EFFECT OF METAL SURFACE COATING ON THE MOISTURE ABSORPTION CHARACTERISTICS OF CFRP

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Approval of the Graduate School of Natural and Applied Sciences

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ABSTRACT

EFFECT OF METAL SURFACE COATING ON THE MOISTURE ABSORPTION CHARACTERISTICS OF CFRP

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In this study, the influence of metal surface coating on the moisture absorption characteristics of Fibredux 914C/T300 Carbon Fibre Reinforced Plastics (CFRP), which contain unidirectional carbon fibres and epoxy resin as a matrix, were investigated.

Copper-gold, copper-nickel-gold, nickel and gold films were deposited on CRFP specimens using vacuum evaporation technique. Decorative copper-nickel-chromium combinations were plated on CFRP specimens with electroplating technique. The coated specimens were aged at $70^{\circ}C$ and 90% RH, by using saturated salt solution technique.

The weight gain of specimens coated by vacuum evaporation technique monitored during ageing shows that the metal films does not affect the moisture absorption rate of specimens. The diffusion coefficient D, was calculated to be $3.4*10^{-7}$ mm^{2}/sec. The examination of aged specimens under the scanning electronmicroscope reveals crack formations on the metal layers. Therefore it is concluded that the vacuum evaporation technique does not provide a sufficient film for Fibredux 914C/T 300 CFRP specimens.

By using electroplating technique, the thicknesses of metal films were increased, but crack formations were also observed with this type of metal films.

Key words : Carbon fibre reinforced plastic, accelerated ageing, moisture absorption of CFRP.

ÖZET

YÜZEY METAL KAPLAMALARIN KARBON ELYAFLI PLASTİKLERİN NEM ABSORBLAMA ÖZELLİKLERİ ÜZERİNE ETKİLERİ

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Bu çalışmada, yüzey metal kaplamaların Fibredüx 914 C/T300 karbon elyaf takviyeli epoksi plastiklerin nem absorbsiyonu üzerine etkileri incelenmiştir. Vakum kaplama tekniği ile karbon elyaflı plastikler üzerine bakır-altın, bakır-nikel-altın, nikel ve altın filmleri elektroliz yöntemi ile dekoratif bakır-nikel-krom filmleri kaplanmıştır. Metal filmler ile kaplanan numuneler doygun tuz çözeltisi yöntemi ile 70 °C de, %90 bağıl nemli ortamda yaşlandırılmıslardır.

Vakum kaplama tekniği ile kaplanmış numunelerin yaslandırma deneyleri sırasında ağırlık artış değerleri alınmış, elde edilen değerler bu teknik ile kaplanan metal filmlerin, numunelerin nem absorbsiyon hızını etkilemediklerini göstermiştir. Difüzyon katsayısı, $3.4*10^{-7}$ mm^2 /sec olarak hesaplanmıstır. Yaşlandırılmış numunelerin elektronmikroskop altında incelenmeleri, çatlak oluşumlarını açığa çıkarmıştır. Bu nedenle vakum kaplama tekniği ile Fibredüx 914C/T300 karbon elyaf takviyeli epoksi plastikleri için istenilen filmin elde edilemeyeceğine karar verilmiştir. Elektroliz yöntemi ile metal filmlerin kalınlıkları artırılmıs, fakat catlaklar bu metal filmler üzerinde de gözlenmiştir.

Anahtar kelimeler : Karbon elyaf takviyeli plastik, ivmelendirilmiş yaşlandırılma, karbon elyaf takviyeli plastiklerin nem absorbsiyonu.

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NOMENCLATURE

C	moisture concentration in the material (gr/mm^3)
Ca	ambient moisture concentration in the material (gr/mm^3)
c	composite density (gr/mm^3)
D	mass diffusivity (mm^2/sec)
F	fibre density (gr/mm^3)
G	parameter defined by Equation(7)(dimensionless)
h	thickness of specimen (mm)
l	length of specimen (mm)
m	moisture content in the material (gr)
M	percent moisture content in the material
Md	weight loss percentage
n	number of specimen
Q	fractional relative humidity
R	resin density (gr/mm^3)
S	standard deviation
t	time (hr)
t_L	time defined in Figure(6) (hr)
t^*	dimensionless time defined in Figure(7)

Tg	glass transition temperature (°c)
Vo	dry resin volume (mm^3)
ΔV	volume difference (mm^3)
W	weight of the material (gr)
w	laminate width (mm)
Wd	dry weight of the material (gr)
Wf	weight of fibre in the composite (gr)
Ww	wet weight of the material (gr)

Subscripts

i	initial state
m	maximum saturation
r	resin

Addenda

CFRP	carbon fibre reinforced plastic
ILSS	interlaminar shear strength
MBB	Messerschmitt-Bolkow-Blohm Gmbh
TMA	thermomechanical analyzer

CHAPTER-1

INTRODUCTION

1.1. GENERAL

The word composite is used to describe the final material resulting from the combination of many different reinforcements and a matrix . Most common plastic matrix composites are reinforced plastics (RP) laminates, high pressure laminate and filled molding compounds.

In recent years, composite materials are widely used in structural applications, because of limiting properties of metals in engineering applications. Since some plastic composites have, for certain applications, favorable performance characteristics in comparison to metals, they have been gaining wide use in commercial, military and space applications. In comparison to current 1000 and 2000 series aircraft aluminum alloys, increase in specific strength of composite materials is by a factor of 3 and in specific modulus by a factor of 2. It also causes economic impacts in aircraft with weight savings.

The use of carbon fibre reinforced plastics in aircraft structure is increasing. The new generations of aircraft take advantage of their attractive structural properties. However, a disadvantage is their readiness to absorb moisture, with consequent degradation of those strength properties of the composite which are matrix dependent particularly at high temperatures. The degradation that these structures will see in service is linked with the level of moisture absorbed during the service life. In aircraft applications epoxy matrices are most prevalent. Special epoxies adhere well to reinforcing fibers and retain a high percentage of their mechanical properties up to $300^{o}F$. The moisture and chemical resistance of epoxies is good at room temperature.

1.2. SCOPE AND OBJECTIVE OF THE THESIS

The objective of this investigation is to determine the influence of metal coating on the moisture absorption characteristics of carbon fibre reinforced plastics.

To study the effect of metal coating on the moisture absorption of the carbon fibre reinforced plastics laminates it is necessary to precondition a structure to a moisture level similar to that which would be a present in an aircraft component during service. This conditioning process needs some speeding up, which is provided by an accelerated ageing technique. During an accelerated ageing process, the moisture can be introduced into a carbon fibre reinforced plastics structure in as short a time as practical, without damaging the composite. Ageing includes the achievement of realistic moisture contents and the superimposing of temperature excursions representative of aircraft experience. This is accomplished by increasing exposure temperature and humidity. To shorten the ageing process, raising the ageing temperature beyond a critical value is not allowed.

1.3. ORGANIZATION OF THE THESIS

This thesis consists of six chapters. Chapter 1 is an introduction to the field of composite material.

A review of previous investigations is presented in Chapter 2.

The experimental techniques are given in Chapter 3.

The experimental results are tabulated and discussed in Chapter 4.

The study is concluded in Chapter 5.

Recommendations are given in Chapter 6.

CHAPTER-2

PREVIOUS WORK

The use of carbon fibre reinforced plastics in aircraft structures continuously increases. However, their usage is limited, since they readily absorb moisture from the atmosphere in service environment.

In this study, various metal films were deposited on the CFRP specimens, to prevent the moisture diffusion into the CFRP, but such a research is not available in the literature up to now.

2.1. THE EFFECT OF MOISTURE ON THE CFRP

Carbon fibre reinforced plastics show a thermal expansion and swelling due to the changes in temperature and moisture in service environment. These two parameters cause a degradation in the mechanical properties of composite materials.

It is known that carbon fibres are not significantly affected by the presence of moisture in environment thus, swelling comes through the influences of moisture on resin matrix material.

Swelling is used to describe volumetric changes due to the moisture content alone, independent of thermal expansion. Thermodynamic arguments have shown that liquid molecules can combine with polymer molecules in the glassy state and actually become part of the glassy structure, establishing an equilibrium between the liquid and the glassy mixed phase [1] . When the polymers mix with a miscible liquid which has a lower glass transition than the polymer, liquid decrease the glass transition temperature of the polymer. In that case moisture behaves like a plasticizer agent for resin system, producing a lower value for the glass transition temperature.

Because of the effect of moisture in lowering the glass transition temperature of the resin, there is considerable interest in determining the mechanical properties of composite laminates at various temperatures in the presence of moisture . Such experimental evaluation requires a knowledge of the moisture diffusion process in order to perform moisture conditioning and to determine moisture content and distribution during elevated temperature tests.

Adamson [1] made experiments in which the thermal expansion and swelling behaviour of an epoxy resin system and two graphite / epoxy composite systems exposed to water were measured. The specimens were moisture conditioned by immersion in distilled water, using a constant temperature bath. Specimen volume was calculated from length, thickness, and width measurements accurate to 0.0002 in. Following the volumetric determination, weight change measurements were performed. Adamson [1] has found that the cured epoxy resin swells by an amount slightly less than the volume of the absorbed water. Figure 1 describes the swelling of 3501 resin as moisture is absorbed at 74°C. This figure shows the percent change in resin volume (compared with the volume of dry resin, Vo) as afunction of the volume of absorbed water calculated from the change in specimen weight. Additionally, a dashed line having a slope of one is shown in Figure 1; it represents swelling that would be expected if the volumes of the dry resin and the absorbed water were additive. All dimensions of the specimens were determined periodically while the specimens were at 74°C. The swelling curve was divided into three regions. Region 1 corresponds roughly to the region of diffusion controlled absorption. This suggests that as water is initially absorbed and diffuses into the resin, some of the water begins to occupy polymer free volume, causing no swelling, while some of the water distrupts interchain hydrogen bonds, causing swelling by hydrogen bonding with the resin. As individu water molecules are removed from the free volume by combining with the resin, they are replaced by diffusion of moisture from outside the specimen; hence, there is nearly one to one correspondence between swelling and volume of moisture absorbed in swelling region 2. Above about 6% moisture concentration, the apparent swelling efficiency drops far below in the first two swelling regions. This low efficiency reflects diffusion into the highly cross linked micro gel particles , which contain some free volume but due to their highly reacted state swell only slightly.

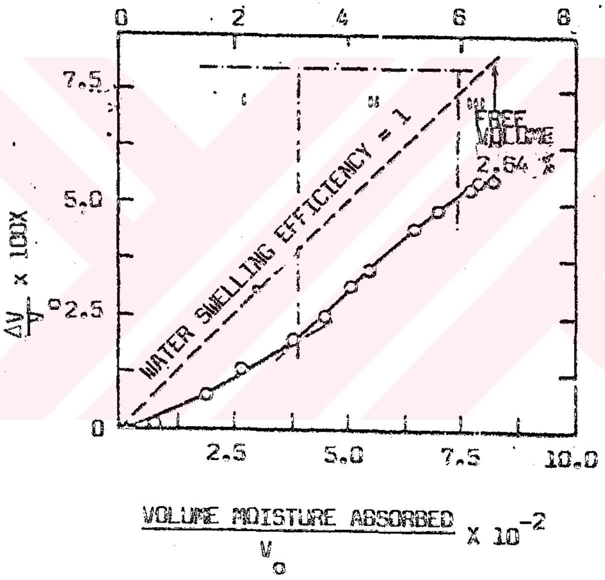

Figure 1 Swelling efficiency of Hercules 3501 resin immersed in 74 °C water [1].

McKague et al [2] made experiments to examine swelling behaviour, thermal expansion behaviour and changes in glass transition temperature of an epoxy resin material resulting from moisture absorption. Narmco 5208 epoxy resin was used for all of the experiments in the study. The dried specimens were placed into hygrothermal conditioning environments. Specimens were periodically removed from environment, weighed and dimensionally measured. A loaded-columnar thermal expansion method was developed which involved the use of Perkin-Elmer TMS-1 thermomechanical analyzer (TMA). Measurements were made with four-place-slip-ratched micrometers which were permanently mounted on indexing fixtures. After specimens reached moisture equilibrium as determined by weight and dimensional measurements, glass transition tests were conducted. For specimens, glass transition temperature was defined as that temperature coinciding with the first significant change in the rate of expansion. Weight versus time data were analyzed for overall diffusion coefficient D, using a regression program based upon a finite difference solution of Fick's law of diffusion assuming concentration independence.

The total volume change due to swelling from a dry state to a moisture equilibrium state can be calculated based upon ideal mixing law [3]. This would predict a volume increase equal to the volume of absorbed water. Thermodynamically, ideal mixing implies no effect of absorption upon the polymer. Figure 2 shows the total volume changes ΔV, that occurred due to swelling from the dry resin state to the various moisture equilibrium states.

The figure shows that the observed swelling is less than that which would be represented by ideal mixing.

McKague et al [2] concluded that moisture absorption by epoxy resin result in dimensional swelling by an amount less than that predicted by ideal mixing. In addition to swelling, this absorption causes a reduction in the glass transition temperature.

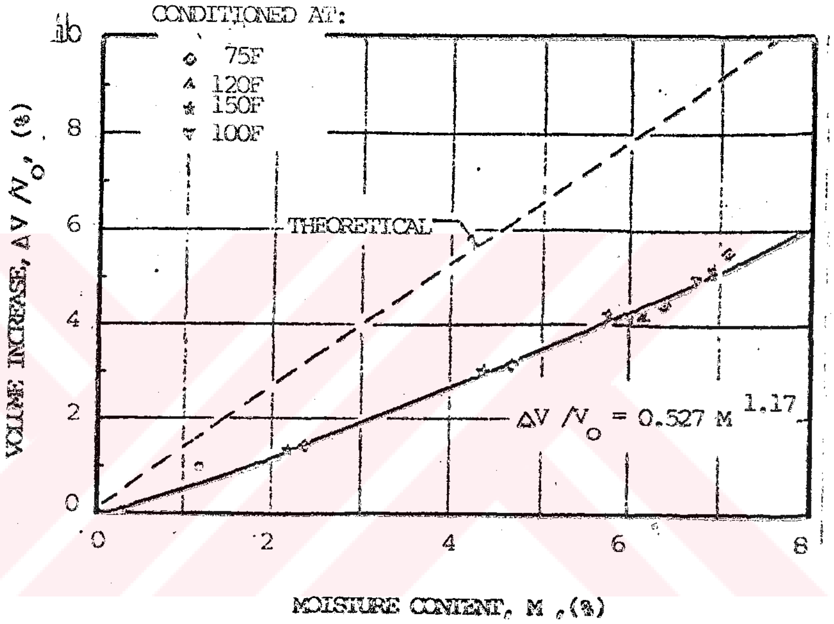

Figure 2 Volumetric swelling of neat Narmco 5208 resin due to absorbed moisture [2].

Wright [3] examined the experimental results of Ecktein [4] who obtained moisture absorption data for 70 different resin formulations. Specimens were immersed in boiling water for 180 hours and weight changes of the specimens were monitored.

The experimental results of Ecktein [4] show that water absorption causes swelling of the resin, above 1% moisture content, Figure 3 shows a linear relationship between the amount of water absorbed and the overall volume change for at least three epoxy resins. Due to the swelling of the matrix and production voids, the interlaminar shear strength of a composite decreases by about 7% for every 1% void content.

The decrease in the glass transition temperature as a function of absorbed moisture is plotted by Wright [3], as shown in Figure 4. Glass transition temperature Tg, is the temperature or narrow range of temperatures, below which an amorphous polymer is in a glassy state, and above which it is rubbery. It may be said that for each 1% water pick up there is a drop in glass transition temperature of about 20 °C. Experimental data obtained by a single

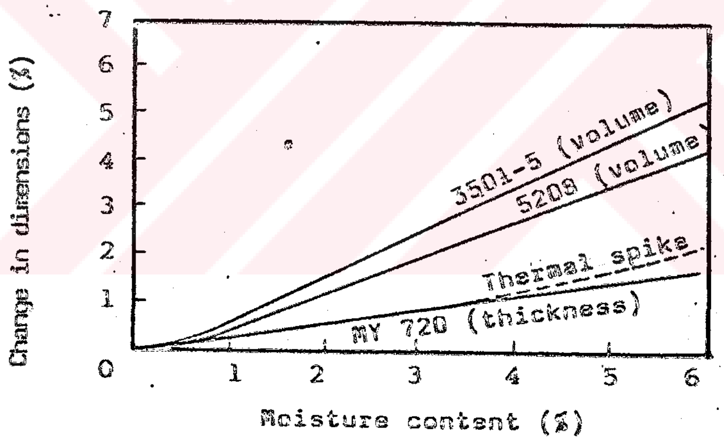

Figure 3 Swelling of epoxy resins by absorbed moisture [3]

investigator are generally in fairly good agreement with the theoretical curve for the effect of a diluent upon the glass transition temperature of a polymer derived by Kelley and Bueche [5].

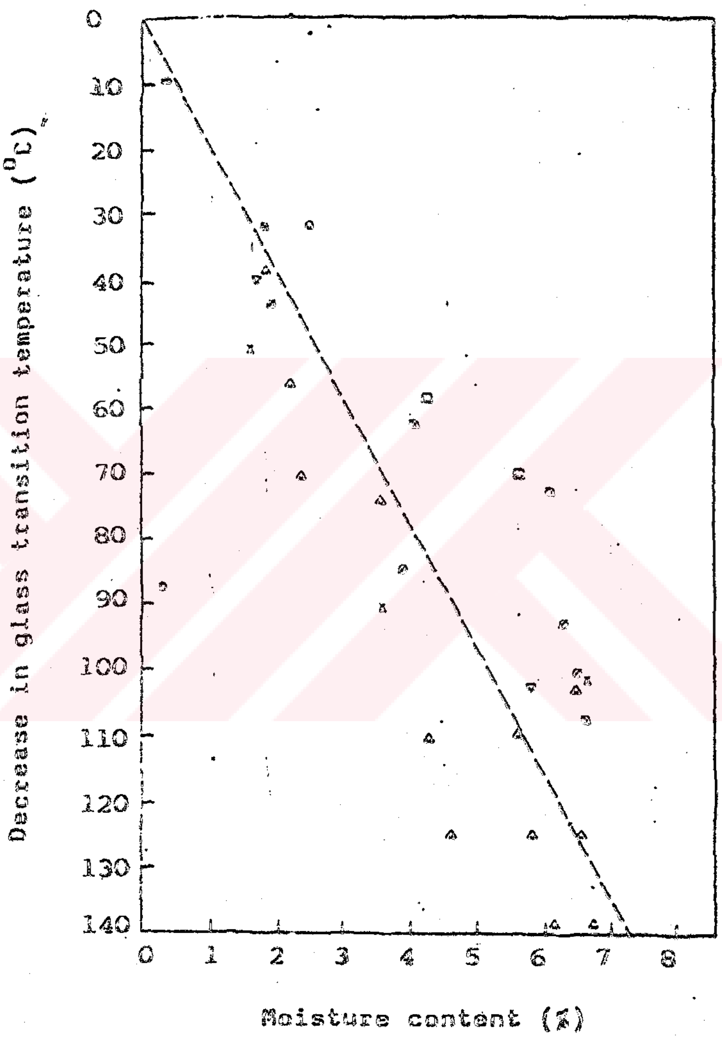

Figure 4 Decrease in Tg of epoxy resin with moisture absorption (each symbol denotes a different epoxy resin) [3].

In a service environment, the carbon fibre reinforced plastics in aircraft structure are exposed to moisture which is absorbed and desorbed by the epoxy resin matrix throughout its service life. So it is important to determine the effect that moisture will have when stress concentrations are present.

Josh [6] made a study to determine the effect of moisture on the mechanical properties of carbon fibre reinforced epoxy resin. He performed experiments with unidirectional composites which were either immersed in boiling water or aged in a hot-humid atmosphere. The specimens were aged at 70°C and 95% RH to accelerate the moisture uptake and then tested at 20°C, 70°C, 110°C and 130°C. Then the interlaminar shear strength (ILSS) of the test specimens were measured at room temperature in short beam bending. ILSS is the maximum shear stress existing between layers of laminated material. Josh [6] reported that the interlaminar shear strength of the composite increased when a small amount of moisture was absorbed. This is shown in Figure 5 and 6. Typically, 0.2 % weight increase in moisture from the dry state increased the interlaminar shear strength value by about 10 %. On further absorption of moisture, the interlaminar shear strength decreased and the specimens become more ductile; the failed specimens

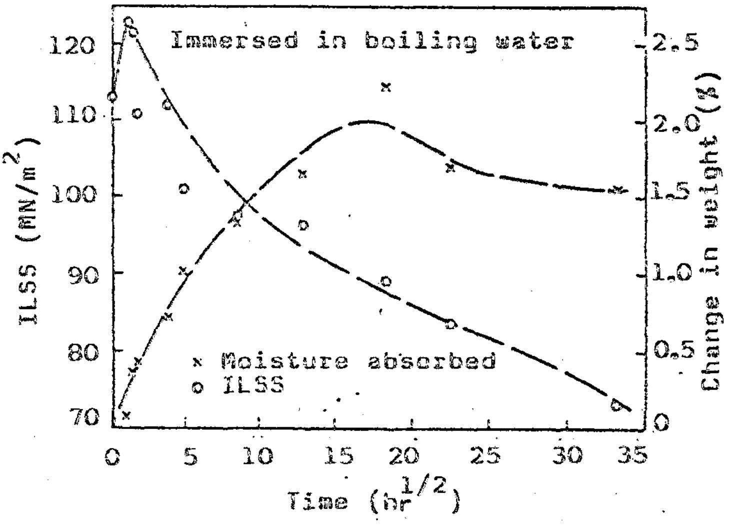

Figure 5 Variation of ILSS and moisture absorption with exposure time for unidirectional carbon fibre epoxy resin composite[6].

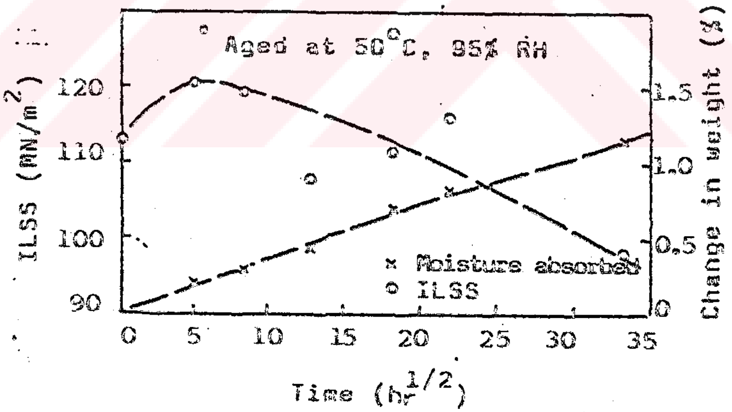

Figure 6 Variation of ILSS and moisture absorption with exposure time for a unidirectional carbon fibre epoxy resin composite[6].

showed a general shear deformation throughout the specimen thickness and some permanent deformation was observed. The values of interlaminar shear strength for both the boiled and aged samples were similar, for the same amount of moisture absorbed.

Bishop [7] determined the effect of absorbed moisture on the notched tensile strength of multidirectional carbon fibre / epoxy laminates with two different play stacking sequences. The shear strength parallel to the fibres affect notch sensitivity. The shear strength depends on the fibre/matrix bond strength which is determined by the level of surface treatment. Therefore two types of test laminates were prepared to be used in the experiments. The first type of laminates were made by using high strength carbon fibre with the standard commercial surface treatment. The second type was prepared by using high strength carbon fibres from a different batch with reduced levels of fibre surface treatment of the standard commercial level. The test specimens from the first set were placed at room temperature in constant humidity environment having approximately 0%, 33%, 65% and 95% RH. Specimens from the second set were stored at 21 °C and 65% RH. All specimens were left for several months until new equilibrium values of moisture content were obtained. Plain and notched specimens were loaded in tension parallel to the 0° direction until failure occurred.

The tensile strength of plain specimens with the standard commercial level of fibre surface treatment was found to be independent of moisture content. The tensile strength of plain specimens from the second set with the reduced level of fibre surface treatment was found to be independent of surface treatment. For different moisture contents no significant differences were observed in the cracking of notched specimens with the standard commercial level of the fibre surface treatment.

The effect of postcuring and thermal spike on the behaviour of carbon fibre reinforced plastics were examined by Etiz [8]. The specimen used in the experiments was 914C/T300 unidirectional carbon fibre reinforced plastics. Specimens were aged at 70^{o}C and 75 % RH. To study the effect of postcuring on interlaminar shear strength, wet samples and dry samples were postcured. The short beam three point bend test was used to measure the interlaminar shear strength (ILSS). A prismatic specimen was subjected to a three point bend loading until fracture occured. For both dried and aged specimens, interlaminar shear strength increased slightly as postcure temperature and time increased. The results obtained at 120^{o}C showed that there is a reduction of ILSS by 30% for the dried and 45% for the aged specimens compared to the values obtained at ambient temperature.

ILSS of dried and aged specimens were tested at room temperature and 120 °C for comparison with the thermal spiked (sudden, large temperature changes) specimens. Aged specimens were thermal spiked at three different temperatures, namely 110 °C, 120 °C and 130 °C. The experimental results showed that ILSS decreases with increasing thermal spike temperature. Thermal spiking also causes permanent changes in the subsequent moisture absorption behaviour of the composite. Again, absorbed moisture decreases ILSS of the thermal spiked specimens.

2.2. THEORETICAL WORK ON MOISTURE ABSORPTION OF CFRP

In most engineering applications, moisture diffusion is through a large surface area with very few edges. As a result, diffusion through the thickness is of primary interest. For such a case, thin composite specimens are utilized in order to approximate a one-dimensional diffusion process.

It has been previously shown that [9] moisture diffusion in laminated composites can be predicted by Fick's second law. For one-dimensional diffusion through the thickness of an infinite plate of constant thickness, h, the diffusion process is described by the relationship:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X}\left[Dx \quad \frac{\partial C}{\partial X} \right] \qquad (1)$$

where C is the moisture concentration, Dx is the effective diffusivity through the thickness, t denotes time, and x is the thickness coordinate.

The initial and boundary conditions are ,

$C=C_i \qquad 0 < x < h \qquad t < 0$ (2)

$C=C_a \qquad x = 0 \; ; \; x = h \qquad t > 0$ (3)

Initially (time $t<0$) the moisture concentration Ci inside the plate is uniform. The plate is suddenly exposed to a moist environment in which moisture concentration Ca, is constant. Effective diffusivity is a function of temperature, moisture concentration and diffusion path x. The material temperature is assumed to be uniform, and is taken as an ambient temperature. Then equation (1) is reduced to the following form,

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial t^2} \tag{4}$$

the solution of this equation is given by Jost 10 ,

$$\frac{C-C_i}{C_m-C_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j+1)} \operatorname{Sin} \frac{(2j+1)\pi X}{h} \exp -\left[\frac{(2j+1)^2 \pi^2 D_x t}{h^2} \right] \tag{5}$$

where, Cm is the maximum moisture concentration at the surface of the material.

In order to obtain the total weight of the moisture, Equation 5 is integrated over the plate thickness,

$$m = \int_0^h C \, dx \qquad (6)$$

the result of this integration yields,

$$G = \frac{m - m_i}{m_m - m_i} = 1 - \frac{8}{\pi^2} \sum_{j=1}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 (D_x \, t / h^2)\right]}{(2j+1)^2} \qquad (7)$$

where

m_i : the initial weight of the moisture in the composite

m_m : the weight of the moisture in the composite when the material is fully saturated, in equilibrium with its environment.

G : a time dependent parameter.

The objective is to determine the percent moisture content M as a function of time t, [9]

$$M(t) = \frac{\text{Weight of moist material} - \text{Weight of dry material}}{\text{Weight of dry material}} * 100 \qquad (8)$$

The percent moisture content M can be written in terms of initial moisture content Mi, maximum moisture content Mm and G.

$$M = G\ (Mm-Mi) + Mi \tag{9}$$

Equation 7 can be approximated by the following expression, it is seen in Figure 7,

$$G = 1 - \exp\left[-7.3\left[\frac{Dx\ t}{h^2}\right]^{0.75}\right] \tag{10}$$

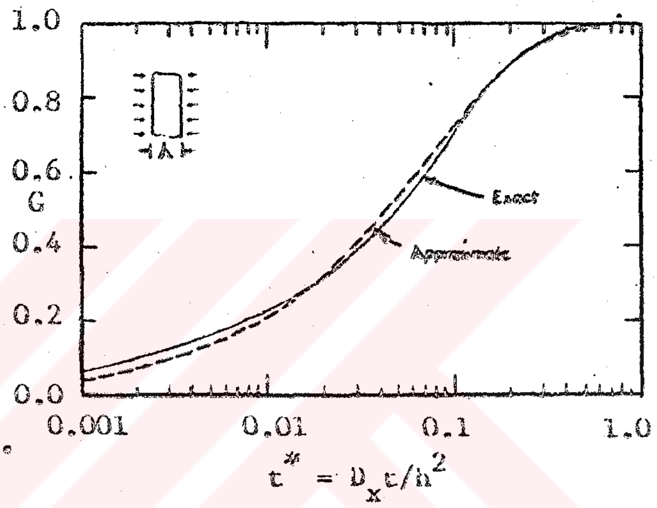

Figure 7 The variation of the parameter G with the dimensionless time $t^* = (Dx * t)/h^2$. Exact : Equation (7); approximate: Equation (10), [9]

In Figure 8, percent weight gain versus square root of time plot is given. Initially, the absorption curve is linear with the square root of time. This linearity suggests that absorption is predominantly diffusion controlled and diffusion rate is constant.

For costant temperature environment [9], the diffusion coefficient may be calculated from equation (11),

$$D = \pi \frac{h^2}{16\ Mm^2}\left[\frac{M_2 - M_1}{\sqrt{t_2}-\sqrt{t_1}}\right]^2 \qquad (11)$$

where M_1 and M_2 are the percent moisture content taken from the linear portion of the M versus $\sqrt{t}$ plot.

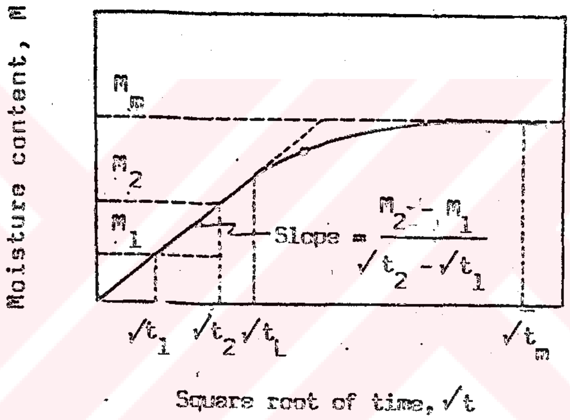

Figure 8 Illustration of the change of moisture content with the square root of time. For $\sqrt{t} < \sqrt{t_L}$ the slope is constant[9].

If the moisture entering the specimen through the edges can be neglected, then Dx becomes equal to D. Including edge effects, for homogeneous material Dx is

$$Dx = D \left[1 + \frac{h}{w} + \frac{h}{l}\right]^{-2} \tag{12}$$

where

w : laminate width

l : laminate length

h : thickness

To test analytical results, a series of experiments using $\Pi/4$ and unidirectional Graphite T-300 Fiberite 1034 composites were performed by Shen and Springer[9]. The maximum moisture content Mm and effective diffusivity Dx were determined experimentally.

The test specimens were prepared in the form a thin plate, so that the moisture enters predominantly through the large surface. After drying of the specimens, they were placed in a constant temperature and humidity environment, and their weights were recorded as a function of time. The moisture content was plotted versus square root of ageing time. The experimental results give the similar curve which is shown in Figure 8. Initially all curves are straight lines, the slope being proportional to the diffusivity of the composite. After a long period of time the curves approach asymptotically the maximum moisture content Mm.

In the past, most attempts to accelerate ageing have used only a single combination of elevated temperature and humidity and these have generally resulted in unrepresentative distributions of moisture through the thickness of a composite.

Collings and Copley [11] developed a technique representing the final condition of a naturally aged composite. By using this technique moisture distribution can be controlled to produce a through-thickness moisture profile that is representative of naturally aged specimens. This technique involves the removing slices of a finite thickness throughout the thickness of a laminate and measuring each slice for moisture content by weighing before and after drying, to give a distribution of moisture at discrete points. The percentage uptake of water by weighing before and after drying, to give a distribution of moisture at discrete points. The percentage uptake of water by weight, M, was found for each slice from

$$M = \frac{(Ww - Wd)}{Wd} \times 100 \qquad (13)$$

where

Ww : wet weights of the laminate

Wd : dry weights of the laminate.

To plot the moisture distribution, it is assumed that the moisture level at the center of each slice is the average value of the slice. Results of some test carried out on a carbon fiber / epoxy resin system are given in Figure 9. Collings and Copley [11] suggested that if the diffusion characteristics of composite materials are available it is possible to predict the through-thickness moisture diffusion, by means of a finite difference method using a Fickian one dimensional diffusion model.

Equation 9 was written in terms of a moisture level M, which is defined as the moisture per unit volume of the laminate as a percentage of the dry weight,

$$\frac{\partial M}{\partial t} = D \frac{\partial^2 M}{\partial X^2} \qquad (14)$$

The equation to be modelled, the boundary conditions are,

$$M = M_{\text{initial}} \qquad 0 < X < h \qquad t=0 \qquad (15)$$

$$M = M_{\text{boundary}} \qquad X = 0\ ,\ X = h \qquad t>0 \qquad (16)$$

The numerical solution of Equation 12 by using Finite difference method, gives the moisture distribution through the thickness of laminates. The through- thickness distribution predicted by using a finite difference method to solve Fick's second law of diffusion is given in Figure 9. In this figure, it can be seen that a quadratic expression gives a good fit to the experimental data(taken from three specimens).

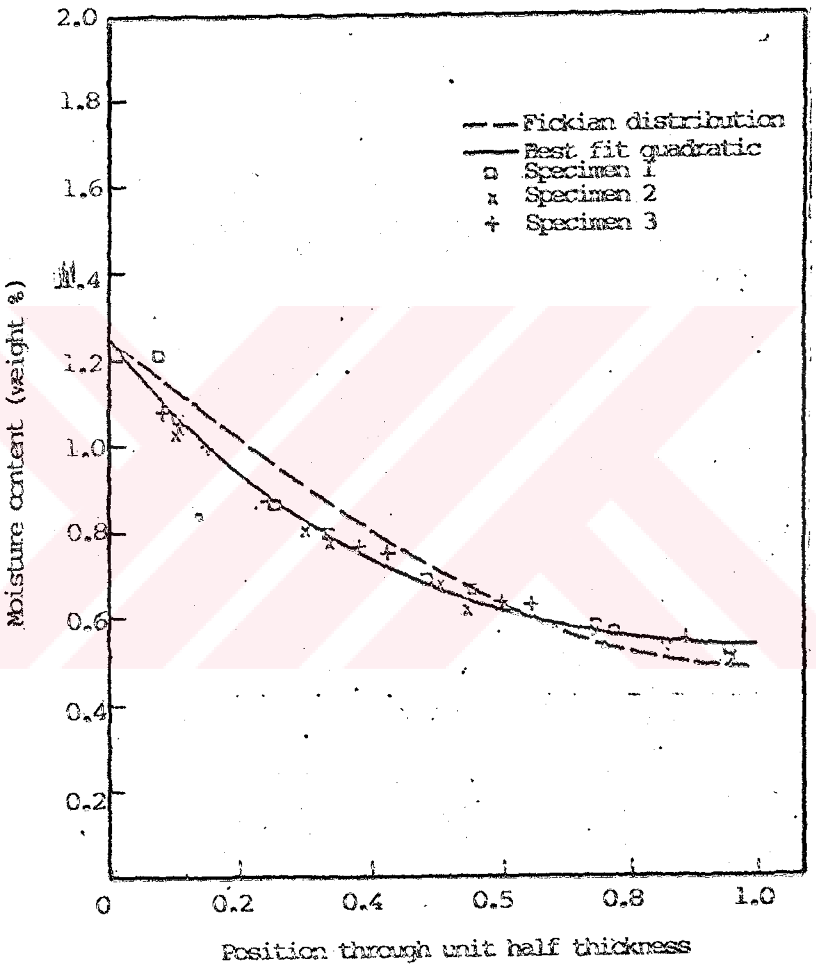

Figure 9 The distribution of moisture through the thickness of carbon fibre/epoxy laminate (XAS/914) after conditioning at 60 °C and 75% for 15 days[11]

Figure 10 compares the moisture uptake against root time for both experiment and prediction using Fick's laws. Although the fit of theory with experiment is not perfect, prediction of moisture diffusion using Fickian theory is adequate for most practical purposes, provided that the resin exhibits approximate Fickian absorption.

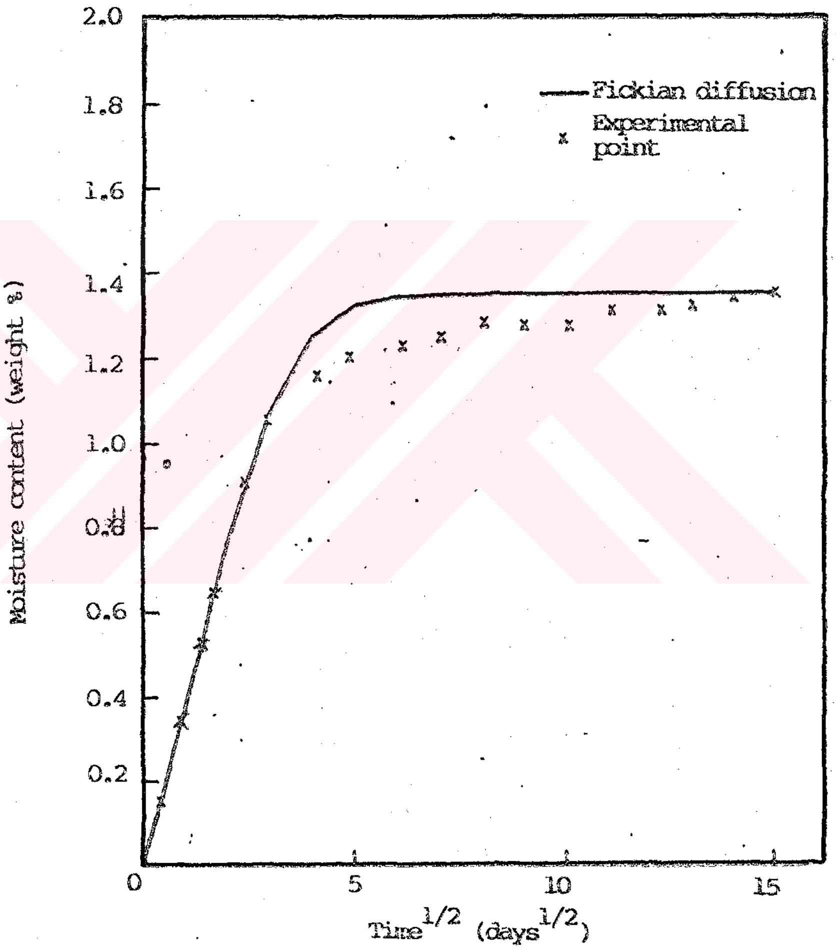

Figure 10 Moisture uptake of a 2mm thick carbon fibre/ epoxy laminate containing 60% fibres by volume conditioned at 60 °C and 75% RH [11].

Most of the previous investigations had been concerned with moisture absorption and desorption of graphite epoxy composites exposed to humid air. Loos and Springer [12] was concerned with the moisture absorption properties of graphite epoxy composites submerged in five different liquids, distilled water, a saturated salt water solution, No.2 diesel fuel, jet A fuel and aviation oil. In the study, moisture content as a function of time, temperature and relative humidity of graphite epoxy composites exposed to humid air were also examined. During tests, the specimens were immersed in liquids, the temperature was kept constant in baths and to humidify the specimens, they were mounted above the surfaces of a pool of water. Their weight gain was monitored by weighing them periodically. For distilled water and salt water the diffusivities D were calculated according to the method outlined by Shen and Springer [9]. For specimens exposed to humid air, the values of the maximum moisture content Mm and the diffusivity D were evaluated from percent moisture content versus square root of time plots according to the procedure in reference [9].

The following general conclusions were obtained by Loos and Springer [12] for graphite epoxy composites.

1) Material immersed in liquid at temperatures 300° to 322° K.

a) The amount of moisture absorbed by materials immersed in No.2 diesel fuel, jet a fuel and aviation oil depends on the immersion time but it is insensitive to the temperature.

b)The amount of moisture absorbed by materials immersed in saturated salt water depends both on the immersion time and on temperature.

2) Material exposed to humid air in the temperature range 322^{o} to 366^{o}K.

a)The maximum moisture content is related to the relative humidity by the expression $Mm=aQ^{b}$, where a and b are constants. The values of these constants can be obtained by fitting a line through the data points. The maximum moisture content as a function of relative humidity is seen in Figure 11. The exponent b, is unity for this material. The maximum moisture content depend on the relative humidity but is insensitive to temperature.

b)The maximum moisture content of a composite can be estimated from the maximum moisture content of the resin, by assuming that the fibers do not absorb any moisture, they are related by the expression

$$Mm = (Mm)r\ (Wr) \tag{17}$$

where

$(M_m)_r$: maximum moisture content of resin

W_r : weight fraction of resin

c) The diffusivity of a composite can be estimated from the diffusivity of the resin.

d) The diffusivity follows the Arrhenius plot up to 390 $^{\circ}$K.

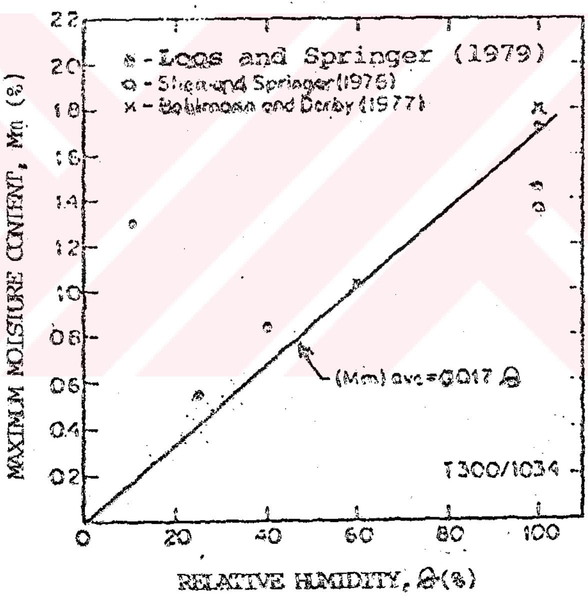

Figure 11 Maximum moisture content as a function of relative humidity for Fiberite T300/1034 composites. Solid line is fit to data[12].

CHAPTER-3

EXPERIMENTAL TECHNIQUES

3.1. Material Specification

In the present study, a series of tests were performed using unidirectional carbon fiber reinforced plastics. Epoxy resin was used in the matrices. The composite materials are manufactured by Messerschmitt-Bolkow-Blohm GmbH (MBB), according to MBB production standard FA 80-F-31-2930, and its commercial name is GEIGY fibredux 914C/ T300.

In this study, to prevent the moisture diffusion in to the unidirectional CFRP, metal films are deposited on the specimen surfaces. Vacuum evaporation and electroplating techniques were used to deposit metal films on the specimens surfaces.

The test specimens coated with copper-gold, copper-nickel-gold, nickel and gold films using vacuum evaporation technique were in the form of thin plate having the dimensions of 2mm thickness, 20mm length and 10mm width.

Before vacuum coating all the test specimens were cleaned and dried.

The test specimens used in the electroplating technique, had dimensions of 2mm thickness, 75mm length and 10mm width. Specimens were cleaned, dried and firstly coated with copper using vacuum evaporation techniques. After the conductive surface was obtained, decorative copper-nickel-chromium combinations were deposited on the surface by using electroplating technique.

Then the specimens were aged in a constant temperature and constant moisture environment and their weights were monitored as a function of time.

3.2. Experimental Methods

3.2.1. Pretreatment of test specimens

a) Determination of resin content

To determine the resin content, ANSI / ASTM D 3171-76 [17] standard which covers the matrix digestion method was used. This method consists of dissolving the resin portion of a weighed composite specimen in a hot digestion medium. Concentrated nitric acid solution was used as the hot digestion medium in the selected procedure. The residue was filtered, washed, dried and weighed. The weight percent of fibre was converted to a volume percent, the calculations are given in Appendix-B.

b) Cleaning of the test specimens

To remove any organic and inorganic contaminants from the specimen surface, trichloroethylene was used since it evaporates easily. To prevent the damage of CFRP specimens, the specimens were kept in trichloroethylene for a very short period of time and dried using an air blower.

c) Drying of the test specimens

CFRP specimens contain some residual moisture after the curing process, this moisture content rises during storage and handling. Before the ageing process, to establish a zero moisture content datum, all of the specimens were dried by following the MBB standards [18], as explained below:

In the drying process, to prevent the laminate damage because of decrease in the glass transition temperature, specimens were dried in three steps. Drying of the specimens was carried out in a drying oven (NUVE EN 500).

Firstly, the specimens were dried at 70^{o} C, with periodical weighing, until 0.5 % weight change was reached. Then the temperature of the oven was increased to 90^{o} C. The specimens were kept at this temperature with periodical weighing, when the 0.03 % weight change was reached, the oven temperature was increased to 110^{o}C. They were kept at this temperature until no more weight change was observed. An analysis balance used in the weight determination gives an accuracy of 0.001 of the specimen weight.

During the periodical weighing, the specimens were taken from the drying oven and cooled to ambient temperature in a dessicator containing silica gel as dessicant.

3.2.2. Vacuum Coating of the Specimens

The vacuum coating unit of Nano Thin Films Ltd., Model Microprep 300 S was used to deposit metal (copper-gold, coppe-nickel-gold, gold and nickel) films.

During the coatings, the deposition rate (1µm/min) the pressure inside the vacuum chamber (10^{-5} torr) and other deposition conditions such as the distance of the substrates from the source (12 cm), and the coating time (5 min for one surface) were kept constant for all specimens.

A filament basket was used for vacuum evaporation of metals. The filament current was increased slowly to ensure melting of evaporants before evaporation took place. The vacuum, at the beginning of coating was about $4x10^{-6}$ torr, and it remained almost constant during evaporation around 10^{-5} torr with small fluctuations.

The diagram of the evaporation apparatus is shown in Figure 12.

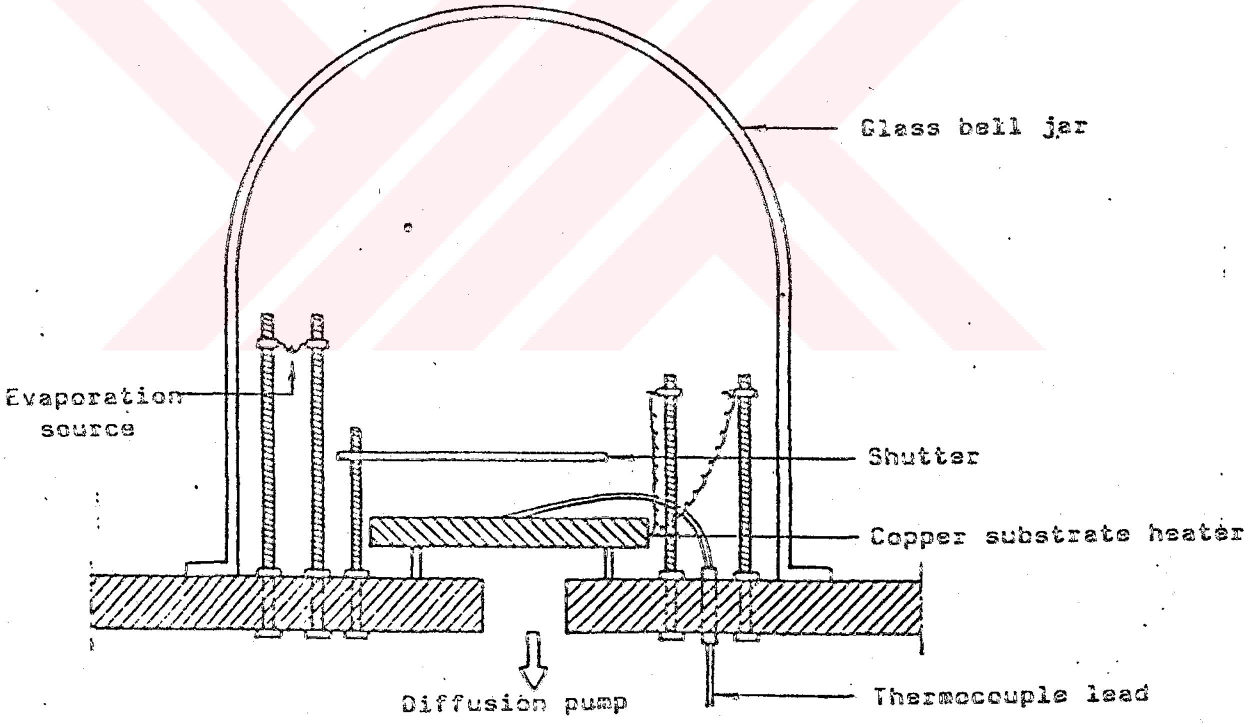

Figure 12 Diagram of the evaporation apparatus

3.2.3 Ageing of Specimens

To study the effect of moisture on the carbon fibre reinforced plastics laminates it is necessary to precondition it to a moisture level similar to that which would be present in an aircraft component. This conditioning needs some speeding up if it is to be of practical use. Then accelerated ageing process is required by which moisture can be introduced into a carbon fibre reinforced plastics structure in as short a time as practical, without damaging the composite or degrading the resin in a manner that is unrepresentative of natural ageing.

Two alternative methods are available for ageing. Ageing of specimens can be carried out in an environmental cabinet with regulation of temperature and relative humidity. The other method is to use saturated salt solutions held in sealable glass chambers which are kept at the required temperatures. Racks are used to hold the specimens in the humidified air space above the solution. The environmental cabinets are not easily obtainable, because of their high prices. So, in the present study saturated salt solution method was used. Since the saturated sodium chloride solution is less sensitive to the temperature changes than other salt solutions, it was selected in this study.

To shorten the ageing process, raising the ageing temperature beyond a critical value is not allowed. The ageing temperature over 70°C can lead to a so called Fickian anomally resulting in much higher saturation levels due to irreversible damage, microcracking in the laminate [17].

In the present study the experimental procedure was as follows:

The saturated salt solution at 70°C was prepared, and placed in a dessicator. Thirty specimens were placed on racks which hold the samples in the humidified air above the solution. It was placed in an oven (NUVE EN500), this is shown in Figure 13. Since the saturation moisture content of CFRP is affected by relative humidity and temperature, accurate control of the conditioning parameters was made during ageing periods. The accuracy of oven thermometer was controlled by additional thermometer immersed in the oven atmosphere. To check the relative humidity of ageing atmosphere, electro-hygrometer of Laboratory Line Instrument Incorporation was used periodically. The relative humidity of ageing atmosphere was kept at 90%.

When the specimens were removed from the dessicator for weighing, they were cooled to room temperature in another dessicator, which was at room temperature and had the same relative humidity as the ageing atmosphere. The recommended cooling time is 5 minutes for CFRP specimens with 2mm thickness [17]. Since the weighing procedure were carried out in uncontrolled humidity environment, the time required for weighing was tried to be kept to an absolute minimum. An analysis balance (Model 2842 Sartorius Balance) used to determine the weight change of specimen gives an accuracy of 0.0001 of the specimen weight.

Figure 13 Environmental chamber used in the ageing.

3.2.4. Examination of the surfaces

Micro examination of the specimen surfaces was done by using a scanning electron microscope (SEM, Cambridge Stereoscan 54-10). Scanning electron micrographs of the specimens were taken, they are given in Chapter 4.

After the examination of micrographs, the electroplating techniques were applied to the other specimens.

3.2.5. Electroplating

The specimens were prepared in 2 mm thickness, 70 mm length and 20 mm width. Firstly, the specimens were cleaned and were dried as it is given in Section 3.2.1.c. Specimens used in the experiments are nonconductive materials, to deposit metal films using electroplating technique, the conductive surface must be obtained. Vacuum evaporation techniques were applied to cover conductive surfaces with copper.

Electroplating system consisted of a power supply, (6261 B DC Power Supply, 0-20 volt, 0-50 amp. with coarse and fine adjustment knobs), glass beaker as a plating bath and two electrodes. The system is shown in Figure 13.

Copper was plated from acid bath. Acid bath contains copper sulfate, sulfuric acid and hydrochloric acid, the composition of bath is given in Table 1. Bath was kept in an oven which is at 20 °C, until it reaches a thermal equilibrium with an oven atmosphere, then copper was plated

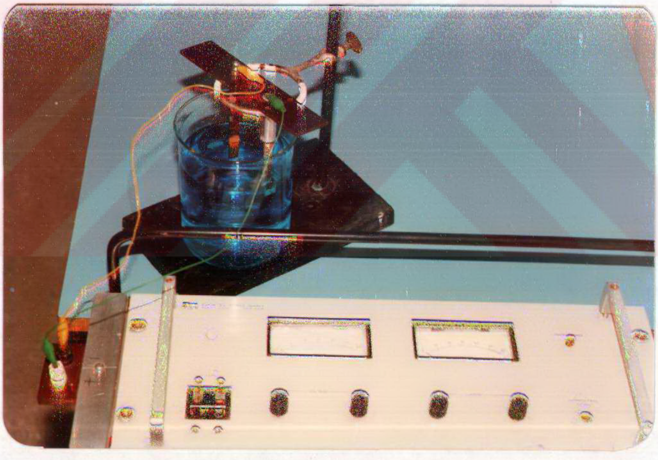

Figure 14 Electroplating system used in the experiments.

at room temperature (18-20 ^{o}C). The copper plating of one specimen took one hour and the temperature of bath was around 20 ^{o}C. The current density was kept at 0.01 amp/cm^{2} with the adjustment of voltage . Depending on the experimental studies current density is kept at a minimum value. Current density was tried to be kept at minimum value, because increasing in the current density causes an increase in the grain size.

Watts bath was used to plate nickel on the copper surface. It contains nickel sulfate, nickel chloride and boric acid. Its composition is also given in Table 1. nickel plating of the specimen took 30 minutes, in this time interval, the temperature of bath was at 20 ^{o}C and current density was kept at 0.08 amp/cm^{2} . Decorative chromium plating bath used for chromium plating, which contains chromic acid and sulfate, the weight ratio of chromic acid to sulfate is 100:1 and plating took 30 minutes.

For all types of plating, lead was selected as the anode, because it is insoluble in these solutions. The pH of the bath was measured with Universal Paper Indicator.

Table-1 OPERATING CONDITIONS OF ELECTROPLATING SYSTEM

BATH TYPE	BATH COMPOSITION		OPERATING CONDITIONS				
			Temperature °C	Curent density amp/cm^2	Voltage	P_H	Anodes
ACID BATH	$CuSO_4.5H_2O$ H_2SO_4 HCl	60g/lt 80g/lt 30mg/lt	20	0,01	2,1-2,2	3	lead
WATTS BATH	$NiSO_4.6H_2O$ $NiCl_2.6H_2O$ H_3BO_3	330g/lt 45g/lt 38g/lt	20	0,06	5	3,4	lead
CHRONIUM BATH	Cr_2O_3 SO_4^{--}	250g/lt 2,5g/lt	20	0,06	4	3,4	lead

CHAPTER-4

RESULTS AND DISCUSSION

In the present study hot-wet ageing data were collected for carbon fibre reinforced plastics coated with metal films. The experimental results are tabulated in appendix A, and related graphics are given in this Chapter.

Firstly, the fibre volume content was calculated by using Equations 1-B and 2-B in Appendix B. The calculated percent fibre content is 67%.

To establish zero moisture content, the specimens were dried before the ageing. Weight loss percentage of the test specimens are given in Table A.1. Weight loss percentages were calculated by using the following equation,

$$Md = \frac{Wd - Wi}{Wi} * 100 \qquad (5.1)$$

where

Md : weight loss percentage

Wd : weight of dried material

Wi : initial weight of material

To minimize the amount of data and to derive specific information, the mean value of weight loss percentage of dried specimens were calculated by Equation 1-C in Appendix C. To characterize the variation in the original data, standard deviations were calculated for weight loss percentage of the dried specimens by equation 2-C. The mean values and standard deviations of the drying data were tabulated in Table C.1.

Mean value of percent weight loss of specimens during drying are plotted , as a function of square root of time in Figure 15. The temperature change during drying is also shown in Figure 15. It is seen from the figure that as the drying temperature increases, rate of desorption increases.

In the first set of experiments, the specimens were coated first with copper and then with gold using the vacuum evaporation technique. At the beginning of ageing, the zero moisture content is required, vacuum evaporation technique helps to attain this zero moisture content.

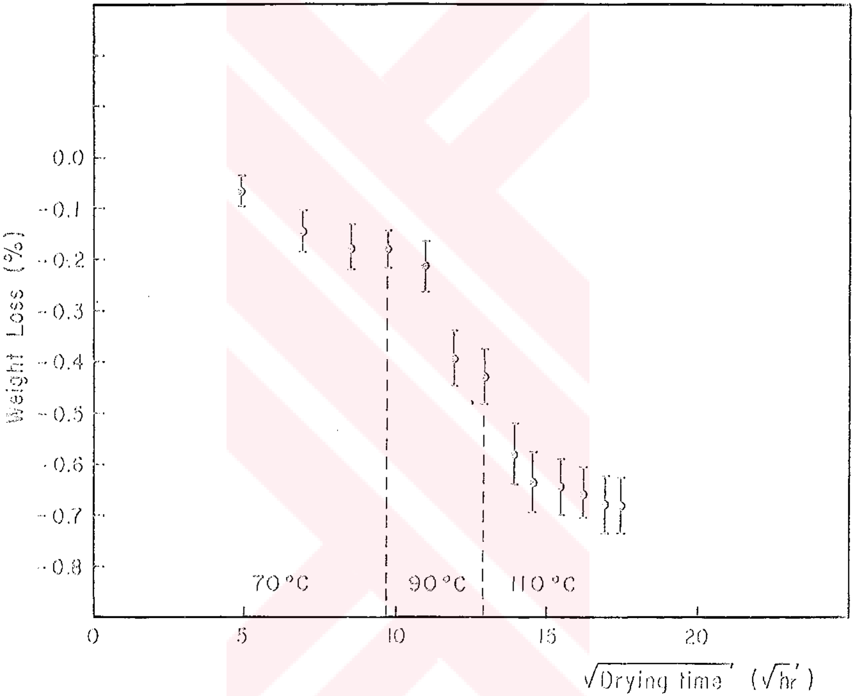

Figure 15 Desorption of Fibredux 914C/T300 Unidirectional Composite

Also, vacuum evaporation does not require a conductive surface which is essential for other coating techniques. Copper gold films were deposited on the dried specimens using vacuum evaporation technique. Copper provides a durable and ductile film but it is subject to rapid tarnishing and staining when exposed to the atmosphere. Gold film was deposited on top of the copper film to prevent the oxidation of copper film.

The specimens coated with copper gold films by using vacuum coating techniques were aged at 70°C and 90% RH. Percent moisture gain of aged specimens as a function of time are tabulated in Table A.2. Percent moisture contents were calculated from weight data monitored during ageing using Equation 8. The mean value of percent moisture content of aged specimens were calculated by Equation 1-C, standard deviations of the data were calculated by using Equation 2-C. The mean value and standard deviation of ageing weight data were tabulated in Table C.1. Figure 16 shows the mean value of percent moisture content versus square root of time for the aged specimens. Up to about 1.4% moisture content the absorption curve is linear with the square root of time. This linearity suggests that absorption is predominantly diffusion controlled [1]. Above 1.4% moisture content, the specimen begins to be filled with moisture and the absorption rate begins to decrease. Finally, equilibrium moisture content is approached, although the rate of approach is extremely slow. These observations suggests that the saturation is approached as asymtotically . The diffusion coefficient D, was calculated from Equation 11, the second part of the equation $((M_2 - M_1)/(\sqrt{t_2} - \sqrt{t_1}))$ is equal to the slope of the linear portion of percent moisture content versus square root of time plot, Figure 16. This slope is calculated by fitting the best line that passes through the mean value of percent moisture content, and the slope is also calculated for the upper and lower limits of the mean value of percent moisture contents, in order to see the deviation in the diffusion coefficient. The moisture diffusion into the specimen through the edges is neglected and the diffusion coefficient through the thickness of the specimen Dx, become to equal to the overall diffusion coefficient D. The diffusion coefficient D, was calculated to be $3.413*10^{-7}$ mm^2/sec for the mean value of percent moisture contents, $3.761*10^{-7}$ mm^2/sec for the upper value of percent moisture contents, $3.044*10^{-7}$ mm^2/sec for the lower values. The percent saturation moisture content is 1.9 ∓ 0.1 % for the specimens coated with copper and gold using vacuum evaporation technique , aged at 70 °C and 90% RH.

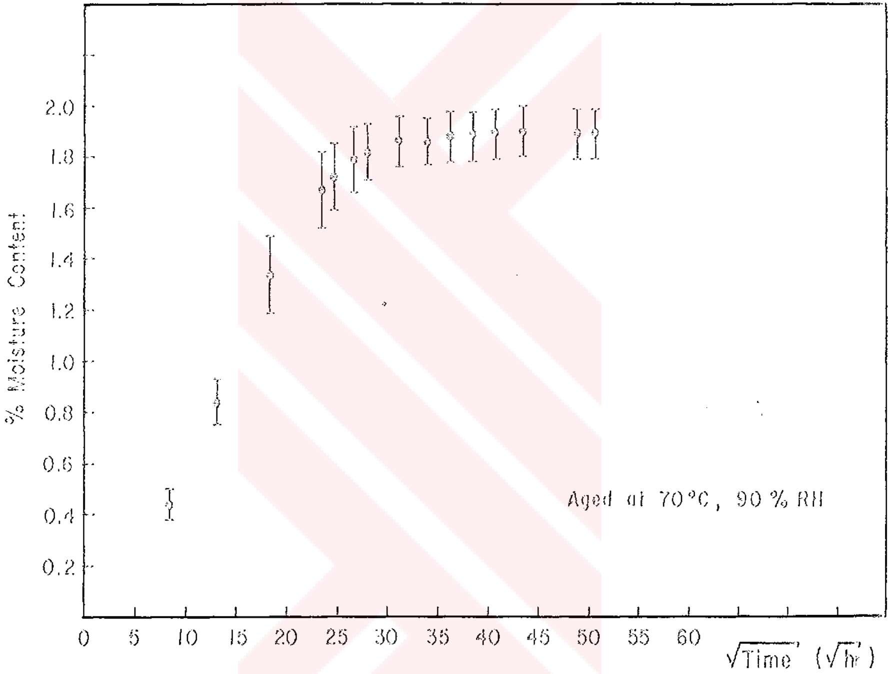

Figure 1.6 Moisture Absorption of Fibredux 914 C / T 300 Unidirectional Composite as a Function of Exposure Time

Etiz [8] used the same composite material (GEIGY fibredux 914 / T300) as in this study. He carried out experiments with uncoated specimens aged at $70^{o}C$ and 75% RH. He found the maximum moisture content Mm, to be 1.5% and diffusion coefficient D, to be $3.5*10^{-7}$ mm^{2}/sec.

The results obtained in the present study were compared with the results obtained by Etiz, and it is seen that the expected decrease in the saturation moisture content has not been obtained. Saturation moisture content is affected by the value of relative humidity (Figure 11) and as relative humidity increases, saturation moisture content also increases. If the specimens used in the present study were uncoated, then the higher value of percent saturation moisture content compared to that of Etiz [8] could be explained by the higher relative humidity used in our experiments. These results show that the copper-gold films deposited with vacuum evaporation technique had no effect on moisture absorption rate.

In order to understand the reason for these results, the specimens were examined under the scanning electron microscope. Micrographs of the aged specimens coated with copper gold films are shown in Figure 17. Each micrograph show a section of the specimen surface at different

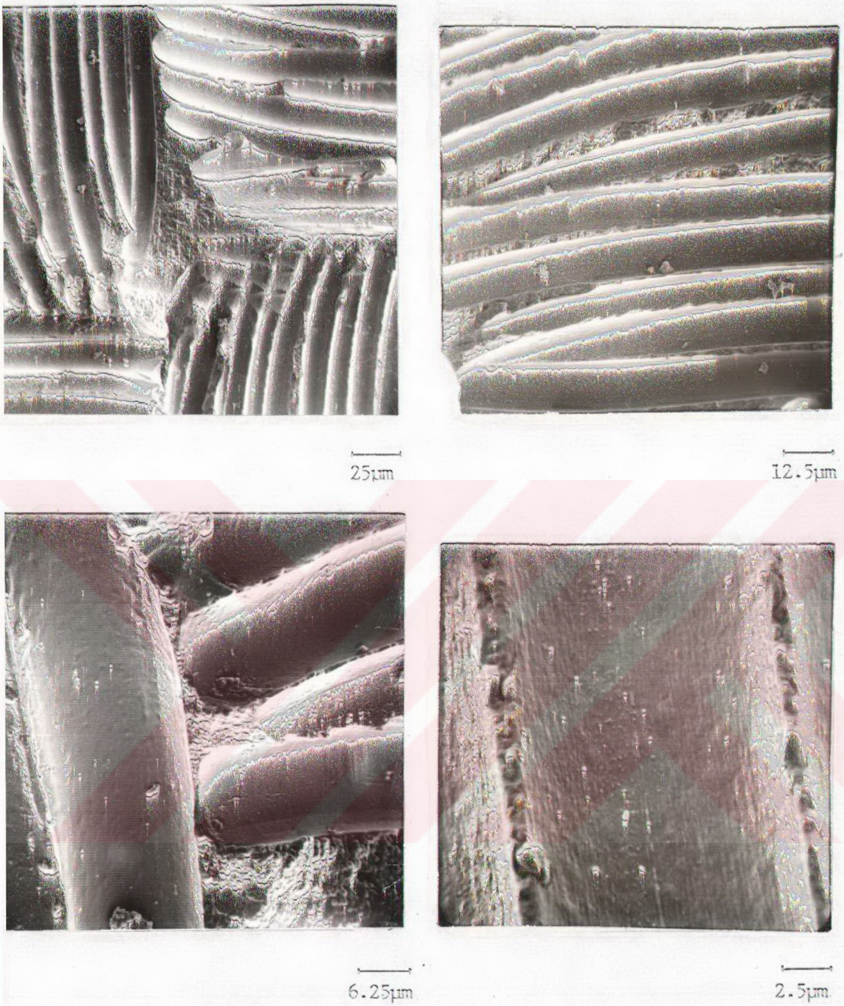

Figure 17 Micrographs of the specimens coated with copper-gold film using vacuum evaporation technique.

magnifications. The magnifications are indicated under each micrograph. During production, the CFRP is pressed leaving woven structure impression on the surface. This structure is seen in the micrographs and is not related with the internal structure of CFRP which has unidirectional fibers. Careful examination of micrographs indicate crack formations on the deeper parts of the specimen surface.

During ageing, specimens were removed from the environmental chamber (at 70° C), before weighing they were cooled to room temperature. This temperature change causes dimensional changes in the metal film. In the second set of experiments, to improve copper-gold coating, nickel was used as an intermediate layer, because the thermal expansion coefficient of nickel is between that of gold and copper. To observe the responses of gold and nickel films, one specimen is plated with gold, another one with nickel. In this set, metal films were deposited only one surface of the specimens using vacuum evaporation technique. The coated specimens were aged at 70°C and 90% RH. At the end of ageing the specimens were examined under the scanning electron microscope. Micrographs of these specimens are shown in Figures 18, 19 and 20. As it is seen in these figures cracks have also developed on this type of metal films.

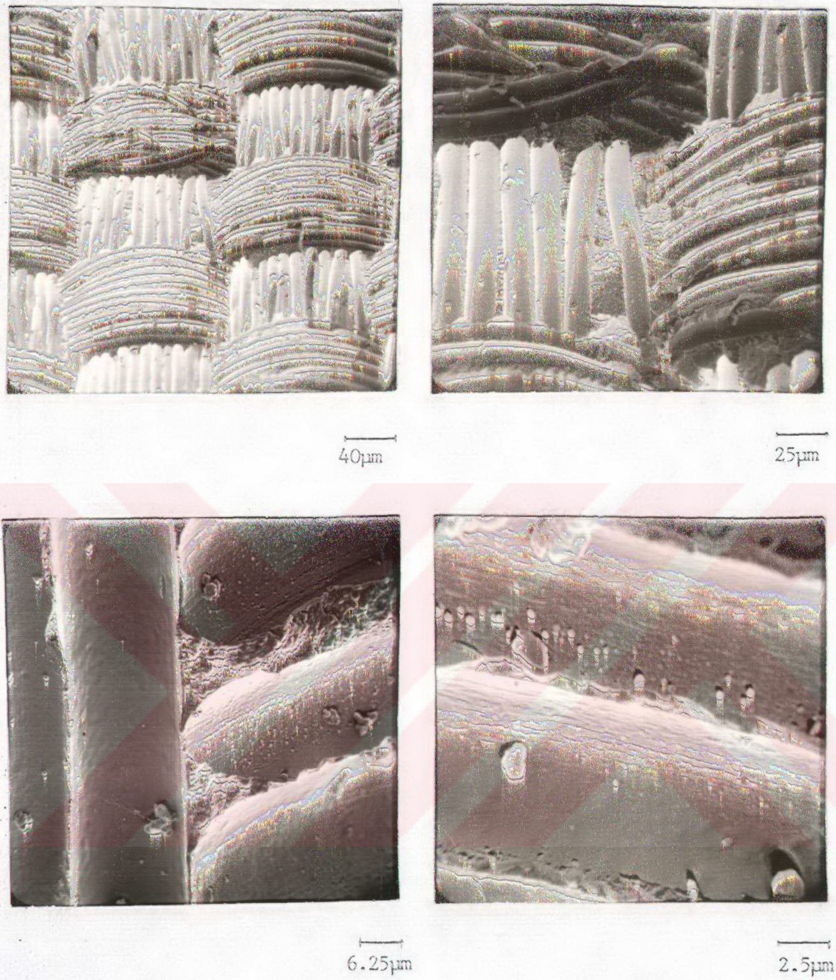

Figure 18 Micrographs of the aged specimens coated with copper-nickel-gold films using vacuum evaporation technique.

Figure 19 Micrographs of the aged specimens coated with gold film using vacuum evaporation technique.

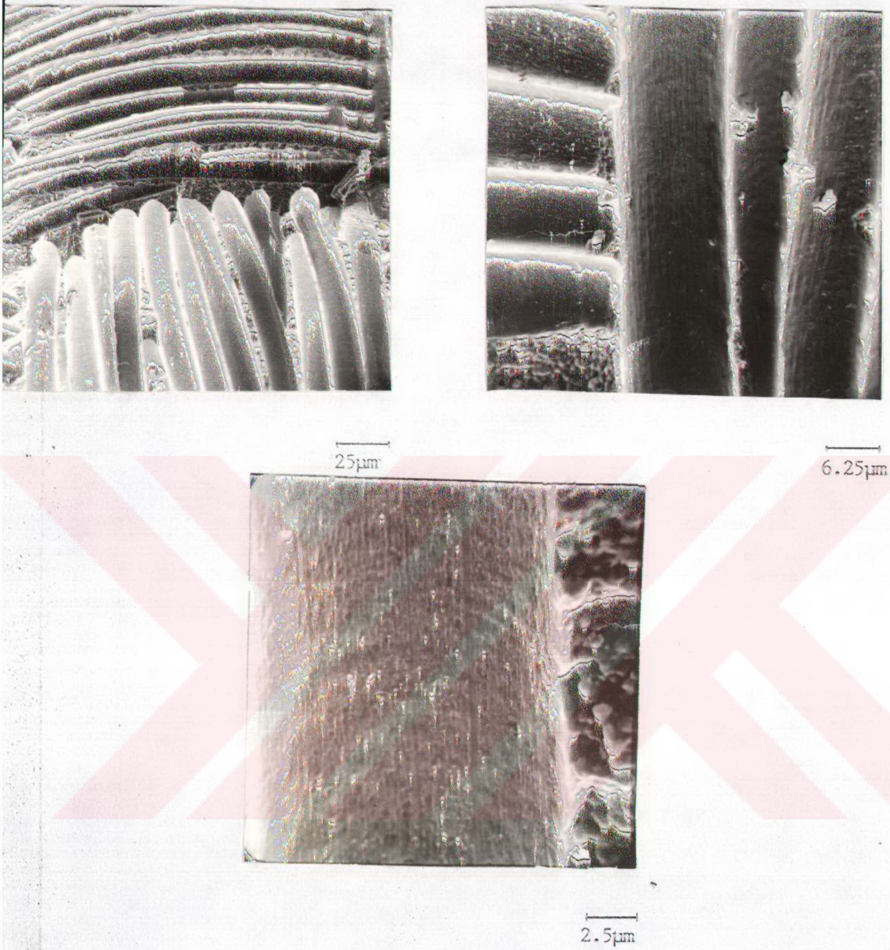

Figure 20 Micrographs of the aged specimens coated with nickel film using vacuum evaporation technique.

Experimental results show that metal films obtained using vacuum evaporation technique are thin and not free from pores. The specimens have rough surfaces, because of the wovenlike structure impression. In the vacuum coating, the metal vapor condense easily on the upper levels but the deeper levels on the surface were poorly deposited. During the ageing process, the moisture penetrate through these pores. It is known that water absorption causes swelling of the resin and above 1% moisture content[2], there is a linear relationship between amount of absorbed water and overall volume change of epoxy resin. Since, the absorbed water causes a change in the dimensions of a composite, cracks were developed on the metal films.

At the end of ageing experiments, the specimens were taken from the environmental chamber and thus they were exposed to the atmosphere. At this time moisture in the specimen diffuses back to the specimen surface, this process cause a deposition of moisture which creates a pressure gradient, and it causes a stress on the metal film. This stress may lead to crack formations on the metal films.

To produce a thicker metal film and also to eliminate pores in the metal film, electroplating technique was used to coat the specimens. In the electroplating technique, decorative copper nickel chromium combinations were selected because of their durability and appearance properties. Copper has an ability to deposit in to the small pores and also provides a more ductile film. Thus it decreases deformation due to the residual stresses mentioned above. However copper film tends to tarnish and stain rapidly when exposed directly to the atmosphere. Therefore it is used as an undercoat in decorative copper - nickel - chromium combinations. Chromium coating exhibits good corrosion resistance in atmospheric exposure and it also affects the durability of total coating. But it is difficult to obtain dense and pore free electrodeposits of chromium. Nickel is used as an undercoat of chromium, to provide pore free, continuous metal films.

Specimens coated with electoplating techniques were aged at the same temperature and humidity conditions (70 °C and 90% RH), for the same time period as the specimens coated with vacuum evaporation technique. The percent weight gain of these specimens in the ageing experiments are given in Table C.3. Diffusion coefficient is calculated to be $2.26*10^{-7}$ mm^2/sec. Comparison of these results with the results obtained using the specimens coated with vacuum evaporation technique show that the rate of absorption is lower in the case of electroplating.

evaporation technique show that the rate of absorption is lower in the case of electroplating.

This can be explained as follows:

Before using the electroplating technique, copper was deposited on the specimens with vacuum evaporation technique to obtain a conductive surface. It is expected that this copper film will also act as a barrier to the diffusion of water molecules in the electroplating bath. The weight gain of specimens during ageing show that copper films deposited using vacuum evaporation could not be sufficient to act as a barrier. Vacuum evaporation technique produce thin film. Therefore the water molecules diffuse into the specimens during electroplating, and thus before ageing, specimens approached to the saturation value. If the specimens were dried before each coating with electroplating, the accumulation of water in the specimens may be decreased.

When the aged specimens coated with electroplating technique were examined under the scanning electronmicroscope (Figure 20), it is observed that cracks have also formed with this coating technique.

The reason of crack formations on the metal film deposited using evaporation technique can be explained in a similar way with crack formations on the metal films

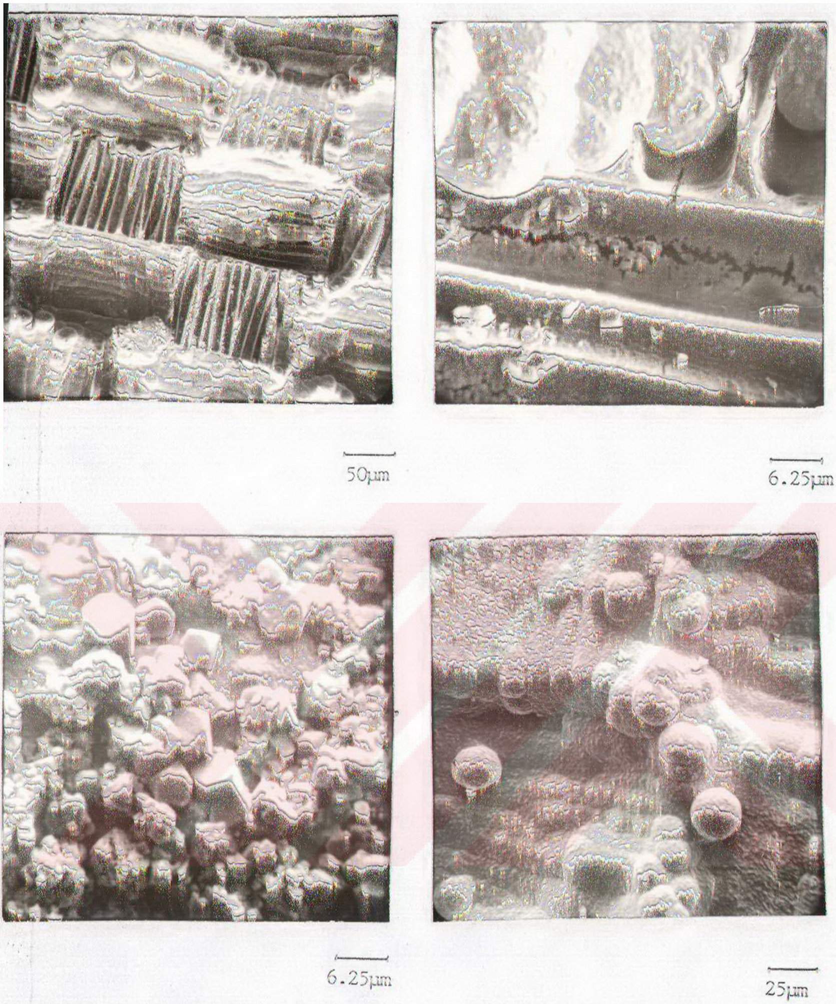

Figure 21 Micrographs of aged specimens coated with copper-nickel-chromium combinations using electroplating technique.

obtained using vacuum evaporation technique. The absorbed water in the specimen cause the swelling of epoxy resin A10, then it cause the cracks on the metal films. Cracks may have also developed when the aged specimens were exposed to the atmosphere, molecules tend to diffuse back to the surface between specimen and metal films. These water molecules create stress on the metal films, this stress lead to crack formations on the metal films.

CHAPTER-5

CONCLUSION

In the present study, various metal films (copper-gold, copper-nickel-gold, nickel and gold) were deposited using vacuum evaporation technique and decorative copper nickel combinations were deposited using electroplating technique on the specimens of Fibredux 914C/T300 unidirectional CFRP, to prevent the moisture diffusion.

The experimental results obtained for vacuum evaporation technique show that the metal films deposited on the CFRP specimens had no effect on moisture absorption rate and saturation moisture content of CFRP specimens. So it is concluded that vacuum evaporation technique does not provide sufficient metal film for Fibredux 914C/T300 unidirectional CFRP.

Examination of specimens coated by electroplating technique under the scanning electronmicrosope show that the thickness of metal layer was increased with this plating technique. However, since water diffuses into the specimens during plating, the weight gain of specimens monitored in the ageing experiments can not be discussed. In order to improve the electroplating technique, the intermediate drying are added between the coating steps.

Also, the reason for the insufficient metal layers obtained by vacuum evaporation and electroplating techniques may be due to the surface structure of Fibredux 914C/T300 unidirectional CFRP. Since specimens have wovenlike structure on the surface, the deeper levels were poorly deposited with both plating techniques used. If pressing during production does not leave an impression and smooth surface is produced, then it may be possible to obtain uniform metal films.

CHAPTER-6

RECOMMENDATIONS

In order to improve the electroplating technique, intermediate drying steps should be added between the coating steps. For instance, when copper is deposited, the specimens should be dried in oven, so that the absorbed water can diffuse back to specimen surface.

Pressing process during the production of Fibredux 914C/T300 unidirectional CFRP leave wovenlike structure impression on the surfaces of CFRP. If that disadvantage is compansated with suitable pressing, then it would be possible to obtain uniform metal films by using vacuum evaporation technique.

REFERENCES

1. Adamson, M.J., 1980. "Thermal Expansion and Swelling of Cured Epoxy Resin Used in Graphite/Epoxy Composite Materials", J. Material Science, Vol. 15, pp.1735-1747.

2. McKague, E.L. et al, 1978. "Swelling and Glass Transition Relations for Epoxy Matrix Material in Humid Environments", J.Applied polymer Science, Vol.22, pp.1643-1654.

3. Wright, W.W., 1981. "The Effect of Diffusion Water into Epoxy Resins and their Carbon Fibre Reinforced Composites", Composites, vol.12 pp. 201-204.

4. Ecstein, B.H.,1978. "Moisture Absorption by Epoxy Laminating Resins", ACS Org,Coatings Plast. Chem. Preprint 38, p.503.

5. Kelly F.N. and Bueche F.., 1961. "Viscosity and Glass Transition Temperature Relations for polymer Diluent Systems",J.Polymer Science p.549

6. Joshi, O.K.,1983, "The Effect of Moisture on the Shear Properties of Carbon Fibre Composites",

Composites, Vol.14,p.196.

7. Bishop S.M.,1983. "Effect of Moisture on the Notch Sensitivity of Carbon Fibre Composites". Vol.14, p.201-205.

8. Etiz, A.,1985. "Effects of Postcuring and Thermal Spike on the Behaviour of CFRP" Master Thesis, M.E.T.U. Ankara

9. Shen, C. and Springer, S.S., 1976. "Moisture Absorption and Desorption of Composite Materials", J.Composite Materials, Vol.10, p.2.

10. Jost W.,1960. "Diffusion in Solids, Liquids,Gases, Academic Press

11. Collings, T.A.,and Copley, S.M.,1983. "On the Accelerated Ageing of CFRP", Composites, Vol.14, p.180.

12. Loos, A.c.,and Springer G.S.,1979. " Moisture Absorption of Graphite Epoxy composites Immersed in Liquids and in Humid Air", J.Composite Materials, Vol.13, p.130-147.

13. Holland, L., 1970. "Vacuum Deposition of Thin films p.1-20.

14. Berry, R.W.,Hall P.M., Harris, M.T., 1968. "Thin Film Technology" p.255-285.

15. Lowenheim, F.A., 1974. "Modern Electroplating"p.87-150

16. ASTM D 3171-76, "Standard Test Method for Fibre Content of Resin Matrix Composites by Digestion".

17. MBB Standards , 824/2559/ECE/SMcP. "Specification for Preconditioning of CFRP Test specimens".

18. Lubin George, 1969.,"Handbook of Fibre Glass and Advanced Plastics composites",p.46-84.

19. Whitney, J.M., et al, 1982. "Experimental Mechanics of Fibre Reinforced Composite Materials".p.237-249

20. Wright, W.W.,1981. " The effect of diffusion of Water into Epoxy Resins and Their Carbon Fibre Reinforced Composites",Composites, Vol.12. p.201-204.

21. Collings, T.A., 1961. "The Effect of Observed Climatic Conditions on the Moisture Equilibrium Level of Fibre reinforced Plastics", Composites, Vol.17, p.33-41.

22. Loos A.C.,1979. "Moisture Absorption of Graphite Epoxy Composites Immersed in Liquids and in Humid Air", J.Composite Materials, Vol.13, p.131-147.

23. John D.M., 1984. " Thermoplastic vs Thermosetting Structural Composites" , Polymer Composites, Vol.5, No.3.

24. Perry R.H. Chilton C.H., 1973."Chemical Engineers Handbook", Fifth Edition.

APPENDICES

APPENDIX A

EXPERIMENTAL RESULTS

Table A.1. Percent Weight Losses Obtained From Drying Weight Data

Specimen Number	DRYING TIME $\sqrt{hr}$												
	4.89	6.92	8.48	9.79	10.95	12	12.96	13.85	14.69	15.49	16.24	16.97	17.66
1	0.105	0.22	0.247	0.264	0.512	0.653	0.724	0.724	0.724	0.724	0.724	0.724	0.724
2	0.017	0.088	0.124	0.159	0.159	0.355	0.39	0.515	0.540	0.550	0.550	0.550	0.550
3	0.06	0.17	0.17	0.17	0.238	0.391	0.425	0.540	0.544	0.544	0.544	0.544	0.544
4	0.095	0.191	0.255	0.255	0.302	0.478	0.526	0.658	0.717	0.749	0.749	0.781	0.781
5	0.065	0.144	0.164	0.180	0.213	0.213	0.394	0.443	0.575	0.657	0.657	0.657	0.657
6	0.108	0.180	0.18	1.198	0.288	0.378	0.552	0.612	0.612	0.612	0.612	0.612	0.612
7	0.081	0.146	0.195	0.2113	0.276	0.455	0.471	0.650	0.715	0.715	0.747	0.747	0.747
8	0.101	0.186	0.203	0.203	0.237	0.441	0.458	0.678	0.678	0.678	0.678	0.678	0.678
9	0.05	0.150	0.183	0.183	0.200	0.350	0.451	0.567	0.668	0.668	0.684	0.701	0.701
10	0.049	0.165	0.181	0.215	0.248	0.446	0.479	0.578	0.661	0.661	0.678	0.678	0.678
11	0.115	0.132	0.214	0.214	0.214	0.413	0.429	0.595	0.677	0.677	0.677	0.677	0.677
12	0.08	0.112	0.145	0.161	0.209	0.402	0.402	0.612	0.676	0.693	0.693	0.693	0.693

Table A.1.(cont'd)

Specimen Number	DRYING TIME $\sqrt{hr}$												
	4.89	6.92	8.48	9.79	10.95	12	12.96	13.85	14.69	15.49	16.24	16.97	17.66
13	0.05	0.134	0.201	0.201	0.218	0.437	0.437	0.571	0.571	0.723	0.723	0.756	0.756
14	0.080	0.192	0.224	0.240	0.240	0.481	0.481	0.561	0.593	0.593	0.641	0.673	0.673
15	0.033	0.099	0.099	0.181	0.198	0.413	0.413	0.611	0.611	0.611	0.660	0.677	0.677
16	0.032	0.164	0.230	0.230	0.246	0.411	0.476	0.608	0.674	0.674	0.690	0.690	0.690
17	0.016	0.135	0.135	0.152	0.152	0.356	0.406	0.525	0.559	0.593	0.610	0.627	0.627
18	0.033	0.066	0.100	0.133	0.133	0.385	0.401	0.535	0.535	0.535	0.636	0.636	0.636
19	0.065	0.147	0.147	0.163	0.180	0.340	0.376	0.540	0.671	0.671	0.671	0.671	0.671
20	0.064	0.146	0.227	0.227	0.227	0.438	0.454	0.648	0.681	0.681	0.681	0.681	0.681
21	0.1311	0.196	0.213	0.223	0.245	0.295	0.499	0.590	0.672	0.672	0.721	0.721	0.721
22	0.116	0.133	0.133	0.133	0.149	0.349	0.349	0.599	0.632	0.632	0.632	0.649	0.649
23	0.084	0.169	0.169	0.169	0.406	0.406	0.541	0.643	0.643	0.643	0.643	0.643	0.643
24	0.096	0.144	0.241	0.241	0.241	0.402	0.418	0.579	0.691	0.692	0.691	0.691	0.691

Table A.1.(cont'd)

Specimen Number	DRYING TIME $\sqrt{hr}$												
	4.89	6.92	8.48	9.79	10.95	12	12.96	13.85	14.69	15.49	16.24	16.97	17.66
25	0.114	0.163	0.163	0.163	0.180	0.392	0.441	0.605	0.687	0.687	0.687	0.687	0.687
26	0.048	0.112	0.177	0.193	0.193	0.386	0.402	0.579	0.595	0.595	0.627	0.660	0.660
27	0.084	0.134	0.134	0.134	0.168	0.353	0.421	0.538	0.639	0.639	0.639	0.639	0.639
28	0.035	0.053	0.0714	0.107	0.107	0.267	0.267	0.303	0.499	0.540	0.549	0.642	0.642
29	0.081	0.146	0.195	0.211	0.228	0.439	0.472	0.635	0.635	0.635	0.716	0.733	0.733
30	0.00	0.066	0.105	0.149	0.165	0.414	0.414	0.579	0.579	0.596	0.794	0.794	0.794
31	0.048	0.161	0.161	0.177	0.177	0.387	0.419	0.629	0.709	0.709	0.742	0.758	0.758

Table A.2. Percent Moisture Content Obtained from Aging Weight Data

Specimen Number	AGING TIME √hr															
	8.48	12.96	18.33	23.49	24.45	26.83	28.14	30.19	31.36	33.94	36.33	38.57	40.69	43.54	48.98	50.67
1	0.354	0.780	1.259	1.401	1.543	1.631	1.720	1.844	1.844	1.844	1.844	1.844	1.844	1.844	1.844	1.844
2	0.356	0.659	1.230	1.622	1.586	1.622	1.765	1.765	1.765	1.765	1.765	1.765	1.765	1.765	1.765	1.765
3	0.461	0.803	1.298	1.503	1.606	1.640	1.777	1.777	1.777	1.777	1.794	1.794	1.794	1.794	1.794	1.79
4	0.400	0.801	1.233	1.634	1.682	1.746	1.794	1.810	1.906	1.89	1.970	1.970	1.970	1.970	1.970	1.97
5	0.412	0.758	1.384	1.582	1.582	1.582	1.648	1.764	1.863	1.863	1.863	1.863	1.863	1.863	1.863	1.86
6	0.342	0.667	1.172	1.262	1.443	1.533	1.533	1.659	1.659	1.659	1.659	1.659	1.659	1.659	1.659	1.65
7	0.490	0.816	1.274	1.830	1.715	1.732	1.732	1.851	1.872	1.895	1.928	1.960	1.960	1.960	1.960	1.96
8	0.374	0.732	1.209	1.515	1.634	1.788	1.788	1.78	1.788	1.788	1.788	1.78	1.788	1.788	1.788	1.78
9	0.503	0.923	1.411	1.898	2.015	2.015	2.049	2.133	2.066	2.49	2.049	2.032	2.032	1.982	2.01	2.01
10	0.498	0.797	1.677	1.760	1.810	1.926	1.942	1.942	1.942	1.876	1.876	1.893	1.959	1.926	1.893	1.8
11	0.531	0.880	1.312	1.677	1.843	2.109	2.113	2.119	2.120	2.123	2.130	2.138	2.140	2.142	2.142	2.14
12	0.404	0.809	1.392	1.732	1.797	1.829	1.862	1.878	1.829	1.829	1.846	1.846	1.846	1.894	1.894	1.89

Table A.2.(cont'd)

Specimen Number	AGING TIME $\sqrt{hr}$															
	8.48	12.96	18.33	23.49	24.41	26.83	28.14	30.19	31.36	33.94	36.33	38.57	40.69	43.54	48.98	50.6
13	0.422	0.912	1.317	1.621	1.621	1.655	1.705	1.70	1.700	1.672	1.756	1.756	1.756	1.755	1.756	1.75
14	0.450	0.982	1.384	1.529	1.594	1.835	1.884	1.932	1.937	1.945	1.970	1.980	1.980	1.980	1.980	1.98
15	0.531	0.896	1.510	1.941	1.941	2.007	2.19	2.035	2.042	2.057	2.077	2.093	2.107	2.107	2.107	2.10
16	0.462	0.891	1.354	1.816	1.865	1.964	1.964	1.998	1.998	1.998	2.047	2.047	2.031	2.031	2.031	2.03
17	0.391	0.731	1.735	1.735	1.735	1.769	1.79	1.851	1.865	1.871	1.875	1.885	1.888	1.888	1.888	1.88
18	0.470	0.772	1.394	1.697	1.781	1.800	1.817	1.825	1.827	1.831	1.838	1.848	1.865	1.881	1.882	1.88
19	0.345	0.789	1.332	1.760	1.859	1.924	1.920	1.900	1.809	1.760	1.760	1.809	1.809	1.809	1.809	1.80
20	0.472	0.846	1.286	1.579	1.660	1.772	1.774	1.774	1.856	1.934	1.936	1.937	1.937	1.937	1.937	1.93
21	0.395	0.806	1.564	1.761	1.827	1.860	1.860	1.893	1.909	1.942	1.940	1.942	1.942	1.942	1.942	1.94
22	0.367	0.852	1.403	1.620	1.670	1.771	1.771	1.787	1.820	1.825	1.830	1.845	1.850	1.854	1.854	1.95
23	0.413	0.844	1.448	1.724	1.776	1.810	1.810	1.810	1.810	1.815	1.820	1.825	1.827	1.827	1.827	1.82
24	0.441	0.798	1.398	1.818	1.852	1.855	1.855	1.860	1.869	1.870	1.880	1.900	1.920	1.920	1.920	1.92

Table A.2.(cont'd)

Specimen Number	AGING TIME $\sqrt{h}$															
	8.48	12.96	18.33	23.49	24.45	26.83	28.14	30.19	31.36	33.94	36.33	38.57	40.69	43.54	48.98	50.67
25	0.468	0.904	1.372	1.840	1.889	1.889	1.889	1.905	1.907	1.910	1.913	1.919	1.920	1.921	1.921	1.921
26	0.312	0.755	1.347	1.643	1.675	1.675	1.725	1.770	1.790	1.794	1.79	1.803	1.807	1.807	1.807	1.807
27	0.485	0.905	1.423	1.617	1.660	1.681	1.827	1.859	1.900	1.912	1.917	1.924	1.923	1.924	1.924	1.924
28	0.507	1.031	1.910	1.926	1.930	1.932	1.937	1.942	1.945	1.949	1.960	1.970	1.973	1.977	1.977	1.97
29	0.458	0.867	1.391	1.620	1.784	1.816	1.784	1.784	1.784	1.800	1.816	1.820	1.821	1.849	1.849	1.84
30	0.432	1.014	1.313	1.745	1.753	1.810	1.812	1.845	1.845	1.848	1.862	1.870	1.878	1.962	1.962	1.962
31	0.355	0.978	1.298	1.412	1.494	1.621	1.779	1.779	1.887	1.889	1.790	1.797	1.797	1.797	1.797	1.79

APPENDIX B

FIBER VOLUME PERCENT CALCULATIONS

Percent fibre volume content of the carbon fibre reinforced plastic used in the experiments, was calculated by using the following Equation,

$$\text{Fibre Vol. Percent} = (Wf/\ W) * (c\ /\ F) * 100 \qquad (1\text{-}B)$$

where

Wf: weight of fibre in the composite specimen

W : weight of the composite specimen

F : fibre density

Resin and fibre density were known, the composite density was calculated by Equation (2-B),

$$c = Wf/\ (1/F + 1/R) \qquad (2\text{-}B)$$

where

R ; resin density.

APPENDIX-C

STATISTICAL ANALYSIS [24]

Symbolically, the arithmetic average or mean value is usually denoted as $\bar{X}$, where the individual values are indicated by Xi and the number of data is indicated by n. The mean value is calculated by Equation (1-C),

$$\bar{X} = (1/n) \sum_{i=1}^{n} Xi \qquad (1\text{-}C)$$

The standard deviation is the square root of the average squared difference between the individual observations and the average value. The standard deviation, usually denoted by the symbol S, would be calculated for the given data as follows:

$$S = 1/(n-1) \sum_{i=1}^{n} (Xi - \bar{X})^{2} \qquad (2\text{-}C)$$

Table C.1. Statistical Analysis For Drying Data

$\sqrt{t}$	4.89	6.92	8.48	9.79	10.95	12	12.96	13.85	14.69	15.49	16.24	16.97	17.66
$\bar{X}$	0.0689	0.144	0.174	0.188	0.213	0.394	0.433	0.581	0.636	0.646	0.667	0.679	0.679
σ_n	0.033	0.039	0.045	0.037	0.055	0.052	0.053	0.061	0.059	0.056	0.055	0.056	0.056

Table C.2. Statistical Analysis For Ageing Data

$\sqrt{t}$	8.48	12.96	18.33	23.49	24.45	26.83	28.14	30.19
$\bar{X}$	0.429	0.838	1.388	1.671	1.729	1.792	1.827	1.857
σ_n	0.059	0.090	0.153	0.154	0.135	0.136	0.115	0.106

$\sqrt{t}$	31.36	33.94	36.33	38.57	40.69	43.54	48.98	50.67
$\bar{X}$	1.865	1.867	1.880	1.887	1.891	1.895	1.895	1.895
σ_n	0.098	0.101	0.103	0.103	0.103	0.101	0.102	0.102

Table C.3. Statistical Analysis For Ageing Data

$\sqrt{t}$	8.48	15.49	20.19	24	27.2	32.86	37.94	46.73
$\overline{X}$	0.227	0.347	0.457	0.456	0.457	0.457	0.457	0.457
σ_n	0.091	0.119	0.182	0.188	0.179	0.179	0.179	0.179