humid air.

Aluminium honeycomb sandwich structures may suffer corrosion problems in hygrothermal environments and are considered as a special case.

3.1 Matrix

The exact chemical composition of the matrix does not need to be known to determine diffusion characteristics or to set up a representative accelerated test. It is, however, vital to ensure that no variations between batches of material exist. It is desirable to use material from the same batch for all tests. If material from more than one batch is required it is necessary to perform mechanical tests to verify the material has identical properties. It is also necessary to ensure that the same cure-cycle for all material of the same type is employed. It is best to have a complete thermal history of the matrix material prior to testing to ensure results are valid. Variations in chemical composition and processing can easily be the greatest influence on variability in mechanical testing results. Tight control on manufacturing and selection of materials for testing is required. Residual stresses may also be present in the cured material and volume fractions of resin may vary. Voids and cracks in the matrix created during processing may produce errant moisture diffusion results. A uniformly consolidated laminate is also required.

Moisture uptake concentration is defined in this paper as a percentage uptake by weight. This may be calculated using Equation 1.

Equation 1

$$\text{Moisture Uptake Concentration \%} = \frac{Weight(final) - Weight(initial)}{Weight(initial)} * 100.$$

The terms moisture uptake, moisture absorbed, moisture concentration and weight-gain are used interchangeably in the literature. All terms refer to moisture uptake of the resin or composite by weight.

Moisture content is an important property as it alters the resin mechanical properties. The glass-transition temperature, T_g, is an important material property as it defines the temperature at which material properties are drastically reduced. The matrix changes

from a glassy stiff state to a pliable one at temperatures greater than T_g. Moisture has the effect of lowering T_g in proportion to moisture concentration.
Differing types of resin will absorb varying amounts of moisture.
Table 1 lists a variety of high-performance resins and their maximum moisture uptake when exposed to high humidity. Values of moisture uptake in composites will be lower due to the presence of fibres.

Table 1 Maximum Moisture Uptake of Selected Resins in Composite Materials

Name	Maximum Moisture Uptake of resin in % by weight
3501-6 Graphite/Epoxy (Hercules) [1]	4.5
FM-73 Epoxy Adhesive [2] (Cytec)	4
MR-45 Bismaleimide (Amoco) [3]	3.1
V398 Bismaleimide (US Polymeric) [3]	5.3
PMR-15 Polyimide (US Polymeric) [3]	4.0
PEEK Thermoplastic (ICI) [3]	0.7

3.2 Moisture Resistant Matrix Resins

It is often useful to evaluate the hot/wet performance of matrix materials prior to choosing them for an application. Many new resin systems have come onto the market which have a greater resistance to moisture uptake. These resins are undergoing development and may appear in the short term. Thermoplastic resins are an example; they have much lower moisture uptake when compared to epoxies. A thermoplastic resin such as PEEK may be saturated with moisture at 0.1% whereas epoxies may take up as much as 4% water by mass. Chemically modified resins designed to withstand moisture uptake have been produced by the Dow Chemical Company [4]. Dow has demonstrated the production of two toughened epoxy resins which have saturation moisture values close to 1%. These new resins retain much of their dry glass-transition temperature (T_g) and modulus values after reaching their saturation moisture content levels.

3.3 Fibre

It has been found that both graphite and boron fibres do not absorb moisture to any significant extent [5]. This makes it easier to assess the diffusion properties of a composite employing these fibres since only the matrix needs to be considered. These fibres are also found to be resistant to the hot/wet environment which degrades the matrix of epoxy based composites.

3.4 Matrix Interface/Interphase

It must be noted that fibres may be coated or 'sized' prior to being coated by the matrix resin to improve fibre to matrix adhesion. This sizing then forms an integral part of the fibre/matrix interface or interphase. The properties of the sizing may need to be considered separately; especially for mechanical tests where the failure mode is by fibre pull-out. Results of fibre pull-out tests [6][7] have shown that the fibre/matrix interface or interphase is especially sensitive to hygrothermal conditioning and may be a 'weak link' in composite performance . It may be important to consider that the glass-transition temperature (T_g) and diffusion properties of this interface/interphase may be different to the bulk matrix. The chemical composition of sizing is often difficult to determine so the properties of this interface may not be known.

3.5 Honeycomb Sandwich Structures

The intrusion of free water into composite sandwich structures can cause several serious problems. It is possible for free water to enter the cells of aluminium honeycomb core and produce corrosion which may cause the skin to separate.

The effects of corrosion are not addressed here. Metallic honeycomb is the most commonly used type in RAAF aircraft and is present in F/A-18 structure. Other types of honeycomb core such as NOMEX are non-metallic and do not suffer from corrosion but may have problems in hot/wet environments similar to composites.

Work by Jackson and O'Brien [8] assessed the possibility of water intrusion into thin-skinned composite honeycomb sandwich structures. They found that impact and fatigue could produce matrix cracks which would form a path for water to enter honeycomb cells. An air-intrusion test devised by the researchers gave a clear indication of the possibility of water intrusion where other NDI methods such as optical examination failed. It is important to test honeycomb structures for the possibility of water intrusion prior to conditioning in any humid or moist environment.

Work by Dexter and Baker [9] showed that corrosion of honeycomb sandwich structure led to a significant decrease in residual strength. Corrosion of honeycomb is likely to reduce it's strength and create a disbond between the honeycomb and the composite skin.

Water within honeycomb cells can generate pressures great enough to force the skin to disbond from the honeycomb if heated to high temperatures. **Figure 1** is a plot of pressure within a honeycomb cell versus temperature. This plot assumes that there is approximately one atmosphere of pressure within the cell to begin with as well as sufficient water to vaporise to achieve the saturated vapour pressure at all temperatures shown. **Figure 1** therefore represents the maximum pressures that can be generated at the given temperatures. Work by Garret at al. provides a more rigorous treatment of the problem. **[10]**.

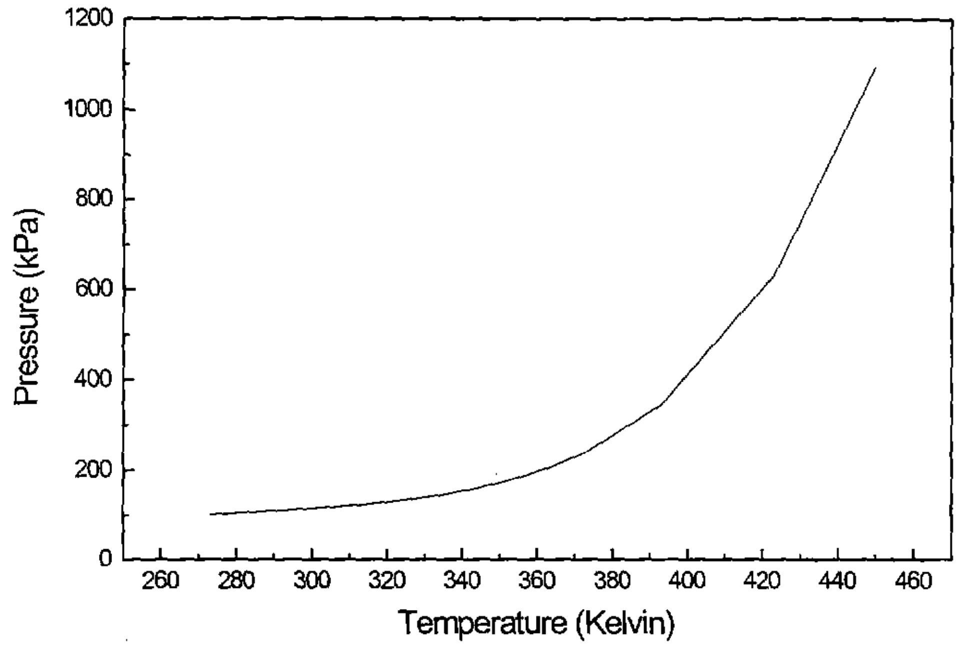

Figure 1 Plot of pressure within a honeycomb cell with water present

The effect of this pressure may be important in repair situations where elevated temperatures are used to cure adhesively bonded repairs.
Work at DSTO-AMRL by Chester and Baker [11] employed novel techniques to demonstrate the tropical environmental durability of honeycomb sandwich specimens under mechanical loading. Excellent durability was found for these specimens even after up to 9 years of exposure.

4. Diffusion of Moisture into Composites

Immediately after manufacture the matrix material in a composite material will begin to absorb moisture from humid air. The manner in which this occurs and to what extent, is crucial in assessing a materials performance. Models of the moisture diffusion process are required to understand the nature of the material changes as well as to optimise accelerated testing regimes for hot/wet testing.
This section covers some of the elementary mathematics of diffusion relevant to composites and the mathematical models which may be used to describe it. The solution of these models may be conveniently performed using computer software.

4.1 Basic Moisture Diffusion

Moisture diffusion characteristics are often quoted in the literature as Fickian or non-Fickian. Fickian behaviour is the simplest to deal with and represents the diffusion behaviour of many aerospace thermoset matrix materials. Non-Fickian behaviour can often be associated with chemical and/or physical changes occurring within the composite. Materials which do not absorb moisture according to Fick's law are difficult to model reliably. Most of the diffusion mathematics and discussion given here are based around Fickian behaviour.

4.2 Fickian Diffusion:

In most cases we are considering common aerospace epoxy resins and fibres in laminate form. This means that the diffusion will be primarily through the laminate faces and only a small effect will be seen from edge diffusion. Fick's first law states that the flux of moisture in the through-thickness direction, x, will be dependent only on the concentration gradient through the sample in that direction:

$$MoistureFlux = -D.\frac{\partial c}{\partial x} \qquad \text{Equation 2}$$

where D is the diffusivity or diffusion constant, c is the concentration of moisture.

Fick's second law defines the differential equation for the diffusion process if diffusivity, D, is independent of x:

$$\frac{\partial c}{\partial t} = D.\frac{\partial^2 c}{\partial x^2} \qquad \textit{Equation 3}$$

The diffusion constant D will be independent of time and is constant through the thickness of the sample. The diffusion constant, however, varies strongly with temperature.

Fickian behaviour is characterised experimentally by an uptake of moisture which reaches an asymptotic value after a period of time. If the mass-gain of a sample exposed to constant humidity and temperature is plotted against the square root of time there will be an initial linear region up to about 60% of the maximum moisture uptake followed by a gradual approach towards an asymptotic value (**Figure 2**). This asymptotic value is the boundary condition and is defined as the concentration of moisture experienced at the surface layer of the material.

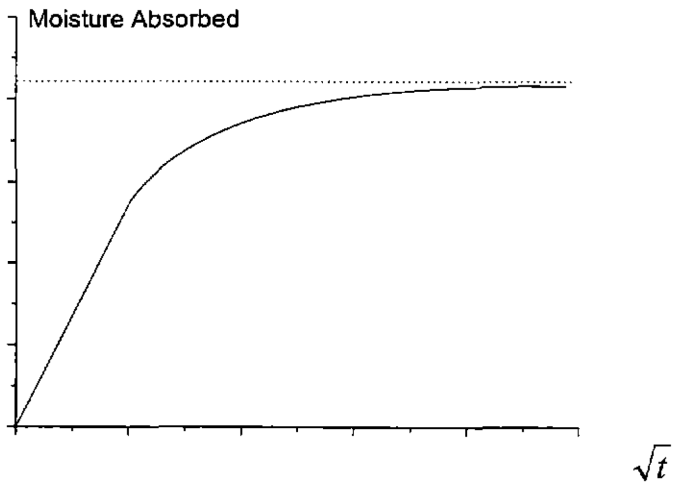

Figure 2 Moisture Uptake versus root time under constant humidity and temperature conditions for Fickian Diffusion Behaviour

The absorption of moisture through the thickness of the composite with time is shown in **Figure 3**. After manufacture the composite is essentially completely dry (t_0). Exposure to humid air allows moisture to begin to diffuse through the outer plies of the composite and through to the specimen centre after time (t_1). After a longer period of time under constant humidity conditions an even moisture distribution arises (t_∞) (See **Figure 3**). It is important to note that at stages other than the fully dry or fully saturated case a profile of moisture concentration will exist in the matrix. Since moisture affects the mechanical properties of the matrix this also implies that a profile of properties will also exist through the thickness. If the humidity conditions are transient (as found in normal weather patterns) a complex profile of moisture through the specimen thickness may result. Weitsman **[12]** demonstrated a method to deduce the concentration profile of moisture within composites from weight-gain data using a numerical approximation. This technique may be used in place of finite difference methods such as those used in the W8GAIN software (see page 13).
The mathematics of diffusion are not within the scope of this report but it is outlined in the book by Hoskin and Baker **[13]**and detailed in the work by Crank **[14]**.

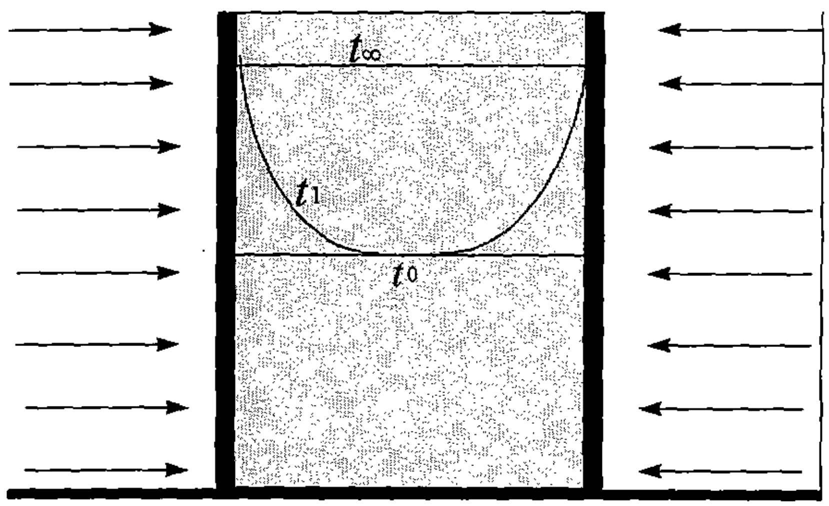

Figure 3 Diffusion of Moisture into Composite over Time

The moisture concentration profile which develops within the matrix is dependent on the boundary condition, material type and the exposure temperature.
Diffusion behaviour is material specific. Each material must be examined experimentally to define it's behaviour under environmental exposure. This may be a costly and time-consuming process but is essential if a thorough understanding of the effects of environment are required.
There are three main steps involved in modelling the diffusion of moisture in composites:

- determine diffusion behaviour type (eg: Fickian, non-Fickian)
- establish boundary conditions (surface concentration value)
- establish the diffusion constant and it's variation with temperature

4.2.1 Diffusion Behaviour Type

It is advisable to first determine the diffusion behaviour type (ie: Fickian, non-Fickian) by exposing a composite coupon to constant humidity and looking at the resulting weight-gain with time. If the results are plotted against $\sqrt{t}$ the diffusion type may be deduced. The diffusion type must also be defined for a particular temperature range since it may change if high temperatures are reached.

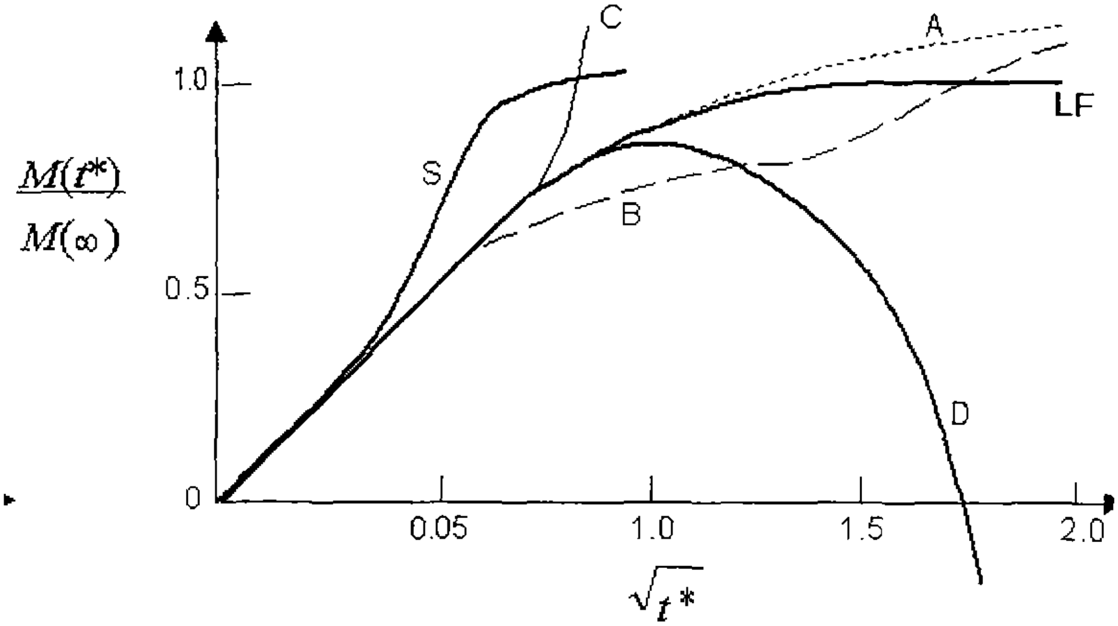

Figure 4 Curves showing both Fickian and non-Fickian weight gain sorption data in polymers and polymeric composites (from Weitsman [15])

A number of different moisture weight-gain sorption curves may result from different types of polymers and polymeric composites. A report by Weitsman [15] shows the results of numerous weight gain sorption data of both Fickian (shown as LF in Figure 4) and non-Fickian (lines A, B, C D, S) type. Curve D shows a weight loss over time which suggests that material is being leached from the polymer matrix. This may be due to chemical reactions such as hydrolysis or other mechanisms. The ratio $M(t^*)/M(\infty)$ refers to values of moisture content normalised by the maximum moisture content values.

The initial part of the weight sorption curve for the Fickian case (LF) is used for the calculation of the diffusion constant D (see section 4.2.3). This is done from the origin to where the weight sorption curve deviates more than 1% from a straight-line.

The maximum temperature at which absorption still follows Fickian behaviour may be a strict upper limit for accelerated testing conditions and service conditions. This may be related to the material glass-transition temperature, T_g. At the T_g a large change in specific volume occurs which allows a greater amount of moisture to be absorbed into the matrix. In determining a maximum testing and service temperature it must be noted that T_g is reduced as moisture content increases. It is advisable to test at temperatures which do not exceed the T_g at maximum moisture content.

4.2.2 Boundary Conditions:

The boundary condition reflects the concentration of moisture at the surface of the composite material. This concentration is proportional to the relative humidity of the exposure environment. For a material exposed to a constant boundary condition for a long period of time a constant moisture concentration profile will develop. This is represented by an asymptotic weight-gain being achieved. In terms of specimen weight this represents the maximum moisture uptake.
Rainfall and humidity are the main source of moisture at the composite material outer layers. The greater the moisture concentration at the composite surface the more moisture will be absorbed by the composite. The limiting boundary conditions are dry air (zero humidity) and immersion in water. For a defined service environment it is important to determine the boundary conditions accurately.
Typical service environments will include many variations in these boundary conditions. High altitude flights result in low humidity while ground storage during the tropical wet season brings very high humidities. The asymptotic value of moisture concentration reached after a very long period of service at a particular location or flight profile will represent an average humidity and diffusion exposure for that aircraft.
An illustration of the effects of varying boundary conditions is shown in **Figure 5**.

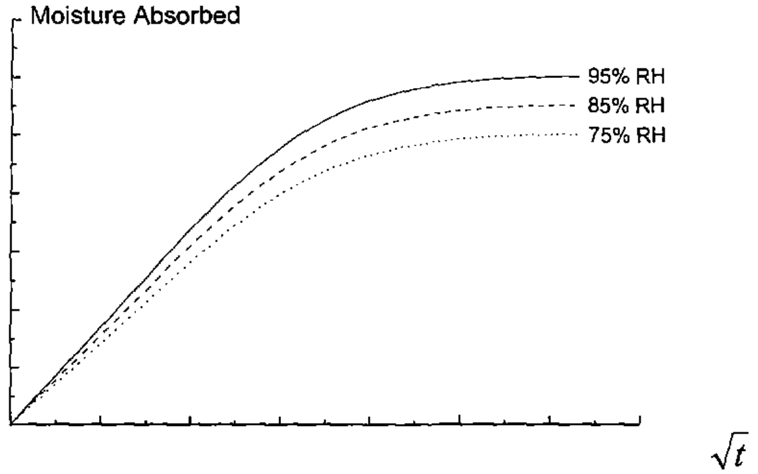

Figure 5 Illustration of the effect of relative humidity on the amount of moisture absorbed with time

It has been shown for many composite materials that the maximum moisture uptake is related to humidity by Equation 4.

$$MaximumMoistureUptake = k.\phi^n \qquad \text{Equation 4}$$

where ϕ is the relative humidity in %, k is a constant and n is close to unity for many aerospace composite materials.

Experimental results produced at DSTO AMRL by Roger Vodicka on a Boron/Epoxy composite system and fitted to this relation are shown in **Figure 6**. The value of n here deviates from unity but the value of k is typical for many epoxy based systems. It may be argued that the deviation from linear behaviour at humidities greater than about 75% shows that a two-step diffusion process is responsible.

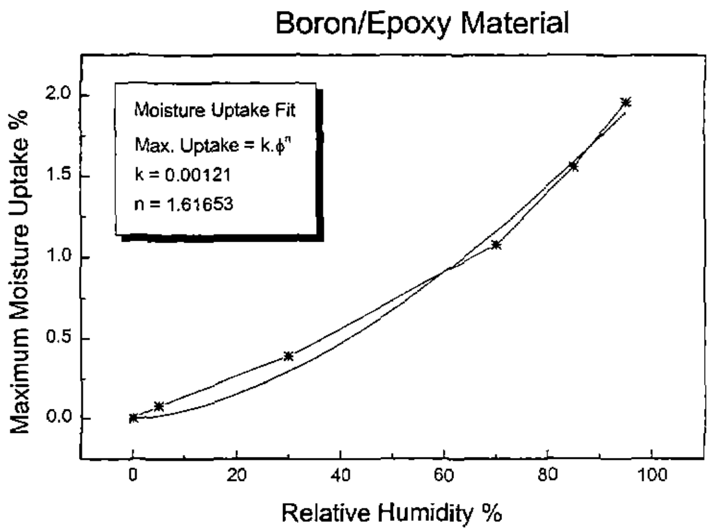

Figure 6 Maximum Moisture Uptake (weight %) for Boron/Epoxy Material

This relation needs to be established in order to model the boundary conditions of the moisture diffusion problem. Shen and Springer show that Equation 4 is independent of temperature for a number of graphite/epoxy composites [16]. The value of n is close to unity for many materials as shown by Shen et. al. [17]. Work at DSTO-AMRL on XAS-914C and AS4/3501-6 graphite/epoxy material also showed n to be close to unity [1].

In general, most research indicates that over a fairly wide operating range the boundary conditions are generally independent of the test temperature. Some work however has identified a minor temperature dependence. This temperature dependence termed "the reverse thermal effect" was observed and examined in detail by Zheng and Morgan [18]. This effect refers to an increase in the equilibrium moisture content on reduction of temperature. They observed that moisture saturated samples of graphite/epoxy which had seen a temperature near the material wet T_g were able to absorb more moisture if the exposure temperature was then lowered. This effect was found to be fully reversible upon drying of the samples.

The difference between free-water and bound-water must be understood before a boundary condition relation is established. Free-water trapped in voids and micro-cracks within the matrix will not affect the matrix in the same way as absorbed moisture. Permanent damage associated with processes such as thermal spiking (section 5.3) will allow free-water to enter the micro-cracks formed. The boundary conditions are not valid if the temperature of the test has been sufficient to cause such irreversible damage to the material. The presence of free-water can be detected by a change in diffusion behaviour or if the boundary condition relation changes after cycling between low and high temperature and humidity exposure.

Note that some moisture will remain chemically bound within the matrix and may not be removed after drying. The importance of fully drying the material before testing to evaluate diffusion behaviour and diffusion constants is demonstrated in the work by Edge [19]. Drying may be performed at a temperature at which Fickian behaviour is observed and within an environment free of moisture such as a vacuum.

4.2.3 Diffusion Constants and Temperature Relation(s)

The value of the diffusion constant, D, for a material must be determined to understand the rate of moisture absorption with time.
Typical values of D for epoxy adhesives exposed at 40° C are:
$D = 10^{-12}\ m^2s^{-1}$
For graphite/epoxy composites (through-thickness diffusion)
$D = 10^{-13}\ m^2s^{-1}$ at 60% fibre volume fraction and 40°C.
The value of D varies strongly with temperature. An increase in temperature of 20°C can double the value of D. **Figure 7** shows the effect of increasing temperature on the profile of weight-gain versus time data plot under a constant humidity level.

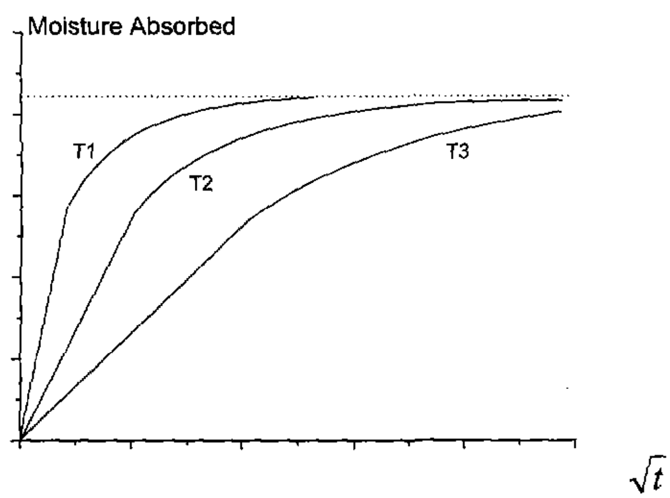

Figure 7 Effect of temperature on the weight-gain profile T1>T2>T3 (constant humidity)

The relationship between D and temperature has been found by [20] to take on an Arrhenius form of the type:

$$D = D_o . \exp[-E_d / R.T] \qquad \text{Equation 5}$$

where D_o is the material permeability, E_d is the activation energy, R is the universal gas constant and T is the temperature in Kelvin. This was found to apply for both neat 3501-5 resin and for unidirectional and bi-directional graphite composites.

The value of D can be deduced from weight-gain versus time data for a material exposed at constant temperature and humidity. The initial slope of the weight-gain when plotted against $\sqrt{t}$ will be linear up to about 60% of the maximum value. *Equation 6* ***may then be applied to this linear region to deduce the value of D.***

$$D = \pi\left(\frac{h}{4M\infty}\right)^2\left(\frac{M_1 - M_2}{\sqrt{t_1} - \sqrt{t_2}}\right)^2 \qquad \textit{Equation 6}$$

where M is weight, M_∞ is the maximum weight, h is specimen thickness and t is time.
When testing composite coupons to determine D there will be a certain amount of moisture diffusion through the specimen edges. This may be avoided if the specimen edges are sealed with a non-permeable material or if the laminate area is

very large compared to the thickness. If the thickness of the coupon is significant compared to the total surface area the value of D generated may be corrected using Equation 7 developed by Shen and Springer [16].

$$D_\infty = D\left(1 + \frac{h}{b} + \frac{h}{l}\right)^{-2} \qquad \text{Equation 7}$$

where D_∞ is the diffusion for an infinite plate, D is the calculated diffusion from the coupon sample, h is specimen thickness, b is breadth and l is length.

4.3 Software to model the diffusion process - W8GAIN

Computer code to predict the moisture content of composite materials under transient conditions was developed by the Mechanical Engineering Department of the University of Michigan in the late 70s [21]. The computer code is written in standard FORTRAN and may be used on a desktop computer. The software requires details of the diffusion and thermal properties of the material as well as information about the conditions under which it will be tested. The code will output the concentration profile of moisture through the composite with time under transient boundary conditions. Output is given in text format at user-specified time and thickness intervals.

From the comments within the software itself W8GAIN is described by the authors:

'This program solves the parabolic, partial differential equation describing the concentration distribution for transient, one-dimensional mass transfer in rectangular coordinates. It is assumed that the left and the right faces become equal to a new temperature and humidity at different times. The initial concentration must be known. An explicit, finite-difference approximation is used to express the governing equation.'

The software allows for the following type of diffusion equations to be modelled.

For the boundary condition, which describes the maximum moisture concentration for a particular humidity level, Equation 4 is used.

The relationship between diffusion and temperature is modelled using the Arrhenius equation (Equation 5). The software allows the modelling of materials where the constants in the Arrhenius relationship change at a particular temperature. Such behaviour would suggest that the moisture uptake mechanism has changed at this temperature. Two equations are given in the software to allow for a material to have a different constants in the Arrhenius equation above and below a temperature T_{limit}. Terminology in the software is such that:

DA1 and DB1 refer to the material permeability D_0

DA2 and DB2 refer to the activation energy E_d

$$D = DA1.\exp[-DA2 / R.T] \text{ for } T < T_{limit} \qquad \text{Equation 8}$$

$$D = DB1.\exp[-DB2 / R.T] \text{ for } T > T_{limit} \qquad \text{Equation 9}$$

Where D refers to the diffusion coefficient, R is the universal gas constant and T is temperature in Kelvin.

The software models straight-line temperature and humidity ramp and hold boundary conditions. The number of straight-line segments allowed is very large so that curved inputs may be adequately represented by straight-line segments. The output of the software shows the profile of moisture concentration at user-specified thickness intervals. It is also possible to model the ingress of moisture from a specimen where one face is insulated from moisture.

Although the diffusion data and boundary conditions required to input to W8GAIN are not easily gained it is worthwhile to determine them as it gives the ability to model just about any type of temperature/humidity profile over time. Verification of the usefulness of the software has been reported by Lundemo [22]. The author found that the software was able to predict the moisture uptake of composites under transient conditions provided the diffusion data for the material modelled was well determined.

The software allows the modelling of many transient boundary condition scenarios applicable to aircraft service. Inputs which represent the yearly climate as well as flight profiles may be used and run through the software many times to represent years or decades of service. The final moisture content and resulting moisture profiles may then be used to understand the state of the material in the future. This may be significant as it may allow these conditions to be replicated in the laboratory and the mechanical properties of the material evaluated well in advance. No damage mechanisms are modelled with this software nor are any other time-dependent degradation mechanisms.

4.3.1 Selected Composite Diffusion Properties

Listed in **Table 2** and **Table 3** below are diffusion properties suitable for input to W8GAIN for three composite materials as measured by Springer and others [28]. All materials show Fickian diffusion behaviour.

Constants suitable for describing boundary Conditions, given earlier by Equation 4, are listed in **Table 2.**

Table 2 Boundary Condition Constants

Material	k	n
AS/3501-5	0.019	1
T300/934	0.017	1
T300/5208	0.015	1

Constants suitable for describing the diffusion constant versus temperature are given in **Table 3**. These constants may then be suitably applied to Equation 5.

Table 3 Arrhenius Relation Constants

Material	E_d/R	D_0 (m²/s)
AS/3501-5	5720	$6.5*10^{-6}$
T300/934	5210	$8.3*10^{-7}$
T300/5208	5170	$5.8*10^{-7}$

4.4 Non-Fickian Diffusion

Deviations from ideal Fickian diffusion may arise for a number of composite materials. In many cases the use of Fickian diffusion mathematics as an approximation will suffice. In cases where gross deviations are found, alternative equations may need to be developed. The modification of the boundary condition to include a time-dependent component has been found to be useful in describing non-Fickian behaviour in many composite systems. A detailed analysis of non-Fickian behaviour is not given here since the actual boundary condition or equations used to describe a particular moisture diffusion process will vary for a range of materials.

Some of the literature references which deal with non-Fickian moisture uptake are described below with the applicable boundary condition suggested. This is not a complete list.

1. Work by Zhou and Lucas [23] describes anomalies in moisture uptake behaviour using a theory which accounts for non-Fickian behaviour through micro-cracks, surface cracks, mass-loss and polymer dissolution. Findings are supported by SEM micrographs which show micro-cracking in the composite.

2. Work by Wilde and Shopov [24] deals with a model which describes the boundary condition as:

   $$C_{d,sur}(t) = C_{\infty,sur}(1-\exp(-\beta t)) \qquad \text{Equation 10}$$

   Where $C_{\infty,sur}$ is the pseudo saturation moisture concentration and $C_{d,sur}(t)$ is the surface concentration at time t. The parameter β is a relaxation constant which reflects changes in the polymer matrix due to absorbed moisture. This model explains the lack of asymptotic weight-gain data.

3. Work by Lee and Peppas [25] discusses a number of diffusion models based on stress dependence, concentration dependence and a combined model of the two. Both 1-D and 2-D models are considered.

4. Work by Tsotsis and Weitsman [26] describes a simple, useful method to fit data to the boundary equation:

   $$c_s = c_0 + (c_{eq} - c_0)\,[1-e^{-\beta t}] \qquad \text{Equation 11}$$

   In this case c_0 refers to a pseudo saturation level and c_{eq} is the maximum concentration recorded from weight-gain data. The relaxation parameter is described by β.

5. Work by Cai and Weitsman [27], is an analysis of non-Fickian behaviour based on visco-elastic boundary conditions. The boundary condition is given by the relation:

   $$C(t) = C_0\,(1-e^{-\beta t}) \qquad \text{Equation 12}$$

   A full mathematical solution for this boundary condition is given as well as equations to analyse weight-gain data to derive the constants C_0 and β. The constants C_0 and β represent the surface concentration, C_0, and the relaxation parameter, β.

6. Work by Whitney and Browning, [20] is a useful reference on two-stage polymer absorption processes.

7. The book edited by Springer [28] is an excellent resource on a whole range of environmental effects issues.

8. Work by Carter and Kibler, [29] offers yet another approach to model moisture weight-gain data.

4.5 Measuring Moisture Concentration Profiles in Composites

The profile of moisture concentration within a composite is very important as it also reflects the profile of properties through the thickness. While weight-gain data is one of the most commonly used means of detecting the ingress of moisture into composites, it tells us nothing about concentration profile. There are numerous experimental techniques which have been used to directly measure the moisture content of polymeric composites. At the time of this report these techniques were not widely used and do not represent a routine moisture evaluation technique.

- Dielectric

The change in dielectric response of polymer matrix materials with moisture has been demonstrated [30]. The use of dielectric techniques on composites with conducting fibres is mostly unsuccessful due to the electrical conductivity of the fibre. A novel microwave dielectric technique developed by KDC Technology Corporation [31] has been shown to be useful to profile moisture in Kevlar and glass-fibre composites [32].

- Positron Lifetime Techniques

This is a technique to determine the amount of moisture in both composite materials and neat resins. The technique uses the interaction of positrons with the matrix to examine the amount of moisture. Preliminary work reported by Singh et al. [33] has shown a correlation between the lifetime of positrons and moisture content. This technique has not yet seen widespread use.

- Deuterium Conditioning

This involves the use of deuterium (D_2O) rather than water to condition samples and then using nuclear reaction analysis to determine the concentration of moisture. Work by Delasi and Schulte [34] has demonstrated the effectiveness of this technique for both composite laminates and adhesive joints. The analysis of adhesive joints by this method was undertaken with much success. The technique can only examine the surface of the sample. Therefore it is necessary to section the sample to quantify the through-thickness moisture concentration profile.

- Sectioning

Collings and Copley [35] reported a method by which a composite coupon of 2mm to 3mm thickness is physically sectioned after exposure to a humid environment to allow the measurement of a moisture profile. The method is attractive since the total time required to extract both the diffusion coefficient and the moisture equilibrium level may be made in a relatively short period of time; about 30 days. Coupons are physically split through-thickness and subsequently dried to evaluate the moisture content by mass. The amount of moisture in the section is calculated and the moisture profile may be determined using multiple sections. The authors claim the method to be accurate.

This method seems sound but is limited by the ability to accurately section and weigh the composite fragments.

- Analytical Techniques

Mathematical solutions may be used to determine concentration profiles. Moisture concentration profiles may be extracted from weight-gain data [27] if the diffusion properties of the material are well known. This also applies to using the W8GAIN software if the boundary conditions and thermal/humidity history are also known.

- Conclusions

None of the techniques listed provide a viable method of measuring moisture contents on in-service aircraft. The technique of most use in the laboratory is likely to be sectioning. This technique is useful to verify the results of diffusion models and constants. It would be especially useful for relatively thick composites (over 2mm thick). Damaged or out of service components may be destructively examined by the technique to understand the state of materials of other aircraft which have been exposed to the same operating conditions.

5. Environmental Effects on Composites

This section deals with the specific types of environmental and service-related exposure which aircraft composite components may see.

5.1 Moisture

The immediate effect of moisture on the mechanical properties of a composite is the reduction of both modulus and glass-transition temperature, T_g. Moisture will act to plasticise the matrix and lead to changes in mechanical properties which can be regained upon drying; assuming no permanent matrix damage such as micro-cracks occurred during this exposure. The glass-transition temperature, T_g, is an important material property as it defines the point at which material properties are drastically reduced. The matrix changes from a glassy stiff state to a pliable one.

A direct correlation between T_g and moisture content needs to be established for any material through experimental testing. This correlation may vary from batch to batch so a series of tests are desirable to evaluate any material variations. The T_g of the matrix may not be uniform through it's thickness if a profile of moisture concentration exists. It is important to consider the possibility that the matrix/fibre interface will also have a T_g different to the bulk matrix. This must be kept in mind in order to preserve the integrity of the fibre/matrix interface. Details of the 'sizing' used on the fibre may be useful. **Figure 8** shows a plot of T_g versus moisture content for neat 3501-5 resin. Data is reproduced from work by Browning et al. **[36]**

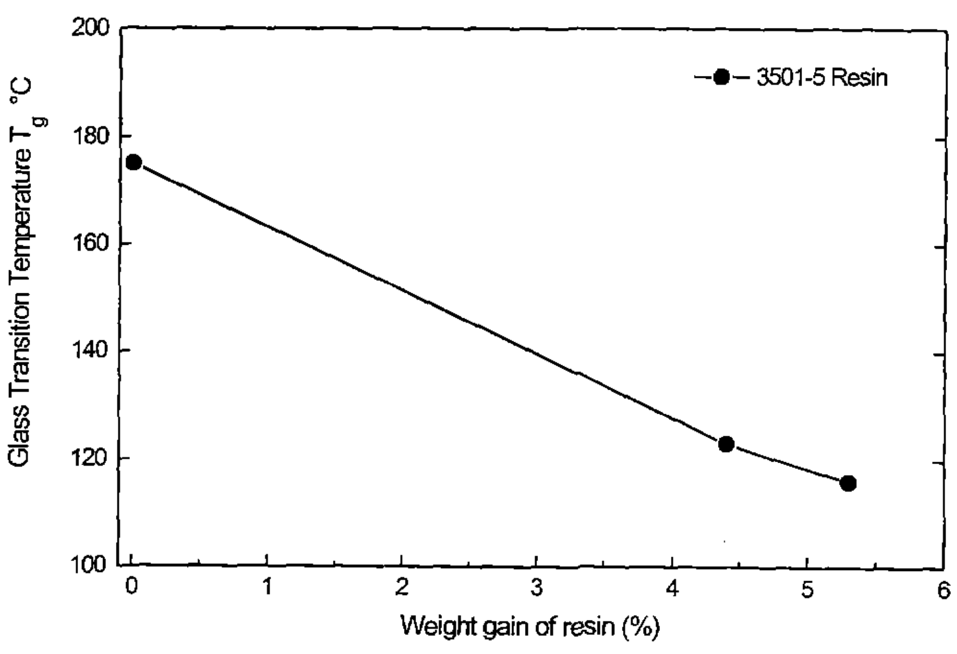

Figure 8 Plot of Tg versus Temperature for neat 3501-5 Epoxy Resin cured at 177°C [36]

Before commencing a mechanical test of any description the concentration profile must be known to make the results meaningful. It is probably best to establish a uniform concentration profile through the sample prior to testing. The outer layers of the composite readily change moisture concentration with changes in boundary conditions. It is therefore likely that the results of mechanical tests in which the composite fails in the outer skin will be compromised. Testing samples which have a constant moisture concentration profile through the specimen thickness is therefore desirable.

The environmental fatigue behaviour of composites is as important as static tests. The effect of moisture on both the static and fatigue response of a number of composite systems was investigated by Jones et. al. [37]. Matrix properties of the resin in carbon-fibre reinforced plastics were not degraded after conditioning to a moisture level of around 0.9%. In fact the authors note that the interlaminar shear strength of the carbon fibre reinforced plastic material was modestly higher than dry specimens attributing the effect to plasticisation of the matrix and a relaxation of some residual thermal stress during processing. They also noted that +/-45° laminates conditioned to 0.9% moisture content had a better fatigue resistance compared to that of dry specimens.
It can be seen that conditioning specimens to levels of moisturise commonly found during service (around 1%) may in fact have a beneficial effect. The use of boiling water to condition specimens can often produce an unrealistic moisture level which does not faithfully simulate a service related exposure. The use of boiling water can roughly equate to a very severe form of thermal spiking (section 5.3) if used indiscriminately.

5.2 Temperature Effects

Temperature acts to degrade the composite matrix in a number of ways. Both reversible and irreversible effects may be observed when a composite matrix is exposed to high temperature. If the temperature exceeds the glass-transition temperature, T_g, the material modulus will decrease markedly. The original modulus will return upon cooling provided no thermal decomposition or other permanent damage has occurred. Thermal decomposition is not an effect which is likely to be important on aircraft except on exposure to fire or other high-temperature sources (over 250°C). Irreversible damage effects will include leaching of volatiles and plasticisers, advancement of the extent of cure of the matrix and residual stresses induced through thermal cycling. Thermal cycling may cause trapped volatiles to expand and create high pressures within matrix voids and cracks. These stresses can lead to permanent mechanical damage and loss of properties.
Service temperature values must be chosen such that:
(i) The material wet T_g value is not exceeded
(ii) No decomposition of the material occurs. This is unlikely for most 177°C curing composites which decompose at temperatures over 250°C.
(iii) The same mode of diffusion is retained
(iv) No damage is introduced into the sample (eg: thermal spiking, section 5.3).

5.3 Thermal Spiking

Thermal spiking refers to exposing a composite to rapid rises in temperature. Thermal spiking is an effect which is investigated to determine the useful maximum operating temperature of a composite. This is designed to simulate a supersonic dash in flight. The literature differs in what it defines to be the maximum service temperature experienced and the rate of heating and cooling during flights. It is important to determine these conditions prior to testing. Thermal spiking tests are often performed when the material is at a moisture level equal to the equilibrium ground exposure level. This is a reasonable approach as long as it is kept in mind that the surface layers of composite change their moisture concentration much quicker than the bulk. A hot and humid day may raise the moisture concentration of the outer plies to greater than average levels and thus it may be worth considering the effect of spiking the composite conditioned at the highest humidity experienced at the exposure site. In any case the moisture profile of the material needs to be established carefully in order to gain quantitative results from thermal spiking.

Spiking is thought to create matrix damage which allows greater levels of moisture to absorb into the composite. A damage mechanism proposed by Clark et al. [1] , as illustrated in **Figure 9** , suggests that there is a critical moisture level M_{crit} above which thermal spiking will cause permanent damage to the composite matrix. Matrix material which has been damaged by spiking will locally reach a moisture level shown by M_{eq} (spiked material). Material in the spiking damage zone will no longer behave according to Fick's law while the bulk of the composite will. Spiking damage is most likely to occur at the surface since heat will affect this area first and the surface plies are likely to have a higher moisture content since it is closer to the environment. The level of moisture measured by weighing the sample will be M_{eq} which is a combination of moisture in the spiking damage zone and the bulk matrix. Moisture will be trapped in the spiking damage zone which will change the moisture profile from the lower black curve to the upper one.

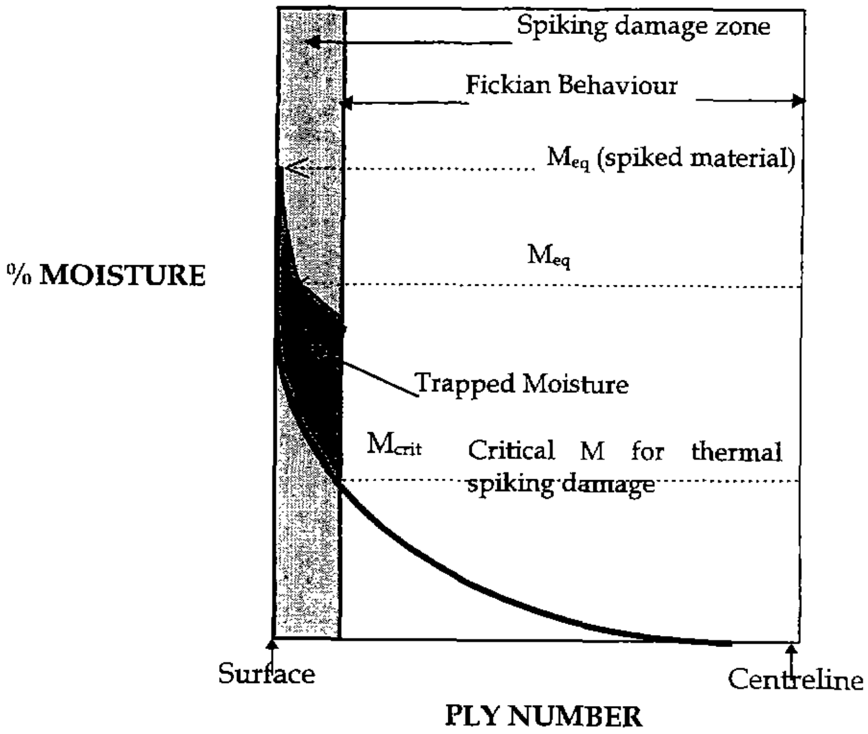

Figure 9 The effects of thermal spikes on the moisture absorption behaviour of a graphite epoxy laminate. Taken from Clark et al. [1]

Irreversible moisture uptake can be used as a measure of thermal spiking damage. There will always be a certain amount of irreversible moisture absorption due to the water chemically binding with the matrix. Large amounts of irreversible moisture uptake or cases where the maximum moisture level increases each time the material is 'spiked' to a high temperature level indicates that the material is undergoing physical damage or permanent changes. The spiked material will also show different diffusion characteristics since the mode of moisture uptake for thermally spiked damaged material may be via free water leaching into matrix cracks within the composite.

Work by Clark et al. [1] shows that spiking creates the most amount of damage when conducted during moisture uptake or at the peak moisture uptake level. Thermally spiking material prior to moisture conditioning did not influence their results. It may be possible to infer that the maximum safe thermal spiking temperature will be equal to or greater than the material T_g.

It must be kept in mind that due to the fact that a concentration profile of absorbed moisture may exist through the composite, spiking damage may occur in some regions and not others. For this reason it may be appropriate to test for sensitivity to thermal spiking at maximum moisture uptake (ie: 100% humidity boundary condition and an evenly distributed moisture concentration through the composite). Surface plies often reach a moisture level much higher than the rest of the laminate; spiking may occur in these layers but the increase in moisture concentration after spiking may not be obvious since only a small fraction of the total laminate is concerned.

5.4 Osmosis

Osmotic pressure results from the passage of a solute across a semi-permeable barrier. It has been suggested that epoxy resins behave as semi-permeable barriers that allow the passage of water but not that of solutes and impurities in the resin. Farrar and Ashbee [38] postulate that osmosis results in a pressure differential across the semi-permeable barrier which can lead to the formation of pressure pockets leading to internal fracture. Later work by Walter and Ashbee [39] attempts to estimate the pressures generated by osmosis using simple calculations. Evidence of interfacial pressure pockets due to osmosis are referred to and an attempt to quantify the pressures required to produce the interfacial debonding that is experimentally observed. They predict a dependence proportional to $time^{1/4}$ to inflate cracks by osmotic pressure. Interfacial failure is a mechanism which needs to be addressed in any composite system exposed to degrading environments.

Another reference addressing osmosis in composites is given by Ghotra and Pritchard [40]. This looks at the identity of the solutes which may be responsible for the generation of damaging osmotic pressures within composites. They examine the effect of osmosis on paint and gelcoats applied to composites. The use of chemical species and materials which are inert to water in resins is advised in order to reduce osmotic effects.

5.5 Swelling Strains

The absorption of moisture by the composite matrix also causes it to swell and exert a resultant strain on the material. The coefficient of moisture expansion defines the way a volume changes when taking up moisture. Volume changes in a composite due to swelling may be represented by the empirical relation given by Delasi and Whiteside [41]:

$$\frac{\Delta V}{V_o} = 0.01.c + \frac{\Delta M}{M_o}.d \qquad \text{Equation 13}$$

Where V_o and M_o represent initial volume and mass and c and d are swelling constants. For 3501-6 resin, swelling constants are given by [41] as c=-0.61 and d=0.87.

5.6 Cryogenic Exposure

Water trapped in voids or cracks within composite materials may freeze when exposed to cold conditions at high altitude. Using the definition of a standard atmosphere we can expect to see temperature decrease by 3°C for every 500m of altitude. It can be seen that even moderately low altitudes can produce freezing conditions. The property of water is such that it expands by 8.3% in volume upon freezing and has a bulk modulus that is three to four times that of epoxy resin. Water trapped within cavities will create pressure on the surrounding material which may result in permanent matrix damage. Such material degradation was reported by Nicholas and Ashbee [**42**]. They concluded that non-spherical disc-shaped cavities would propagate cracks if water froze within them. It is therefore important to consider the potential problems associated with free water entering voids and micro-cracks in composites.

5.7 Ultraviolet Damage

Ultraviolet damage in composites is usually characterised by erosion exposed layers of the matrix material. Such damage can be minimised by the application of U.V resistant coatings. High quality paints are equipped to deal with high U.V levels and prevent the matrix from being affected. U.V damage is restricted to the topmost layers of the composite and is unlikely to affect the bulk properties of a composite laminate.

5.8 Erosion

The effects of erosion on composites is similar to that of ultraviolet damage. Material is removed from the exposed layer of the composite which may lead to fibres being exposed and potentially reduced mechanical properties. Erosion can be minimised by the application of protective coatings in the form of paint or other resins. Erosion effects are often a problem in helicopter blades if the composite is left exposed. The addition of a simple metallic cover eliminates erosion effectively in most cases.

5.9 Stress Effects

The effect of stress superimposed onto a hot/wet condition can produce a greater detriment to composite mechanical properties than each of these factors alone. This was noticed by Gillat and Broutman [**43**]. They found that the level of moisture uptake increased with increasing stress level and that the behaviour could be modelled using Fick's law. The greatest effect was on the value of diffusivity which increased with applied stress. The equilibrium moisture content value was also found to be proportional to the applied stress level.

The consideration of mechanical pre-loading a composite prior to exposure to hot/wet conditions should be considered. Work by Jones et al. [37] showed that pre-loading the composite material up to 80% of it's failure load before conditioning took place did not affect moisture uptake levels. This may indicate that a more realistic approach would be to load the specimen during and after hot/wet exposure.

A mathematical treatment of stress assisted diffusion is provided by Weitsman [44]. Stress assisted damage in the form of micro-cracks will increase the equilibrium moisture uptake level. Moisture present within these micro-cracks will have a significantly different effect than moisture absorbed by the matrix. Stressing the composite during exposure may be an important test to carry out. Viscoelastic relaxations within the resin may occur at sustained stress levels which may alter the diffusion properties. In any case it is important to identify the difference between induced damage and changes in the viscoelastic nature of the matrix due to stress.

5.10 Processing Effects

The processing and manufacturing conditions under which a composite is made affects the residual stress state of the material. Cooling a composite laminate at a fast rate after curing can induce warping and cracking due to differential cooling between the surface and inner plies. It is important to consider the viscoelastic response of the material and take this into account to ensure residual stresses are not induced. This is even more critical for composite repairs and doublers adhesively bonded to metallic structure where thermal coefficient mismatch between materials is quite large.

5.11 Chemical Reactions

Time may have an effect on the matrix due to chemical reactions which may occur on a long-term basis. The matrix may leach volatile chemical components which will affect it's T_g and mechanical properties. The reaction of moisture with some of the matrix chemical components may also need to be considered.
These reactions are likely to be hastened by increased temperature. The long-term chemical stability of most aerospace resins is excellent and generally does not need to be determined unless the suitability of the matrix for a particular environment is in doubt.
Galvanic corrosion may also play a factor in degrading a structure. The bonding of composites with electrically conducting fibres such as graphite to some metallic structures may cause corrosion. This will be a time-dependent process and will be accelerated by the presence of moisture.

5.12 Effects of Voids

The effect of voids on the moisture uptake behaviour of composites was examined by Harper et al. [45]. They found that greater void content produced a higher equilibrium moisture content level. Low void laminates (about 1%) had an equilibrium moisture content level of about 1% while high void contents (about 5%) increased this to over 1.4%.

5.13 Influence of Layup Configuration

The long-term moisture absorption behaviour of angle-ply laminates was investigated by Blikstad et al. [46]. They found that the layup angle influenced the moisture diffusion behaviour due to the residual stresses in these laminates. They noticed that residual compressive stresses had the effect of retarding diffusion and lowering the maximum moisture content. The issue of layup configuration is likely to be closely related to the residual stresses in the matrix.

5.14 Conclusions

It is chiefly the effect of hot/wet conditions that will significantly degrade the mechanical performance of most composite materials. Forms of environmental damage such as erosion and U.V damage can be simply avoided. If other damage mechanisms such as thermal spiking are evident this indicates that the material is unsuitable for the required task or it is being used outside it's design limits.
The effects of the hot/wet environment should be reversible to a significant extent with mechanical properties recovered in the dry state. Moisture diffusion should follow a well-defined diffusion behaviour type for the entire service operating envelope.

6. Composites in Service

Composite materials have been flown in a variety of service conditions on commercial aircraft for over 20 years. Their service performance has been impressive and they remain an attractive structural material for future commercial and military aircraft. Initial concerns about environmental durability by NASA Langley and the U.S Army in the early 1970s led them to investigate their suitability as replacements for metallic structure. These concerns included the effects of moisture absorption, ultraviolet damage, temperature cycling, lightning strikes and long-term sustained stress.
The performance of most graphite/epoxy composite structures has been very good. The greatest environmental problem for composite structures may not even involve temperature and moisture effects over time but more random events such as lightning strikes and foreign object damage.
The flight service environmental effects on composite materials and structures was closely examined by the NASA Langley Research Centre and summarised in the paper by Dexter and Baker [9]. Results of long term exposure for a number of material systems are reported including glass fibre, Kevlar and graphite composites.

6.1 NASA Langley Research Centre Experience

The results of the NASA Langley environmental flight test assessment involved a range of materials on a number of aircraft including helicopters. Below is a summary of a subset of the report focussing on graphite/epoxy and boron/epoxy structures. The report on which these observations are based was completed in 1992 and reported by Dexter and Baker [9].

6.1.1 B737 Graphite/Epoxy Spoilers:

These spoilers used aluminium honeycomb sandwich structure using T300/5209, T300/2544 and AS/3501 graphite/epoxy composite. Damage to this structure was primarily through physical contact followed by corrosion of the honeycomb core. Corrosion was manifest in sandwich structures in which debonding of the skin occurred or in which other damage had taken place. Undamaged spoilers showed no loss of strength even after 15 years of service. Spoilers with significant corrosion damage still retained at least 75% of their original strength even after 15 years of service. This reflects the excellent environmental durability of these structures but stresses the importance of detecting disbonds in honeycomb structures as early as possible. The work by Jackson et al. [8] highlights a method to detect water intrusion in thin-skinned sandwich structures based on an apparatus which quantifies the rate of water entering a damaged or debonded composite skin. NASA Langley Research Centre utilised x-rays to detect water in honeycomb cells in a DC-10 Graphite/Epoxy Vertical Stabiliser.

6.1.2 B727 Graphite/Epoxy Elevators

Damage to this component occurred during ground handling and lightning strike. No other environmental damage was found to affect the service of the component.

6.1.3 DC-10 Graphite/Epoxy Rudder and Vertical Stabiliser

After over 5 years of aircraft service a DC-10 rudder was removed from service and tested. It's mechanical response showed no evidence of degradation. Lightning strike was the only type of damage recorded for this part. The vertical stabiliser was inspected regularly and no damage was found using ultrasonic and X-ray NDE techniques.

6.1.4 L-1011 Graphite/Epoxy Ailerons

During a 9 year evaluation period of this component no major problems were noted. Loose fibres around a fastener on one component were repaired using a simple procedure and the part was returned to service.

6.1.5 C-130 Boron/Epoxy Reinforced Wing Box

Boron/epoxy wing boxes were manufactured and put into service on two C-130 aircraft in 1974. No damage or degradation has been observed. Testing of this boron/epoxy wing-box showed it to have a greater fatigue life compared to equivalent metallic structures.

6.1.6 Ground Exposure

Coupons were produced for a ground based exposure trial at a number of locations worldwide. After a 10 year period most graphite/epoxy coupons had absorbed between 0.7% and 1.0% moisture. Coupons were also placed on a 737 aircraft and the moisture content determined regularly. It was found that the painted flight service coupons absorbed less moisture than the unpainted ground exposure coupons. Matrix-dominant properties were reduced by around 20% after a 10 year exposure period compared to baseline testing data. The researchers also conclude that the ground-based exposure was sufficient to assess the degradation and that the effect of solar radiation produced no discernible difference in results. Mechanical testing of coupons of AS1/6350 at Sikorsky [9] provided a close correlation between a 9 year environmental exposure and an accelerated laboratory environmental test. The accelerated testing scheme utilised 88°C and 87% R.H.

6.2 Other Results

Results from the service experiences of some NATO group military operators can be found in [47]. These results show that composite materials are highly suited to aviation environments with little or no degradation observed. The examination of composite parts for physical damage and water intrusion was found to be important in order to keep components serviceable and without loss of properties. The brittle nature of many graphite/epoxy composites makes them subject to damage from mishandling and foreign object damage. Aluminium honeycomb sandwich structures may be particularly sensitive to corrosion and water intrusion after this type of damage.

7. Simulating Environmental Conditions Experienced in Aircraft Service

The service environment which a material sees may be reproduced in the laboratory in a number of ways. Since hot/wet conditions are of most concern in certification and performance a number of hygrothermal conditioning schemes to simulate the effects of long term exposure are sought.

The hygrothermal conditioning of composites involves essentially three variables which interact to determine the final outcome. These are temperature, moisture conditions (humidity or immersion in water) and time. It is a combination of these three which act to define the final hot/wet performance of the composite. An accurate model of the diffusion process as discussed earlier is essential in defining a laboratory-based environmental conditioning scheme.

The most common approach taken to determine environmentally induced changes in materials is to expose the material to a particular environment and then compare the mechanical properties before and after. Mechanical tests used to qualify or certify the material for service are the logical choice. More discriminating mechanical tests which may detect much more subtle changes in the matrix material are also very useful in predicting long-term effects.

A number of approaches are possible. These are:

(1) Intensify the exposure levels:

This technique uses increased levels of exposure to indicate long-term degradation. This will also increase the severity of the degradation and may cause the mode of degradation to alter. The variables that may be intensified include the temperature, moisture levels, UV radiation levels and any other conditions present in the operating environment. In many instances it is the temperature that is intensified. In any case it will probably be necessary to identify the relationship between the increase in exposure intensity and the property that is to be measured. This makes it difficult to determine the results of an accelerated test without first making a comparison to other long-term exposure data. The relation between temperature and a property such as failure lifetime is often non-linear and may need to be established prior to using such results in a design situation.

(2) Increase the frequency of exposure to degrading conditions:

This scheme attempts to replicate the conditions of real conditions and then increase the frequency of exposure to the most damaging conditions. Thus the conditions of a very hot and humid day which may occur for only a part of a yearly seasonal cycle may be increased to a year long exposure. The decision must also be made whether to cycle between two extreme climatic conditions or to expose materials to long periods of each.

(3) Simulation of environmental conditions by load enhancement:

This involves using load enhancement factors or intensifying another material testing parameter. For example the effects of a hot/wet environment may be simulated by testing a dry structure at higher loads. This is covered later in more detail (section 10). The mode of failure is important in this case and must be identical for the load enhanced test and the hot/wet test in order for the results to remain valid.

7.1 Conditioning Levels

Conditioning levels must be accurately defined in order to reflect the service environment.

7.1.1 Temperature Conditioning Level

As outlined previously, the conditioning temperature must be chosen such that the mode of diffusion is unchanged and that the damage mechanisms introduced through the use of higher temperatures are not different from those experienced during real-time exposure.

7.1.2 Moisture Conditioning Level

It has been shown that the moisture uptake rate is related to the moisture level at the boundary and the temperature of exposure. The upper limits of the moisture level and temperature need to be chosen such as to produce the fastest rate of moisture diffusion yet retain the same type of diffusion mechanism. That is, if the diffusion rate is determined by Fick's law at conditions similar to the real environment then it must be ensured that greater temperatures and moisture levels retain this mode of diffusion.

The target moisture level must also relate to a value given by either the level found under real environmental exposure conditions or that derived from an average humidity level of the exposure site. The final saturation moisture level will largely depend on the material type used so it is not representative to saturate composites of differing types to an identical moisture level. It is better to establish an average humidity level for a particular site which relates to the equilibrium moisture level found in a long-term exposure moisture coupon. For example if a final equilibrium moisture level of a composite is found to be 1.2%, the humidity which will produce this saturation level can be calculated if the boundary conditions are known (Equation 4). This way all materials may be conditioned to a saturation moisture level corresponding to this average humidity value.

It must be kept in mind that other forms of irreversible matrix degradation may occur which may not be represented accurately by the maximum moisture uptake relation (Equation 4). Free water may pool in cracks in the composite matrix and give the false impression of an enhanced diffusion of moisture.

Moisture uptake trials from coupons under ground based exposure may take many years. Work by Chester and Baker at DSTO-AMRL [11] has shown that exposing 3mm thick AS4/3501-6 graphite/epoxy material took over 9 years under both temperate and tropical conditions to reach saturation levels.

7.2 MIL-STD-810

This U.S military standard defines a large number of operating environments under which to test both materials and equipment. A number of sections in the standard are applicable to defining environmental parameters for materials testing. These are shown in **Table 4**:

Table 4 Some Environmental Exposure Types in MIL-STD-810

Test Type	**MIL-STD-810 Reference**	**Comments relevant to Australian conditions**
Humidity	Method 507.3	Daily temperature/humidity cycles defined using RH between 95% and 100%.
Rain	Method 506.3	Tests for rain erosion and water penetration into components
Solar Radiation	Method 505.3	Effects of solar heating over and above ambient air temperature. Test for U.V, I.R and Visible radiation effects
High Temperature	Method 501.3	Australian hot ambient condition are given as 30°C to 43°C
Low Temperature	Method 502.3	Australian cold ambient are defined as -6°C to -19°C
Temperature Shock	Method 503.3	Aircraft flight exposure from high ground temperatures to cold air

Detail is given of the exact conditioning procedure which replicates the daily weather changes in the given category. The possible effects of the given environment on materials, electronics and other devices is briefly outlined. Although these standards are not based exclusively for an aerospace operating environment they are a very useful to define conditions to simulate ground exposure in a number of world climate locations.

7.3 Types of Environmental Exposure

The aircraft operating environment may be reproduced using a number of different techniques.

7.3.1 Ground-Based Exposure

This method of conditioning exposes coupons of material to conditions representative of the environment at ground level. Since most of an aircraft's life is spent on the ground this provides a useful guide to determine the effects of different locations on aircraft material and the effects of storing aircraft under differing conditions. It will not give an indication of the effects of flight cycles. This must be determined by flight exposure coupons, if necessary. Ground-based exposure is still very suitable in defining the levels of moisture present in a sample. It can take many years for a composite coupon to become fully saturated with moisture from humid air.
Subsequent exposure of these ground-based exposure coupons to flights alters the moisture level in only a very thin layer at the composite surface. This is due to the

fact that flights are short in comparison to time spent on the ground and diffusion rates are quite slow for composites. Therefore the bulk moisture content comes to an equilibrium after a long period of time and does not alter much after that. This limiting value is of great importance as it defines the moisture level to which accelerated moisture coupons should be pre-conditioned.

Work conducted by NASA [9] found that ground exposure produced higher levels of moisture uptake compared to coupons placed on aircraft. Ground exposure is therefore a more severe evaluation of the 'wet' condition.

Material surface temperatures at ground level will depend on the ambient temperature, the solar absorptivity of the material, the incident solar radiation and the movement of air. The ENSTAFF specification (see section 9.1) defines an upper surface temperature of 85°C based on the sun being at the zenith, still air, ambient temperature of 49°C and a solar absorptivity of 0.5 (equal to light green or light yellow paint). At this temperature thermal spiking (section 5.3) is unlikely to occur for ground-based exposure coupons.

7.3.2 Flight Exposure

Flight exposure coupons are similar to ground-based exposure tests except that the coupons are attached to aircraft and therefore see the entire exposure environment of the aircraft. This gives a realistic guide to the actual absorption of the aircraft structure as the coupons may be placed at various locations and subjected to varied flight patterns. Work by Dexter and Baker [9] showed that good correlation between the mechanical properties of ground-based exposure and flight exposure coupons could be made. This led them to conclude that ground-based exposure was sufficient to predict the long-term behaviour of the material. This reduces the complexity and cost of a long-term exposure test.

7.3.3 Environmental Chamber Exposure

Here the material is exposed to a temperature and moisture level defined by an artificial environment in the laboratory. The moisture level may be a set humidity or the sample may be fully immersed in water. This type of environment is necessary to define diffusion properties of materials as exacting conditions need to be maintained. For accelerated testing an environmental testing chamber is desirable to produce controlled conditioning.

Coupons or structures which require conditioning using transient environmental exposure will require the use of a complex and expensive environmental chamber. If the exposure requirements only dictate to moisturise to a particular humidity or moisture level at constant temperature then the use of a much simpler and cheaper conditioning apparatus may be used. Humid air above saturated salt solutions provide a constant and well-defined humidity level. For example, a closed container half-filled with a saturated solution of sodium chloride and distilled water will provide a constant humidity level of around 75% at 25°C. There are a number of different saturated salt solutions which give a variety of constant humidity levels from 5% to 95%. The limiting cases are vacuum (0%) and pure water (100%). The procedure is detailed in ASTM E104. The ASTM simply requires the use of a closed container in which the amount of air-space above the salt solution is kept to a minimum (**Figure 10**).

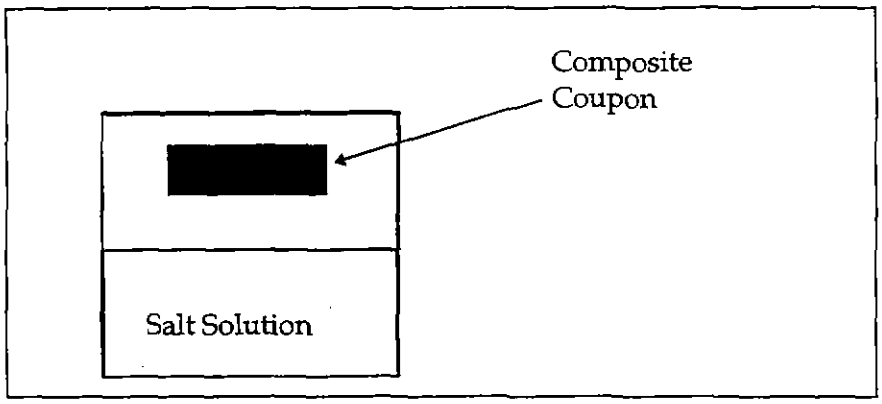

Figure 10 Experimental setup as per ASTM E104 for maintaining constant humidity environments for coupon conditioning

The closed environment must be kept at constant temperature as some solutions produce different humidities according to temperature. A complete survey of a wide range of saturated salt solutions is given by Greenspan [48]. **Figure 11** shows the relative humidity produced by a saturated solution of Lithium Chloride at a range of temperatures (x-axis) from 5°C to 70°C

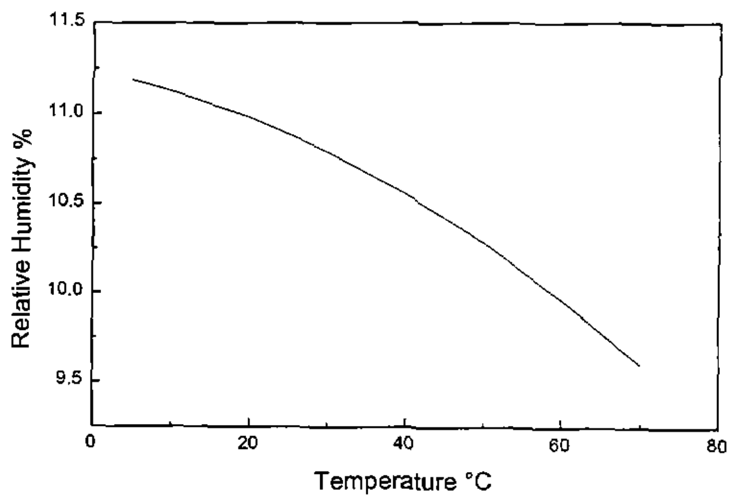

Figure 11 Relative humidity produced over a saturated solution of Lithium Chloride over temperatures between 5 and 70°C

The use of such environments to condition composite coupons has been examined by R. Vodicka at DSTO, AMRL using five different salt solutions. It was found that for containers where the headspace volume (volume above the salt solution) to the surface area of salt solution ratio was kept to less than 10, the target humidity level would be reached in about 30 minutes after closing the container. This was verified using a calibrated humidity probe. **Figure** 12 shows the result of a test on a humidity environment using pure water (100% RH). The x-axis shows the time after closing the container.

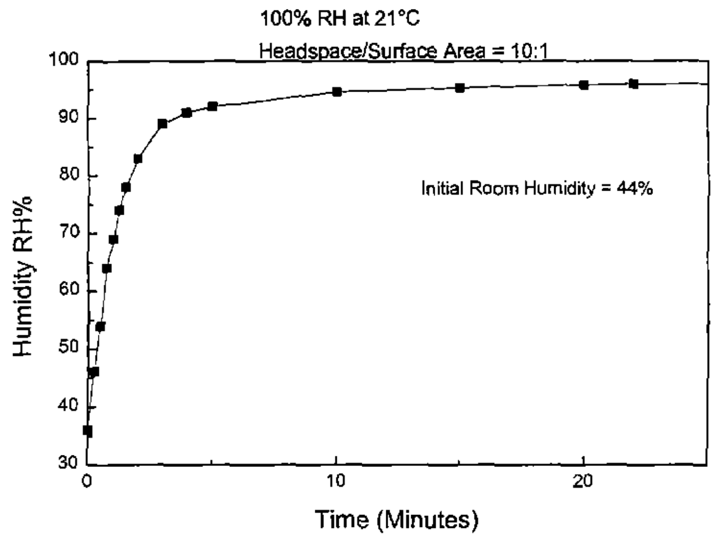

Figure 12 Establishing a constant humidity environment (100%) in a closed container using pure water

7.3.4 Simulating Supersonic Flight

Although supersonic flight constitutes only a small fraction of the total service time, it exposes a material to many environmental extremes. Supersonic flight may involve high temperatures, high heat-up and cool-down rates as well as large temperature differentials. The effect of supersonic service on diffusion was examined by McKague, Halkias and Reynolds [**49**]. The authors found that subsonic service had hardly any drying effect on the composite while supersonic speeds in which the temperatures rose up to 149°C caused noticeable drying. Low pressures and cold temperatures experienced at high altitude (30,000 feet) did not cause rapid drying. The major effect of supersonic flight was due to thermal spiking (see section 5.3). Sub-zero temperature exposure did not alter the diffusion behaviour of the laminate.

The results of this study indicate that the effects of supersonic flight may be demonstrated in the laboratory using thermal spikes as discussed in section 5.3. The re-absorption behaviour of the composite after thermal spiking may give a good indication of any damage introduced. Significantly larger amounts of moisture may be diffused into materials after thermal spiking. It is best to define a thermal spiking test in which the heating rate, cooling rate and maximum temperature experienced during flight is faithfully reproduced.

8. Accelerated Moisture Conditioning

Accelerated moisture conditioning is a useful tool in composite testing. If used correctly it can provide valuable answers on the suitability of materials for a given environment in a relatively short period of time. The method of accelerated testing must be chosen wisely with a complete knowledge of the material properties, diffusion properties and the service environment.

Most accelerated testing techniques are concerned with getting moisture to diffuse rapidly through the composite to simulate the moisture concentration found after many years of service. Much work has been reported on the use of a constant high humidity environment while others have utilised high humidity at the initial stage and then switch to a lower level commensurate with the final target moisture uptake level. While immersion of samples in boiling or hot water seems to be an attractive proposition for accelerated conditioning it is unlikely to represent service conditions faithfully and may in fact lead to unrealistic results. Work by Edge [50] has shown that immersion in water is not fully representative of a composite which will spend most of it's time at average humidity (about 65%). It was also shown to produce much more severe irreversible degradation of properties than naturally exposed specimens.

The use of severe environments which do not represent real exposure may give the wrong impression of a material's suitability to the task. Many cost-effective materials may be found unsuitable by such methods where in fact they are quite adequate.

Below are described a number of methods from the literature which show much promise for accelerated testing. The particular method to be chosen will depend on the environmental conditions to be simulated and the type of item that will be exposed.

It is important to keep in mind that many of these methods are suitable for material coupons or structures in which the material type and thickness do not vary. In complex structures with multiple thicknesses of material, different parts of the structure may reach equilibrium moisture levels at different times. The accelerated testing method must be optimised for the entire structure in order to faithfully represent moisture levels seen in service.

8.1 Two-Step Method:

This method was published by Ciriscioli, Lee and Peterson [51] and describes a method for the accelerated testing of graphite/epoxy composite coupons which has been validated using mechanical testing. Tests were performed on Fiberite T300/976 material coupons 2mm and 2.8mm thick. The method accelerates moisture conditioning by varying the humidity only. The target moisture level is determined and related to a humidity level as per Equation 4. Conditioning begins at 100% R.H and is maintained until a change-over time is reached. The change-over time is determined using a simple calculation and an easy to use nomogram given in [51]. At this change-over time the humidity is reduced to the target level. By utilising the 100% R.H humidity level at the start the conditioning process is accelerated as greater concentrations of moisture are allowed to diffuse deep into the specimen centre. The time taken to reach target moisture level at 68% R.H is illustrated for the case of a 6.4mm graphite/epoxy composite laminate. The accelerated scheme achieves the target level in 170 days while the regular method of holding humidity at 68% R.H requires 800 days. This is a factor of 4 time saving.

The authors conducted tensile, compressive and short beam shear strength tests as per ASTM standards and found that the accelerated conditioning regime did not affect these mechanical properties compared with conditioning in a stable humidity environment. It is important to verify accelerated testing techniques in this way but it may not be practical to do so since a comparison with coupons exposed for long periods may not be available or such tests may not be feasible due to time constraints.

This method is quite straightforward as it does not introduce the complication of temperature. It must be noted that the diffusion characteristics, particularly the boundary conditions (Equation 4) of the material must be pre-determined. Also, it

may not always be possible to use 100% R.H in a situation where conditioning at this level changes the mode of diffusion markedly. An upper limit for humidity would be the point where the boundary condition equation is no longer linear or where the material shows non-reversible diffusion behaviour at high humidity levels.
This technique produces a uniform distribution of moisture through the sample thickness. This is representative of a composite which has had long term exposure.

8.1.1 Two-Step Conditioning For Composite Materials Using Traveller Coupons

The use of traveller coupons to monitor the moisture uptake of a structure is useful if the structure and coupon are made using identical materials under identical conditions. The two-step method (section 8.1) requires conditioning for a certain period at 100% R.H before switching to the target humidity defined by the material boundary conditions (Figure 13).

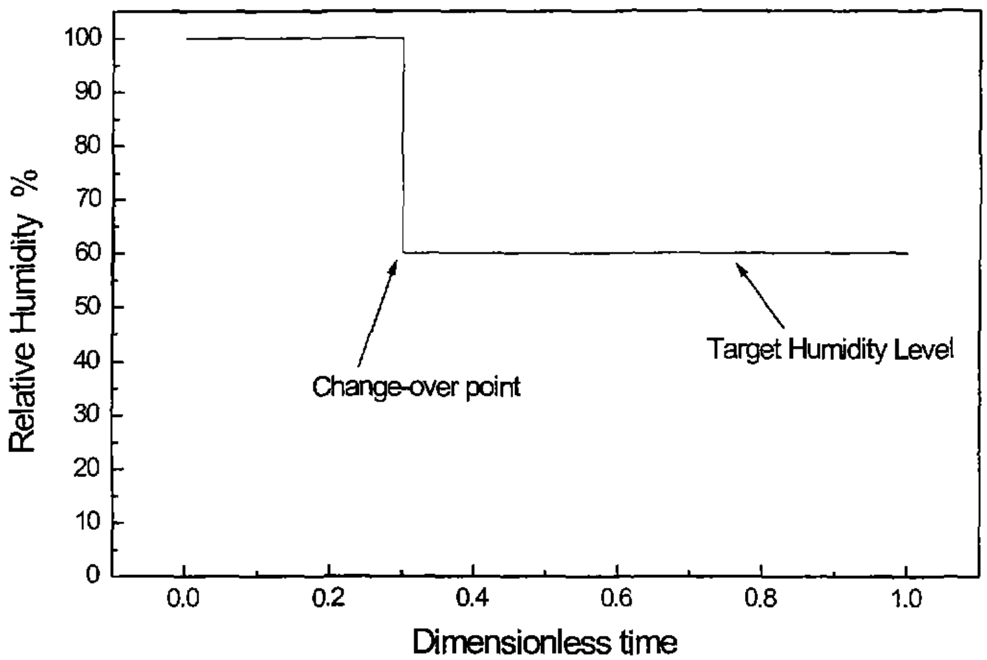

Figure 13 Two-step humidity conditioning example

The change-over time may be deduced from traveller coupons using the dimensionless change-over moisture content described in [51]. The traveller is exposed to 100% R.H with the component to be conditioned until the change-over moisture content is reached. The materials are then transferred to the target humidity environment and the weight of the traveller monitored until it reaches equilibrium. The change-over moisture content may be calculated from Figure 14.

Dimensionless parameters are defined as follows:

$$M_c^* = \frac{MoistureContent}{MaximumMoistureContent} \qquad \text{Equation 14}$$

$$c_d^* = \frac{MoistureConcentration}{MaximumMoistureConcentration} \qquad \text{Equation 15}$$

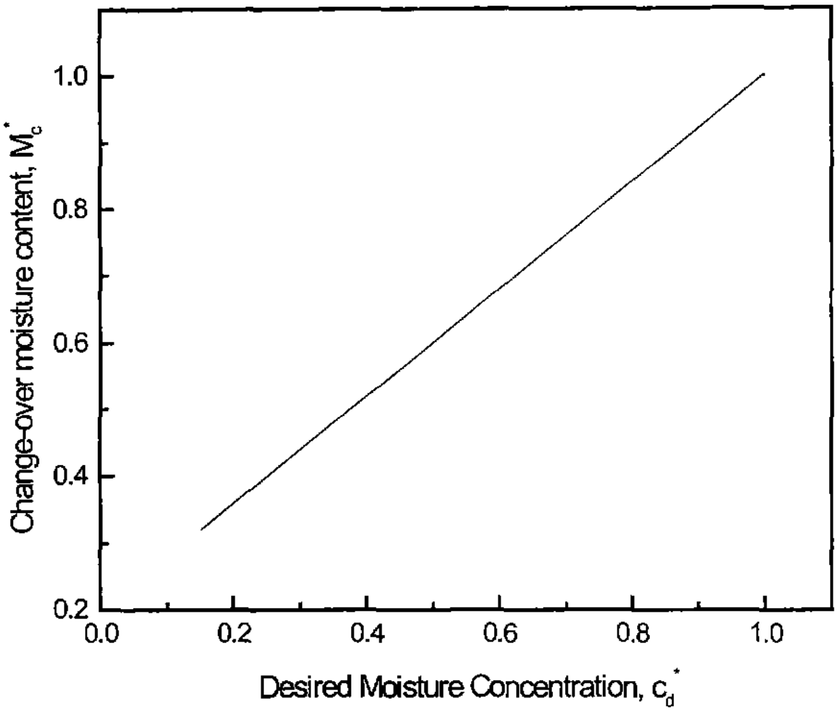

Figure 14 The dimensionless change-over moisture content versus the dimensionless moisture concentration from [51]

The resulting weight-gain curve from this two-step conditioning scheme will appear as shown in Figure 15 for a typical epoxy-based composite with Fickian diffusion behaviour.

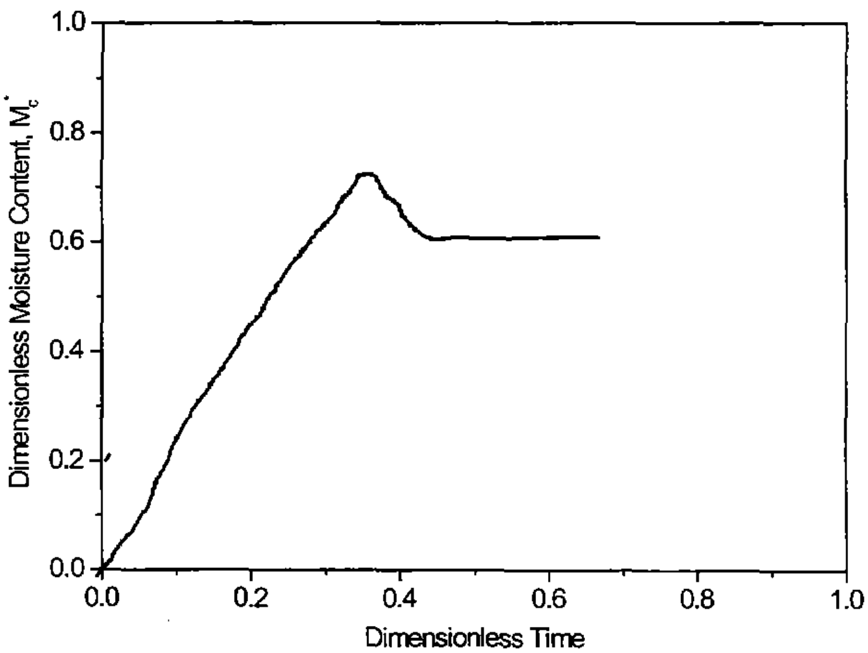

Figure 15 Weight-gain curve for two-step conditioning

Example: Conditioning a specimen to 1% moisture content.

A traveller is produced using identical material, layup and cure conditions. Both the traveller and component are exposed to 100% R.H until the change-over moisture content is reached. For 5521 F/4 Boron Epoxy laminate a 50% humidity level will produce an equilibrium moisture concentration of about 1%. The maximum moisture content possible at 100% R.H is 2.2%. The target dimensionless concentration level is therefore $\frac{1}{2.2}$ or about 0.45. From Figure 14 this gives a dimensionless change-over moisture content of about 0.55. This equates to a weight-gain concentration of 0.55*2.2 = 1.21%.

The traveller weight is then monitored when exposed to 100% R.H until it reaches 1.21% weight gain. The traveller and component are then transferred to the target humidity (ie: 50% R.H) until the weight of the traveller equilibrates.

8.2 Three-Stage Method

Collings and Copley [35] demonstrate a three-stage moisture conditioning method which may be used to provide a moisturised composite coupon with an even moisture concentration throughout it's thickness. The method uses the fact that the centre of the laminate takes up moisture slowly and reaches saturation after a long period of time whereas the exposed surfaces changes moisture content in relatively short times.

The three stages used to condition the specimens are:

1. **Accelerated ageing stage:** This stage utilises high temperatures and humidities to put as much moisture deep into the laminate as possible. The temperatures and humidities chosen should be those at which Fickian behaviour still applies.
2. **Drying Stage:** The first step provides more moisture to the laminate surface than the centre. To address this imbalance the surface of the laminate is dried in vacuum at 35°C.
3. **Equilibrium stage:** This stage uses a lower temperature and humidity than Stage 1 such as to produce a constant moisture concentration through the laminate thickness. The final humidity should represent the average moisture content of the real environment that is to be simulated.

The moisture profile produced by the temperatures and humidities chosen for each stage are estimated using a computer model called DIFF 4. This is most likely similar to the W8GAIN software mentioned in section 4.3 since it also uses a finite difference calculation method. Material diffusion parameters must therefore be determined beforehand. The authors stress that the temperature range over which the diffusion parameters are valid must be clearly defined before conditions for all three stages are chosen.

Validation of the moisture uptake data of the three-stage method using software is a good way to create an optimised moisture conditioning procedure and also enables the software model to be further refined. Software such as W8GAIN (section 4.3) can aid to determine conditioning regimes for composite components of non-uniform thickness or those made up of multiple layers of different material types.

The authors use software to point out that typical composites approximately 10 mm thick reach a constant through-thickness moisture profile in about 25 years of service life if exposed on both sides. **Table 5** taken from [35] shows the effectiveness of the three-stage accelerated conditioning scheme. The columns show the time in days taken for the composite (exposed on both sides) to reach a moisture concentration level of 1.06%. From the boundary conditions of the problem this moisture content represents exposure at 59% RH for the material in question. This is the moisture content which was found to be absorbed after a long service period (25 years). It must be noted that laminates less than 10 mm will reach a constant moisture profile well before 25 years of exposure. For exposure at a constant 60°C 96%RH the material reaches the final moisture content quicker than the three-stage method but the moisture distribution is not even and does not reproduce long-term exposure results.

It is valid, however, to compare the three-stage method to the 60°C 59%RH exposure since this exposure produces the correct moisture concentration through the specimen thickness when the specimen weight comes to equilibrium. It can be seen that the three-stage method conditions specimens up to 4 to 5 times quicker. Comparison to real-time exposure given by the 20°C and 59%RH column shows that the time saving here appears to be closer to 20 times.

Table 5 Part of a table reproduced from [35] showing the time taken (days) to condition carbon fibre composite to a moisture content of 1.06%

Thickness (mm)	20°C 59%RH	60°C 59%RH	60°C 70%RH	60°C 96%RH	3-Stage method
2	736	144	39	17.5	29
5	4580	896	240	109	187
7	8960	1760	470	213	344

This method was later utilised by Westlands Helicopters Ltd. [52] in their evaluation of Fiberdux 913 epoxy reinforced with graphite fibres.

The three-stage method seems most appropriate for thick laminates or laminates where the final moisture content through the thickness is quite low (around 60%).

9. Accelerated Environmental Testing

The combined mechanical and environmental testing of composite materials is of prime importance. A number of methods are identified in this section which address the issues related to mechanical strength degradation and the accurate simulation of combined mechanical and environmental effects. Aircraft certification issues relate to these testing methods and are addressed in section 10.

9.1 ENSTAFF (ENvironmental FalSTAFF)

The ENSTAFF method of accelerated testing works on a similar principle to FALSTAFF (Fighter Aircraft Loading Standard for Fatigue evaluation); the mechanical equivalent. ENSTAFF combines mission profiles, cyclic loads, environment and associated temperature excursions during typical combat aircraft usage. A service condition including loads and environment is defined for each aircraft component and these conditions are then applied in a reduced time-frame. This allows many 'flights' to be performed within a relatively short time-frame and allows the prediction of the part performance over an extended period. The standard is designed specifically for testing of composite materials for the wing structure of combat aircraft operating under European conditions. ENSTAFF has been acknowledged by European aircraft manufacturers to cover the design criteria for composite structure in new fighter aircraft. It is applicable for tests performed at both coupon and structural level. The standard was developed by West Germany, the Netherlands and the Royal Aircraft Establishment U.K.

Temperature changes due to ambient temperature, aerodynamic heating, temperature variation with altitude and solar radiation are all included and superimposed onto the load which may be experienced at these stages. A moisture level in the sample representing exposure to a humidity of 85% RH is maintained at all times. This is achieved by pre-conditioning the sample before testing and re-conditioning when moisture is lost.

ENSTAFF is conservative in its approach in that all loads and temperature cycles are carried out at the maximum moisture content produced at 85% RH. During service actual moisture content may fall below this level. However, testing at this level the material is more prone to thermal spiking damage (section 5.3) which can potentially produce greater reductions in mechanical properties.

Although ENSTAFF represents the most 'realistic' way of accelerated testing it must be noted that long-term degradation mechanisms (if present) may not be adequately represented by this method. This includes mechanisms such as U.V exposure, erosion or chemical reactions which may change the material properties.

A report on the ENSTAFF procedure is compiled in [53]. This report details the mission profiles defined for ENSTAFF, the management and testing of samples as well as the ground-based environments experienced.

9.1.1 ENSTAFF Flights

The flight sequences are defined from load/environment data gathered during real flights. The definition of the environment now also extends to include temperature rises and falls at specified rates. Supersonic elements of flights may also be included if the testing environment can be changed fast enough. Seasonal variations may also be included which reflect the extremes of summer and winter exposure. The given ENSTAFF 'flight' sequence will be unique for a particular aircraft component at a defined geographical location. It is assumed that all parts of the aircraft see the same humidity level.

9.1.2 ENSTAFF Ground Storage

Most moisture picked up by the composite material will occur during aircraft ground storage. Ground storage simulation must therefore be included since it allows the material to take up moisture to an equilibrium level. A relative humidity of 85% is chosen by ENSTAFF to represent a global average. ENSTAFF recommends that flight testing (load/temperature) should occur during the day with the moisture recovery period performed overnight. Humidity exposure levels during this period may be increased to 95% in order to restore as much moisture as possible. Although this will produce a moisture gradient within the surface layers this is acceptable to the ENSTAFF test regime.

Ambient temperatures will define the surface temperature during different times of the year. Material surface temperatures due to solar heating at ground level are assumed to rise to no more than 85°C.

9.1.3 ENSTAFF Traveller Coupon and Specimen Management

The ENSTAFF specification defines the requirements for traveller coupons, pre-conditioning and levels of temperature and humidity.
ENSTAFF recommends that:

- Traveller coupons are to be cut from adjacent material to that tested.
- Pre-conditioning is to be done to equilibrium weight-gain on exposure to 85% relative humidity.
- Multi-stage conditioning (sections 8.1 and 8.2) may be used in this case to accelerate moisture uptake provided the final stage is carried out to 85% RH to produce a constant moisture distribution.
- Theoretical modelling of the material diffusion properties is conducted prior to testing.
- Drying temperatures are to be less than 70°C for 180°C cure thermoset materials and 45°C for 120°C curing thermosets unless proven otherwise by experiment.
- All weights are to be measured on a balance capable of measuring 0.0001g.

9.1.4 ENSTAFF Applicability to Australian Conditions

The definition of conditions for the ENSTAFF test is critical if it is to be representative. It may also be possible to single-out a particular environment which causes the most degradation and combine this with the associated mechanical loading. The hot/wet test condition is a good example of this. The combination of high temperature and a fully moisturised test article will be a severe test of material durability.
The ENSTAFF specification is certainly representative of the type of aircraft and mission profiles that are experienced by the RAAF. Both the average humidity level of 85% and maximum surface temperature of 85°C appear to be representative of Australian operating environments. Low temperature excursions experienced on the ground in parts of Europe are unlikely to be seen in most parts of Australia. The section on Cryogenic Exposure (section 5.6) examined low temperature excursions and found that they are not particularly damaging unless water is trapped in damaged structure.
MIL STD 810E (section 7.2) has definitions for many world climate zones. These are useful for defining conditions suitable for determining ground exposure. Flight profiles and exposure conditions are likely to be very similar worldwide and may be defined using the international standard atmosphere definition. It is therefore likely that ENSTAFF flight profiles would be applicable to Australian conditions.

9.2 National Research Council of Canada - National Aeronautical Establishment Testing Facility

The design considerations for an environmental test facility for composite materials and structures proposed by the National Aeronautical Establishment, Canada is outlined in the Technical Report by Komorowski and Simpson [**54**]. The facility allows the use of varying load and hygrothermal loading spectra. This allows the simulation of real-life exposure or the use of accelerated testing regimes.

9.3 Predictive Models Based on Accelerated Testing Results

A review of a number of techniques which may be used to predict the durability of materials under accelerated testing conditions is given in [55]. The techniques use a series of functions to extrapolate long-term behaviour from accelerated tests. The author points out the limitations of such tests:

- Statistical uncertainty due to quantity and number of test results
- Quality of accelerated data in terms of test conditions being sufficiently valid to relate to service conditions
- Validity of extrapolation procedure

Life-time prediction may also be assessed using cumulative-damage theory. Work by Shah and Patni [56] uses a mathematical treatment of damage accumulation within a material to predict its final service life. It requires careful selection of accelerated conditions and careful monitoring of the damage that is being introduced. This method seems best suited to the accelerated testing of materials in which multiple-damage modes are likely to be introduced during service operation. Since a combination of environmental effects lead to the mechanical degradation of composites such an approach is well suited although it requires a large study into each damage mode and it's effects.

9.4 Recommendations from MIL Handbook 17

The MIL-Handbook 17 (MIL-HDBK-17-1D Change Notice 1 1995) document contains information on determining the effects of moisture and gives guidelines on the conditioning of samples for environmental testing.

The bulk of the information on moisture effects is given in Volume 1, Chapter 2. The document points out that moisture effects are limited to the matrix except in the case of aramid fibres which are degraded by moisture themselves. Thus it is only necessary to look at the properties of the matrix in the operating environment. The reduction in matrix properties with moisture uptake is represented by the term Maximum Operational Limit (MOL). The MOL is the limit where a "drastic reduction in properties" takes place. This is likely to be close to the T_g of the material where the matrix loses much of it's stiffness. Since T_g is reduced by moisture uptake MOL must be determined experimentally for matrices which are saturated with moisture to a level representative of the operating environment. One technique to determine MOL uses the value of the wet glass transition temperature with some safety factor built in. A value of MOL 28°C less than the wet T_g is proposed for epoxy based composites.

The handbook also proposes a conditioning humidity of 85% to represent the world-wide average service environment. This value is the same as that used by the ENSTAFF conditioning procedure (section 9.1). A maximum conditioning temperature of 77°C is recommended for 177°C curing epoxies and 68°C for 121°C curing epoxies. An even distribution of moisture through the sample is required prior to mechanical testing. It recommendeds that exact conditioning times are not specified as the time should be based on a constant sample weight being achieved. It is stressed that although temperature may be used to accelerate the ingress of moisture the mode of diffusion must not significantly deviate from Fickian behaviour. Two-step conditioning schemes such as the one detailed earlier (section 8.1) are acceptable provided the maximum humidity used is 95%. Traveller coupons may be used provided the length to thickness ratio is at least 10:1 or that the edges of the samples are shielded from moisture. Drying temperature for specimens is recommended not to exceed 121°C for 177°C curing epoxies and 93°C for 121°C curing epoxies.

9.5 Accelerated Conditioning Research - Grumman Aerospace

This work was done for the US Air Force in 1983 under a contract to Grumman Aerospace Corporation and examines a particular method of accelerated testing. The difference in conditioning during a long-term flight loading test versus pre-conditioning the sample before testing is primarily examined. There is an obvious advantage in not having to pre-condition samples, especially large structures, due to the long time involved.

The approach to accelerated testing carried out by Demuts and Shyprykevich [57] is made with an emphasis on limiting the severities of the test variables; in particular the test temperature. The authors begin by determining an average operating climate. They determined this as 14°C and 67% R.H for a temperate climate and 32°C and 85% R.H for a tropical climate. From these average climates they deduced the final equilibrium moisture level using one-dimensional Fickian diffusion theory. These moisture levels became the end of test moisture goals (EOTM). Two types of environmental conditioning were conducted.

a) Precondition the samples to EOTM and test with flight loading. Lost moisture is replaced between tests at 100% R.H exposure.
b) Reach the desired EOTM by conditioning at periods between mechanical tests. Moisture conditioning was performed overnight and on weekends only.

The authors correctly note the importance of exposing samples to temperatures below their 'wet' T_g; that is the T_g at the EOTM level. Matrix dominated compressive strength tests were used to determine the unfavourable effects of the conditioning environment.

Thermal spiking was also performed at 127°C; which is 6°C above the 'wet' Tg of 121°C.

The authors found no statistically significant difference between conditioning methods a) or b). It was also found that there is no synergistic effect of environment and loading which may allow the determination of suitable knock-down factors from ambient mechanical tests to predict the effect of the environment.

9.6 Simulating the Effects of Hot/Wet Environment on Strength

There are a number of approaches which may be taken to examine the hot/wet behaviour of composites. At the coupon level tests may be performed to determine the diffusion behaviour and matrix mechanical properties under varied hot/wet environments. In order to reproduce this in a structure for the structural substantiation of components and sub-components there are a number of options. In all cases the failure modes of specimens or components subjected to simulated conditions must faithfully reproduce those seen in long-term service.

- **Condition the structure using accelerated moisture uptake schemes and test at elevated temperature.**

This type of testing is currently used for much of the structural certification performed for environmental durability. This is currently the most conservative and representative way of ensuring service conditions are reproduced accurately. An example of this is the ENSTAFF scheme. Accelerated moisture absorption schemes may be used to bring the structure to a moisture level consistent with it's service environment after long-term exposure. This type of test was performed recently by DSTO-AMRL under contract to Hawker de Havilland in the structural substantiation testing of the C130J flap [58]. There may be problems in the accelerated conditioning of structures if they contain sections of different thicknesses. Different parts of the structure would come to equilibrium at different times. Sufficient time must be allowed to develop an even moisture distribution throughout the component such that the entire structure is seeing a representative moisture content.

- **Apply a load enhancement factor to the structure to represent the degradation of matrix mechanical properties under hot/wet conditions at the coupon level.**

This is suggested in the certification procedure described by Rouchon [62]. This would involve determining the reduction in matrix mechanical properties under hot/wet environments at the coupon level and then increasing the load on a dry/room temperature test to reflect this loss. It is vital to ensure that the mode of failure is reproduced in the load-enhanced test article to ensure no other failure modes are present which may invalidate this type of approach. It must be kept in mind that moisture will tend to plasticise the matrix of the composite which may improve it's toughness and could cause a change in failure mode. Analysis of the failure mode is therefore a very important part of the testing procedure. Changes in failure mode may indicate that this sort of approach may be unsuitable. In this case a more conservative approach such as testing under representative hot/wet conditions is preferred.

- **Apply a test which replicates the increased strain experienced by the matrix under testing- equivalent strain approach.**

The strain experienced by the coupons under hot/wet environments are made equivalent to the load experienced by a dry composite to produce an equivalent strain. Again the failure modes must be equivalent also.

- **Apply a elevated temperature testing scheme to reflect the behaviour of a matrix plasticised by the absorption of moisture.**

This seems to be a logical approach since moisture decreases the Tg of the matrix. Elevated temperature could then be utilised to reflect this change. This method also eliminates the need to moisture condition the structure yet the test includes temperature effects. Work by Collings et al. [59] utilises this approach. The authors argue that the temperature enhancement required should be equal to the decrease in Tg seen after moisture conditioning. For many 180°C curing epoxy matrices a depression in Tg of about 30°C-40°C is found when moisture of a level representative of typical service is present. The authors examined the wet and dry mechanical performance of a series of composite materials for a range of temperatures. They utilised Interlaminar Shear Strength, 0° Compression strength and +/- 45° tension tests. Results comparing the wet and dry mechanical properties showed that the mechanical properties of the wet specimen were similar to that of the dry material at a higher test temperature. This supports the theory that a simple increase in temperature for a dry specimen will predict the behaviour of a wet specimen. Resin T_g values decreased by an average value of 33.5°C after moisture

conditioning. The temperature increase required to simulate moisture in the specimen was found to be an average of 36.75°C.
This is an important result as it shows a close link between the T_g of the material and the temperature increase required to simulate the same effect in a dry specimen. The authors point out the shortcomings of this method as being:

- Time dependent effects such as U.V surface degradation are not simulated
- In multi-thickness structures thermal gradients may develop giving an unrepresentative result
- Structure masked by bolts or metal components will be represented as fully degraded. This may not be the case in service.

This method would require enough mechanical tests to establish

- the decrease in T_g of the moisture conditioned matrix
- a relation, at the coupon level, between the wet and dry mechanical properties over a range of representative service temperatures
- a careful examination of the failure modes to ensure they are the same for both the wet and dry cases.

This approach may be performed at the coupon level and then transferred to structures provided all the above points are satisfied.

9.7 Airforce Wright Aeronautical Laboratories Research

This work took place in the late 1970s and examines the environmental sensitivity of advanced composites during both ground exposure and flight service. The material examined is AS/3501-5A. The three volume reference [60] gives excellent details on weather conditions at a number of U.S Airforce Bases including the minimum, maximum and average conditions experienced. Detailed flight profiles and skin temperatures observed during the operation of a B-1 aircraft are also provided. The report also encompasses a whole series of mechanical tests examining the effects of hot/wet environment and exposure time on mechanical properties. The program represents a large volume of work which is indispensable when considering environmental effects on composites.

Some important conclusions are made in this report which are relevant here:

- Aircraft flights reduce the average moisture content of composite materials - more frequent flights give further reduced moisture levels
- Exposure to solar radiation produced a lower overall moisture content
- The effects of thermal spiking (section 5.3) were observed to be reflected in the number of T_g exceedances the material had encountered. Thermal spiking increased the diffusivity and moisture content and degraded mechanical properties
- Microscopic examination revealed laminate cracks when specimens were exposed to high humidity levels for a period of 15 months. This was also evident in the lower compression strengths observed
- Moisture content is a good indicator of compressive strength regardless of previous moisture content history
- Residual tension and compression strengths after real flight profiles applied over long periods were identical if the samples were pre-conditioned to a particular moisture level or if they were conditioned during testing.
- No synergistic effects of fatigue-loading and environment were observed.

10. Certification Issues

Information for this section comes from the workshop held in Canberra, Australia in 1996 [61]. The presenter was J. Rouchon from DGA (Delegation Generale pour l'Armement - Centre D'Essais Aeronautique De Toulouse), France.

This section briefly outlines some issues which are relevant to the certification of aircraft structures for environmental durability. The certification requirements presented here as those as defined by DGA (Centre D'Essais Aeronautique De Toulouse, France) and presented by Jean Rouchon at the "Improved Certification of Composite Aircraft Structures - Trends and Prospects" workshop held by the 'Co-operative Research Centre - Aircraft Structures' and the 'Civil Aviation Safety Authority' in Canberra August 8th-9th 1996.

The requirements with respect to environment (corrosion) were described as:

Humidity effect of moisture uptake is assumed to be reversible and asymptotic:
This implies that the composite material has clearly defined boundary conditions (Equation 4) which are applicable throughout the operating temperature range of the aircraft. The need for asymptotic behaviour implies that the material must follow Fickian behaviour.

Since most aerospace composites use carbon fibres only matrix governed properties are under concern:
This involves establishing that the fibre used is not degraded by moisture and temperature. This is the case for carbon fibre but may not be for glass or aramid (Kevlar). Matrix-governed properties such as compression and shear strengths as well as the reduction of T_g with moisture uptake need to be shown for the dry, semi-saturated and fully saturated case.

Combined Effects of Fatigue and Environment:
This effect is quoted as:
"Assuming that the fatigue resistance can be expressed by the residual static strength existing at the end of the application of a representative combination of fatigue loads and environment:

- no significant effect of fatigue combined with thermo-hygrometric mission profile has been found
- the residual static strength level depends on the moisture level absorbed by the composites only"

The mission profiles used by DGA have a maximum temperature of 50°C for civilian mission profiles and 100°C for fighter mission profiles. Humidity exposure is elevated to 90-95% R.H at certain parts of the profiles as shown in Figure 16 and Figure 17

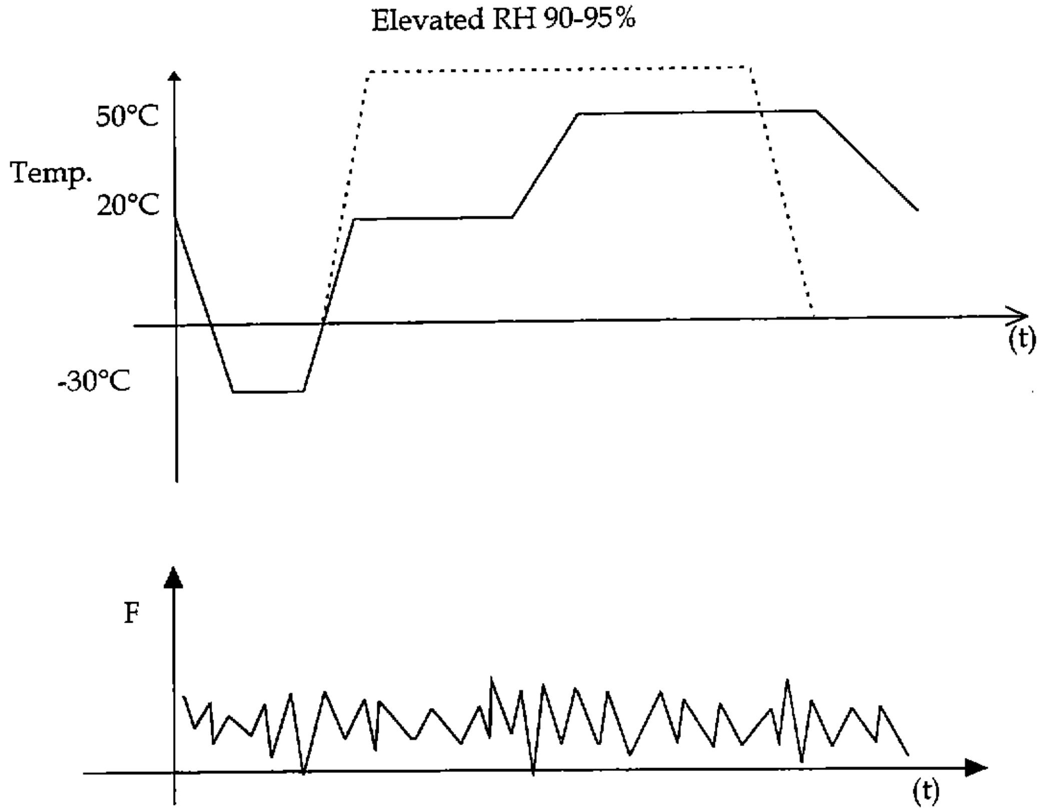

Figure 16 ***Civil Aircraft Mission Profile [61]***
Temperature/humidity versus time profile (top)
Force Applied versus time (bottom)

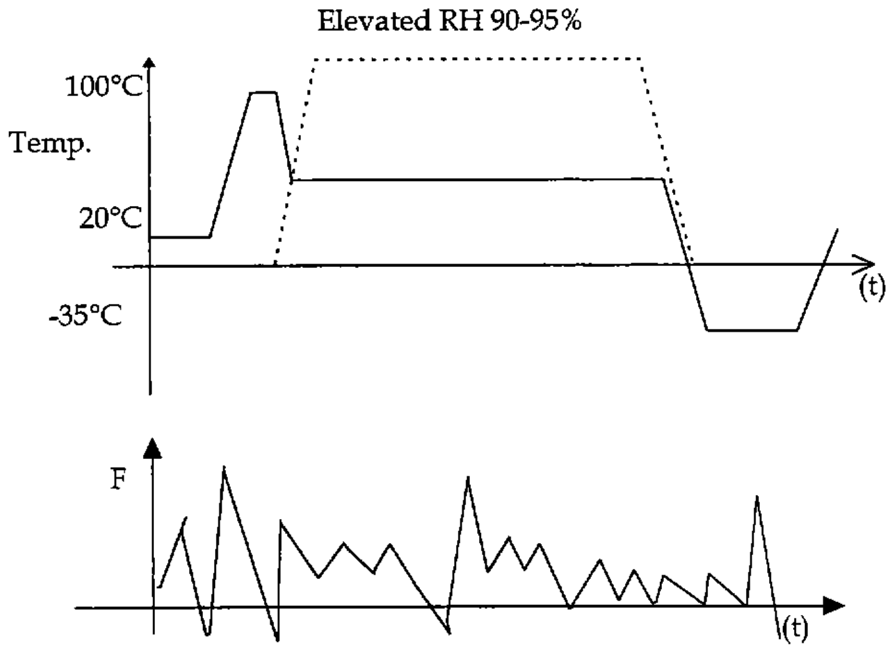

Figure 17 ***Fighter Mission Profile***
Temperature/humidity versus time profile (top)
Force Applied versus time (bottom)

Humid ageing is accounted for in structural substantiation by assuming:

- There is a relationship between moisture content and residual mechanical properties
- Mechanical property degradation depends only on the moisture content of the sample and not the previous temperature/humidity history
- Static strength may be demonstrated by accelerated conditioning or by using a load enhancement factor to account for mechanical property degradation
- It is assumed that there is no combined effect with fatigue. Fatigue is carried out with samples moisture conditioned to a moisture level 60% of that which will be experienced in service.
- Temperature extremes for subsonic aircraft are a maximum of 55°C according to Airbus and 51°C recommended by the FAA.
- In structural substantiation a humidity value of 85% RH is assumed to represent the average global environment.

  In the philosophy used by DGA it is necessary to verify that materials certified by this method behave in the manner that is assumed. That is:
- Material undergoes Fickian diffusion behaviour (asymptotic) under all conditions in the mission profile
- The boundary conditions (Equation 4) of the diffusion process are shown to exist over the temperature profile that the material will experience in service. The boundary conditions must not change if temperature and humidity are cycled within the mission profile
- The fibres undergo no environmental degradation
- The environmental profiles chosen accurately represent service conditions
- Mechanical properties do not decrease with exposure time during humid ageing

All these assumptions need to be confirmed with experimental tests to ensure that the certification approach taken is valid ie: accelerated ageing or load enhancement. Materials which do not comply with these assumptions may be very difficult to deal with as there will be time-dependent degradation mechanisms which may be extremely difficult to simulate in reduced time frames without a long-term test to substantiate the accelerated testing regime.

Further details on the fatigue and damage tolerance aspects for composite aircraft structures are given in the reference by Rouchon [62]. This work suggests that for hot/wet conditions the properties of composites are reduced by 10% for tensile loads and 20% for compressive loads. Rouchon points out that certification of Airbus components for fatigue required the part to maintain a moisture level of 60% to 100% of the maximum value expected at the end of lifetime.

11. Conclusions

The testing of composite materials to ensure their suitability for their intended operating environment is crucial. This testing must include the effects of long-term exposure to both flights and ground storage. Accelerated testing is required to simulate these long-term effects in order to predict their behaviour in a practical time-frame.

There is a wealth of data on the environmental behaviour of a wide range of composite materials. A number of factors can influence the mechanical integrity of the material under environmental exposure. These include temperature, moisture content, thermal spiking, erosion and UV exposure.

There are however some common elements which must be addressed for all composite materials before their environmental durability can be accurately assessed. A summary of these is listed below:

1. The environment to be simulated by accelerated testing must be carefully defined
2. An understanding of the impact of environment on composite performance must be assessed
3. Temperature and moisture produces a combined effect which significantly reduces matrix dominated composite properties. They are the most significant factors in environmental testing in most cases.
4. An understanding of the diffusion behaviour of the composite matrix must be first established.
5. Simulation of environmental effects on mechanical properties must be carried out such that the failure modes are consistent

   Accelerated environmental testing and moisture conditioning methods are available which replicate the moisture uptake of composites over their operating life. These can greatly reduce the amount of time taken to pre-condition samples with moisture prior to mechanical testing.

   Guidelines given by ENSTAFF, French DGA, MIL-HDBK-17 and MIL-STD-810 are available to help define ground-storage, flight conditions and acceptable testing parameters for laboratory evaluation of composite coupons.

12. Bibliography

"Hygrothermal Effects in Continuous Fibre Reinforced Composites"
J. P. Komorowski
National Research Council Canada, National Aeronautical Establishment

Part I: Thermal and Moisture Diffusion in Composite Materials
Aeronautical Note NAE-AN-4 NRC NO. 20974, January 1983

Part II: Physical Properties
Aeronautical Note NAE-AN-10 NRC NO. 22700, September 1983
Part III: Mechanical Properties 1
Static Tests
Aeronautical Note NAE-AN-11 NRC NO. 21299, September 1983
Part IV: Mechanical Properties 2
Fatigue and Time Dependent Properties
Aeronautical Note NAE-AN-12 NRC NO. 21300, September 1983
This series of aeronautical notes from the National Aerospace Establishment, Canada were released in 1983 and provide an excellent review of research on hygrothermal effects on composites.

13. References

1 G. Clark, D.S. Saunders, T.J van Blaricun and M. Richmond, "Moisture Absorption in Graphite Epoxy Laminates", Composites Science and Technology, Vol. 39, 1990, pp355-375

2 W. Althof, Royal Aircraft Establishment, Library Translation 2038, February 1980

3 C.M Demonet, 21st International SAMPE Technical Conference, September 25-28, 1989, pp 231-238

4 Ed Woo, Materials Performance, April 1991 pp68-69

5 L.C. Bank, T.R. Gentry and A. Barkatt, "Accelerated Test Methods to Determine the Long-Term Behaviour of FRP Composite Structures: Environmental Effects, J. Reinforced Plastics and Composites, Vol. 14, June 1995, pp 559-587

6 M.J. Rich and L.T. Drzal, "Interfacial Properties of Some High-Strain Carbon Fibers in an Epoxy Matrix", J. Reinforced Plastics and Composites, Vol. 7, March 1988, pp 145-154

7 L.T. Drzal, "Adhesion of Graphite Fibers to Epoxy Matrices. III The Effect of Hygrothermal Exposure", J. Adhesion, Vol. 18, 1985, pp 49-72

8 W.C Jackson and T.K. O'Brien, "Water Intrusion in Thin-Skinned Composite Honeycomb Sandwich Structures, Journal of the American Helicopter Society, October 1990, pp31-37

9 H.B. Dexter and D.J. Baker, 'Flight Service Environmental Effects On Composite Materials And Structures', Advanced Performance Materials, Volume 1 Number 1, 1994, pp51-85

10 R.A Garrett, R.E Bohlmann and E.A. Derby, 'Analysis and Test of Graphite/Epoxy Sandwich Panels Subjected to Internal Pressures Resulting from Absorbed Moisture', ASTM STP 658, 1978, pp 235-253

11 R.J Chester and A.A. Baker, 'Environmental Durability of F/A-18 Graphite/Epoxy Composite', Polymers and Polymer Composites, Vol. 4, No. 5, 1996, pp315-323

12 Y.J. Weitsman, "A Method To Determine Moisture Profiles From Total Moisture Weight-Gain Data In Polymeric Composites", Report for the Office of Naval Research Arlington Virginia U.S.A, ESM91-1.0-MECH, September 1991

13 B.C Hoskin and A.A. Baker Editors, 'Composite Materials for Aircraft Structures', Chapter 9, AIAA Education Series, New York, 1986.

14 J. Crank, "Mathematics of Diffusion", London, Oxford University Press, 1959

15 Y.J. Weitsman, "Effects of Fluids on Polymeric Composites - A Review", Contractual Technical Report MAES 95-1.0 CM Office of Naval Research Arlington, Virginia, U.S.A

16 Shen and Springer, Moisture Absorption and Desorption of Composite Materials, J. Comp. Mat., Vol. 10, January 1976 p2-10

17 Shen and Springer, Moisture Absorption of Graphite-Epoxy Composites Immersed in Liquids and Humid Air, J. Comp. Mat., Vol. 13, April 1979 p131-147

18 Q. Zheng and R.J Morgan, Journal of Composite Materials, Vol. 27, No. 15, pp1465-1478, 1993

19 E.C. Edge, "Effect, on moisture absorption experiments, of failure to dry specimens prior to exposure, Composites, April 1980, pp101-104

20 J.M. Whitney and C.E Browning, 'Some Anomalies Associated with Moisture Diffusion in Epoxy Matrix Composite Materials', Advanced Composite Materials - Environmental Effects, ASTM STP 658, J.R Vinson Editor (1978)

21 G. S. Springer, "Moisture Content of Composites Under Transient Conditions", J. Composite Materials, Vol. 11 January 1977, pp 107-122

22 C. Y. Lundemo, "Experience From The Use Of The Transient Moisture Response Computer Program W8GAIN For Composite Materials", The Aeronautical Research Institute of Sweden, Technical Note HU-2043, 1979

23 Jiming Zhou and James P. Lucas, 'The Effects of a Water Environment on Anomalous Absorption Behaviour in Graphite/Epoxy Composites', Composites Science and Technology, 53, (1995) pp57-64

24 W.P De Wilde and P.J Shopov, 'A simple model for moisture sorption in epoxies with sigmoidal and two-stage sorption effects', Composite Structures, 27, (1994), pp243-252

25 M.C Lee and N.A Peppas, 'Models of Moisture Transport and Moisture Induced Stresses in Epoxy Composites', Journal of Composite Materials, Vol. 27, No. 12, (1993) pp1146-1171

26 T.K Tsotsis and Y. Weitsman, 'A simple graphical method for determining diffusion parameters for two-stage sorption in composites', Journal of Materials Science Letters 13, (1994) pp1635-1636

27 L-W. Cai and Y. Weitsman, 'Non-Fickian Moisture Diffusion in Polymeric Composites', Journal of Composite Materials, Vol. 28, No. 2, pp130-154, (1994).

28 Environmental Effects on Composite Materials, G.S Springer (Editor), Volumes 1 and 2. Technomic Publishing. Published 1981 (Vol. 1) and 1984 (Vol. 2).

29 H.G Carter and K.G Kibler, 'Langmuir-Type Model for Anomalous Moisture Diffusion in Composite Resin', Journal of Composite Materials, Volume 12, pp118-131.

30 A.O Kays, Determination of Moisture Content in Composites by Dielectric Measurements, Lockheed-Georgia Company, Technical Report AFDL-TR-79-3086, (1979).

31 KDC Technology Corporation, 2011 Research Drive, Livermore CA 94550, U.S.A

32 M. Werner and R. King, 'Microwave Sensors for Imaging Moisture and Flaws in Composite Materials', Review of Progress in Quantitative Non-destructive Evaluation, Vol. 15, 1995, Plenum Publishing Corporation

33 J.J Singh, W.H Holt and W. Mock Jnr., 'Moisture determination in composite materials using positron lifetime techniques', NASA Technical Paper 1681, July 1990

34 R.J Delasi and R.L Schulte, 'Experimental determination of the effects of moisture on composite-to-composite adhesive joints', NASA Contactor Report 3387, 1981

35 T.A. Collings and S.M. Copley, 'On the accelerated ageing of CFRP', Composites, Vol. 14, No. 3, July 1983

36 C.E Browning, G.E Husman, J.M. Whitney, 'Moisture Effects in Epoxy Matrix Composites. STP 617, ASTM, 1977, pp 481-96.

37 C.J. Jones, R.F. Dickson, T. Adam, H. Reiter and B. Harris, 'The Environmental Fatigue Behaviour of Reinforced Plastics', Proceedings of the Royal Society, London A 396, pp315-338 (1984)

38 N.R Farrar and K.H.G Ashbee, "Destruction of epoxy resins and of glass-fibre reinforced epoxy resins by diffused water", J. Phys. D: Applied Physics., Volume 11, 1978 pp1009-1013

39 E. Walter and K.H.G Ashbee, 'Osmosis in composite materials', Composites, October 1982, pp365-368

40 J.S. Ghotra and G. Pritchard in Developments in Reinforced Plastics - 3, Elsevier Applied Science Publishers, Ed: G. Pritchard, 1984, pp63-95

41 R. Delasi and J.B Whiteside, "Effect of Moisture on Epoxy Resins and Composites", Advanced Composite Materials - Environmental Effects, ASTM STP 658, J.R Vinson Ed. 1978, pp2-20.

42 J. Nicholas and K.H.G Ashbee, "Further Destruction of composite materials by the freezing or boiling of phase separated water J. Phys. D: Applied Physics., Volume 11, 1978 pp1015-1017

43 O. Gillat and L.J Broutman, "Advanced Composite Materials - Environmental Effects" ASTM STP 658, Ed: J.R. Vinson, pp61-83

44 Y. Weitsman, "Stress Assisted Diffusion in Elastic and Viscoelastic Materials", J. Mech. Phys. Solids, Vol. 35, No. 1, pp73-93, 1987

45 B.D Harper, G.H Staab and R.S Chen, "A note on the effects of voids upon the hygral and mechanical properties of AS4/3502 Graphite/Epoxy", Journal of Composite Materials, Vol. 21, March 1987, pp 280- 289

46 M. Blikstad, P.O.W Sjoblom and T.R Johannesson, "Long Term Moisture Absorption in Graphite/Epoxy Angle-Ply Laminates", Journal of Composite Materials, Vol. 18, January 1984, pp 32-46

47 AGARD Conference Proceedings No. 288 "Effect of Service Environment on Composite Materials", AGARD-CP-288, Sections 18 to 21, April 1980

48 L. Greenspan, 'Humidity Fixed Points of Binary Saturated Aqueous Solutions', Journal of Research of the National Bureau of Standards-A. Physics and Chemistry, Vol. 81A, No.1, January-February 1977 p 89-96

49 E.L McKague, Jr., J.E Halkias and J.D Reynolds, "Moisture in Composites: The Effect of Supersonic Service on Diffusion", J. Composite Materials, Vol. 9, January 1975, pp2-9

50 "The Implications of Laboratory Conditioning of Carbon Fibre Composites, E.C. Edge, AGARD Conference Proceedings No. 288 "Effect of Service Environment on Composite Materials", AGARD-CP-288, Section 1, April 1980.

51 P. R. Ciriscioli, W.I Lee and D.G. Peterson, "Accelerated Environmental Testing of Composites", Journal of Composite Materials, Vol. 21, March 1987, pp225-242

52 N. Marks and A. Dalziel, "Artificial Ageing of Fibre Reinforced Composite Materials - Three Stage Method", Developments in the Science and Technology of Composite Materials ECCM 3, Bordeaux, France, 20-23 March 1989, pp587-593

53 J.J. Gerharz, 'Standardised Environmental Fatigue Sequence for the Evaluation of Composite Components in Combat Aircraft ENSTAFF = Environmental FalSTAFF, National Aerospace Laboratory NLR, The Netherlands, Report NLR TR 87053 U. Also published as LBF Report No. FB-179(1987), IABG Report No. B-TF 2194 (1987) and RAE Report No. TR 87048

54 J.P. Komorowski and D.L. Simpson, "Design Considerations Environmental Testing Facility for Composite Materials and Structures", Laboratory Technical Report LTR-ST-1505, June 1984, National Research Council Canada - National Aeronautical Establishment

55 R.P. Brown, "Predictive Techniques and Models for Durability Tests", Polymer Testing, 14, 1995, pp403-414

56 C.S. Shah and M.J. Patni, Accelerated Aging and Life Time Prediction Analysis of Polymer Composites: a New Approach for a Realistic Prediction Using Cumulative Damage Theory", Polymer Testing, 13, (1994) pp295-322

57 E. Demuts and P.Shyprykevich, Accelerated Environmental Testing of Composites, Composites, Vol. 15, No. 1, January 1984, pp25-31.

58 J. Lubacz, C130J Flap Test, AMRL Report

59 T.A. Collings, R.J Harvey and A.W. Dalziel, Composites, Vol. 24, No. 8, 1993, pp625-634

60 Environmental Sensitivity of Advanced Composites, Wright AirForce Aeronautical Laboratories U.S.A, AFWAL-TR-80-3076 Volumes 1, II and III, May 1977 - May 1980.

61 "Improved Certification of Composite Aircraft Structures - Trends and Prospects" workshop held by the Co-operative Research Centre Aircraft Structures and the Civil Aviation Safety Authority in Canberra, Australia August 8th-9th 1996

62 "The Fatigue And Damage Tolerance Aspects For Composite Aircraft Structures", J. Rouchon, Fatigue and Damage Tolerance of Aircraft Structures, Delft, March 1995, ICAF-DOC-2051

Page classification: UNCLASSIFIED

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
DOCUMENT CONTROL DATA

1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)

2. TITLE Accelerated Environmental Testing of Composite Materials	3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION) Document (U) Title (U) Abstract (U)
4. AUTHOR(S) Roger Vodicka	5. CORPORATE AUTHOR Aeronautical and Maritime Research Laboratory PO Box 4331 Melbourne Vic 3001

6a. DSTO NUMBER	6b. AR NUMBER	6c. TYPE OF REPORT	7. DOCUMENT DATE
DSTO-TR-0657	AR-010-516	Technical Report	July 1997

8. FILE NUMBER	9. TASK NUMBER	10. TASK SPONSOR	11. NO. OF PAGES	12. NO. OF REFERENCES
M1/9/406	97/093	AIR/ASI	50	62

13. DOWNGRADING/DELIMITING INSTRUCTIONS	14. RELEASE AUTHORITY
-	Chief, Airframes and Engines Division

15. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT

Approved for Public Release

OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE CENTRE, DIS NETWORK OFFICE, DEPT OF DEFENCE, CAMPBELL PARK OFFICES, CANBERRA ACT 2600

16. DELIBERATE ANNOUNCEMENT

No Limitations

17. CASUAL ANNOUNCEMENT Yes

18. DEFTEST DESCRIPTORS

Composite materials, Matrix materials, Accelerated tests, Environmental tests, F/A-18 aircraft, Bonding, Components

19. ABSTRACT
Composite materials are found to lose mechanical on exposure to aircraft operating environments. This is mainly due to absorption of moisture from humid air by the matrix material. Composite materials are extensively used by the RAAF for both major structural components on the F/A-18 and for bonded repairs and doublers. The performance of these materials under long-term environmental exposure is an important aspect of both aircraft certification and in the understanding of how the components will age. This report provides a broad overview of environmental effects on composite materials and methods which may be used to predict their long-term behaviour. The use of accelerated testing environments in the laboratory is an attractive proposition as it enables tests to be carried out in reduced time frames. A number of accelerated testing methodologies and their implications are outlined here. Accelerated testing can be carried out with confidence if the exposure conditions are representative and the failure modes of the material during mechanical tests reflect those seen in service.