Aramid Reinforced Aluminium Laminates: ARALL

Adhesion Problems and Environmental Effects
Vol. B: Environmental Effects

November 1986

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Adhesion Problems and Environmental Effects
Vol. A: Adhesion and Delamination
Vol. B: Environmental Effects

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This report contains Volume B.
Volume A in a separate report (LR-503)
ARAMID ALUMINIUM LAMINATES: ARALL

Adhesion Problems and Environmental Effects

Volume B: Environmental effects on delamination

In a separate volume: Volume A: Adhesion and delamination

Abstract

Fatigue crack growth in the new hybrid material ARALL is accompanied by some "controlled" delamination in the wake of the crack in the thin aluminium sheets. The aramid fibres are bridging the crack, which highly reduces the stress intensity at the crack tip and thus leads to a very low crack growth rate or crack arrest. The delamination in the thin intermediate layers, consisting of aramid fibres and metal adhesive, is the main topic of the present thesis. The investigation has revealed new insights into several questions related to (1) phenomenological details of the delamination mechanisms in ARALL, (2) environmental effects on delamination, (3) usefulness and limitations of different types of specimens to study delamination under mode I, mode II and combined modes of loading, (4) the application of fracture mechanics to understand the delamination behaviour, and (5) the application of diffusion models to analyse moisture absorption by ARALL. Topics (1), (3) and (4) are covered in Volume A, topics (2) and (5) in Volume B.

Acknowledgement: The author gratefully acknowledges
- prof.dr.ir. J. Schijve for his continuous efforts to make this work what it is today,
- ir. B. Vogeleisang for being an outstanding mentor and colleague,
- ing. J. Snijder, ing. A. Burgers, F. Oostrum and K. Paalvast for their technical support,
- J. Jongenelen and W. Spee for making the drawings,
- F. Schaberg and M. Grob for doing part of the typing,
- L. van der Laan and F. Verkaart for doing part of the experimental work,
- all the members of the B2 department: for letting me win all these chess games (joyful moments in sometimes difficult periods),
- STW (Stichting Technische Wetenschappen) for their financial support which made this study possible,

"If I consider the number of people I have to acknowledge, I start doubting whether I did anything myself"
## Contents

**Chapter 1: Introduction**  
PP. 1

**Chapter 2: Literature survey**

2.1: diffusion mechanism in aramid fibres  
PP. 3

2.2: diffusion mechanism in an epoxy matrix  
PP. 4

2.3: influence of moisture on the aluminium/adhesive interface  
PP. 6

**Chapter 3: Moisture absorption of ARALL**

3.1: Introduction  
PP. 9

3.2: Theoretical aspects; a literature survey  
PP. 9

3.3: Moisture absorption of ARALL  
PP. 14

3.4: Experiments  
PP. 16

3.5: Results of the experimental programme  
PP. 18

3.6: A theoretical comparison between the moisture absorption of ARALL and carbon and aramid composites  
PP. 23

3.7: Influence of diffusion retardation by protective coatings  
PP. 25

3.8: Moisture profile of ARALL  
PP. 30

3.9: Discussion  
PP. 37

3.10: Conclusions  
PP. 40

**Chapter 4: Influence of absorbed moisture on the aramid fibre/matrix adhesion**

4.1: Introduction  
PP. 41

4.2: Standard materials  
PP. 42

4.3: Definition of the possible delamination paths in an adhesive or prepreg intermediate layer  
PP. 42

4.4: Environmental testing  
PP. 43
4.5: The influence of absorbed moisture by means of the Bell-peel test 47
4.6: The influence of absorbed moisture by means of the thick adherend specimen 50
4.7: The influence of moisture absorption by means of the interlaminar shear test 52
4.8: The influence of environmental exposure by means of the width tapered double cantilever beam test 54
4.9: The influence of absorbed moisture by means of the wedge-edge test 63
4.10: The influence of absorbed moisture by means of the delamination specimen 67
4.11: The influence of the environment on relaxation of the residual stress 70
4.12: Evaluation of the environmental test series 74

Chapter 5: Summary 78
Chapter 6: Samenvatting 84
References 90
Tables 96
Figures 105
Chapter 1: Introduction

This report covers the second part of an investigation on adhesion problems and environmental influences related to the new material ARALL (Aramid Aluminium Laminate). The hybrid material ARALL consists of very thin aluminium alloy sheets, bonded to a laminate by prepregs consisting of a metal adhesive and unidirectional aramid fibres. ARALL is fully described in chapter 2 of the first report, where reference is made to its most outstanding property, which is the very high fatigue resistance. The first report mainly deals with adhesion phenomena between aramid fibres and the adhesive matrix. The delamination behaviour is analysed theoretically and experimentally including delamination under peel loads (mode I loading) and shear loads (mode II loading). A large variety of experiments has been carried out. Environmental effects on the delamination were not yet considered in the first part of the investigation.

In this second part, presented in a separate report, the influence of environmental exposure on the delamination behaviour of ARALL is examined. A brief literature survey concerning the diffusion mechanisms of moisture in composites and its influence on material properties is presented in chapter 2. In the next chapter the moisture absorption behaviour of ARALL is extensively treated. First a theoretical two-dimensional diffusion model is developed which allows a reliable prediction of the amount of absorbed moisture (section 3.3). The experimental data, essential for the usage of the theoretical model, are presented and discussed in the sections 3.4 and 3.5. Using a three-dimensional analytical diffusion model, in section 3.6 the moisture absorption of ARALL is compared with two composite systems (carbon fibre and aramid fibre reinforced plastics). In section 3.7, possible diffusion retardation by means of protective coatings is examined using a one-dimensional numerical diffusion model. The same model is applied to determine the influence of a fibre/matrix combination on moisture profiles (section 3.8). Chapter 3 is concluded with an overall discussion (section 3.9) and conclusions (section 3.10).

Chapter 4 is dealing with an evaluation of the influence of absorbed moisture on the delamination behaviour. As in the first part of the investigation, some standard materials and possible delamination paths are defined (section 4.2 and 4.3). After some general remarks concerning environmental testing (section 4.4), a survey
of the environmental test series is presented which includes seven different test methods and a wide range of environmental conditions (section 4.5 to 4.11). Chapter 4 is concluded with an evaluation of the environmental test series (section 4.12).

The results and conclusions obtained in the first and in the second part of the investigation are recapitulated in chapter 5. This chapter should serve as an extensive summary of the full investigation.
Chapter 2: Literature survey

The available literature concerning the influence of moisture on composites is extremely comprehensive. A successful effort to cover the available literature has been presented recently by Komorowski (ref.1). In the present survey, the attention is focused on three main topics which are all essential for the ARALL material:

- diffusion mechanism in aramid fibres and the consequences of moisture absorption on aramid properties
- diffusion mechanism in epoxy adhesives and the consequence of moisture absorption on the epoxy properties
- influence of moisture on the adherend (aluminium)/adhesive interface strength

A literature survey on a fourth important topic (moisture absorption rate) is presented in chapter 3, which deals with the moisture absorption of ARALL. Here, only general phenomena concerning moisture absorption will be treated.

2.1: diffusion mechanism in aramid fibres

In ref.2, the moisture absorption and the related degradation of properties is attributed to the susceptibility of the aramid linkages in PpPTA to hydrolyse, and therefore induce chain scission:

![Chemical reaction](image)

The rate of hydrolysis will be accelerated by H₂SO₄ or NaOH impurities present in the fibre (ref.3). H₂SO₄ will act as a catalyst, while it remains chemically unmodified. NaOH will accelerate the hydrolysis and react into a salt macromolecular endgroup (COO⁻Na⁺).

The influence of moisture absorption on the strength and stiffness properties of the aramid fibres is examined in the refs. (2), (3) and (4). In fig.1 it is shown that no decline of fibre properties is present after 21 days of exposure to a 80°C, 95% relative humidity environment (tests performed at different temperature levels, ref.4). On the contrary, hot dry aging in the presence of oxygen resulted in a serious decrease of the tensile strength of the fibres (fig.2). In contradiction with
ref.(4), the authors of ref.(2) and (3) found much faster degradations (200xfaster) for fibres exposed to high relative humidities as compared to dry specimens (same exposure temperature level). A surprising result was found by Deteresa (ref.5): he found an improved interface strength after soaking the fibre in water (single filament test). In ref.(2), an analytical solution is presented for the fibre strength degradation as the result of environmental exposure:

\[ dS = \frac{-(E - K_5S_b)}{RT}.k_t.t.e \] (1)

where \( dS \): strength degradation
\( R.H. \): relative humidity of the environment
\( k_t \): constant
\( t \): time
\( E \): activation energy for hydrolysis
\( K_5S_b \): lowering of the activation energy for hydrolysis due to an externally applied stress level
\( T \): temperature
\( R \): universal gas constant

Since in ref.(2) an experimental confirmation of eq.(1) is absent, the usefulness of this equation is not clear.

2.2: diffusion mechanism in an epoxy matrix

Water molecules, diffusing in an organic matrix can attach to polar groups such as hydroxyl or amine groups by hydrogen bonding (ref.6, 7). It should therefore be clear that, in the absence of crack or voids, the adsorbed water is not present as a liquid but in the form of hydrogen bonded molecules or clusters within the polymer (e.g. ref.8). In the presence of cracks or voids, liquid can be trapped in the material through capillary actions.

The hydrogen bonding results primarily in a decrease of the glass transition temperature of the polymer (e.g. ref.6,7,8,9) which can cause increased plasticizing effects. The hydrogen bonding will also cause significant swelling of the material.

The effect of moisture on the glass transition temperature \( T_g \) has been extensively discussed in the literature (for a review, see ref. 1). In general, two models are proposed to describe the relation between \( T_g \) and the moisture:
1: A free volume model, which applies only satisfactorily to polymer/moisture couples which do not have strong mutual molecular interactions (Kelley-Bueche equation, ref.10):

\[ T_{gw} = \left[ \frac{\alpha_p v_p T_{gp} + \alpha_d (1-v_p) T_{gd}}{\alpha_p v_p + \alpha_d (1-v_p)} \right] \]  

where \( \alpha \): expansion coefficient  
\( v \): volume fraction  
\( p \): polymer  
\( d \): diluent  

Using an approximation of the glass transition temperature of water \((-134^\circ C < T_{gd} < -138^\circ C)\), Morgan and Mones (ref.11) found a large discrepancy between experimental and theoretical results as obtained with eq.(2) mainly because of:

- hydrogen bonding is not accounted for in eq.(2)  
- inhomogeneous absorption of moisture  

Browning (ref.12,13) found a very good agreement between experimental and theoretical results if a \( T_{gd} \) of \( 4^\circ C \) was used although this value has no direct physical meaning.

2: An entropy model, preferentially used if strong mutual interactions are present between polymer and moisture (ref.14):

\[ T_{gw} = T_{gp} \cdot \frac{1 - R \cdot y(r)/(M_s \cdot \Delta C_p)}{1 - R \cdot y(r)/(M_s \cdot \Delta C_p)} \]  

where \( y(r) = r \cdot \ln(1/r) + (1-r) \cdot \ln(1-r) \)  
\( r = M_s/M_w \)  
\( R \): universal gas constant  
\( M_w \): molecular weight of water  
\( M_s = N_A/N_s \): effective formula of the hydrogen bond sites  
\( N_A \): Avogadro number  
\( N_s \): number of hydrogen bond sites per gram of resin  
\( \Delta C_p \): change of specific heat at the glass transition  

Because there are still problems for determining \( \Delta C_p \), the full potential of the entropy approach is not yet realized. However, it is already confirmed experimentally that for a number of resins, eq.(3) gives a much better correlation with experiments than the free volume model of eq.(2).

The relation between the wet glass transition temperature of a polymer and moisture can be disturbed
if moisture is trapped as a liquid in internal cracks or voids. On a microscale, these cracks can occur as a result of osmotic pressures (ref.15, 16) or because of thermal cycling or spiking (ref.8, 17, 18, 19).

Swelling as the result of moisture absorption has been thoroughly examined by, among others, Gazit (ref.20), Shirell and Halpin (ref.21, 22). However, for high cross-linked epoxies, it seems that there is no theoretical model which can predict swelling within a reasonable accuracy. In an analysis of Weitsman (ref.23), a model is presented to calculate the extra stresses and strains in an adhesive bond as the result of the swelling processes.

2.3: influence of moisture on the aluminium/adhesive interface

Because of the large importance of durability for adhesive joints, publications on the effect of moisture on the adherend/adhesive interface are numerous and comprehensive. Publications deal with different adherends (e.g. steel or aluminium), different pretreatments (e.g. etching, anodising, priming) and different adhesives (e.g. phenolics or epoxies). There are excellent surveys, among others by Minford, and also several textbooks (e.g. ref. 24). In most publications, the influence of moisture on the adherend/adhesive interface is assumed to be twofold:

1: degradation of the interfacial forces between adherend and adhesive
2: degradation of the oxide layer on the adherend surface

ad 1: Although there is still some disagreement about the type of bonds between an adhesive and an oxide layer, most authors agree that these bonds are of a chemical nature. However, this does not mean that these bonds should be water stable. In some references (e.g. ref.25, 26) it is demonstrated with a thermodynamical model that such a stability is absent in the presence of water.

In an inert environment, the reversible work of adhesion $W_a$ can be written as:

$$W_a = \gamma_{ad} + \gamma_{ol} - \gamma_{ad,ol}$$  \hspace{1cm} (4)

where $\gamma_{ad}$: surface free energy of the adhesive

$\gamma_{ol}$: surface free energy of the oxide layer

$\gamma_{ad,ol}$: interfacial free energy
In the presence of a liquid, one finds for eq. (4):

$$W_{al} = \gamma_{ad,1} + \gamma_{ol,1} - \gamma_{ad,ol}$$  \hspace{1cm} (5)

The interfacial free energies can be found using the general equation (e.g. ref. 27, 28):

$$\gamma_{x,y} = \gamma_x + \gamma_y - 2\left\{\left(\gamma_x^d \gamma_y^d\right)^{1/2} + \left(\gamma_x^p \gamma_y^p\right)^{1/2}\right\}$$  \hspace{1cm} (6)

where the superscripts d and p refer to the dispersion and polar components of the total surface free energy ($\gamma = \gamma^d + \gamma^p$).

Substitution of eq. (6) in both eqs. (4) and (5) results in:

$$W_a = 2\left\{\gamma_{ad}^d \gamma_{ol}^d\right\}^{1/2} + \left(\gamma_{ad}^p \gamma_{ol}^p\right)^{1/2}$$  \hspace{1cm} (7)

$$W_{al} = 2\left\{\gamma_1 - \left(\gamma_{ad}^d \gamma_1^d\right)^{1/2} - \left(\gamma_{ad}^p \gamma_1^p\right)^{1/2} - \left(\gamma_{ol}^d \gamma_1^d\right)^{1/2} - \left(\gamma_{ol}^p \gamma_1^p\right)^{1/2}\right\}$$  \hspace{1cm} (8)

After substitution of the surface free energies of the adhesives and aluminium oxides, the work of adhesion was found to be:

$$W_a = 232 \text{ MJ/m}^2 \text{ (epoxy + oxide layer on aluminium)}$$

$$W_{al} = -137 \text{ MJ/m}^2 \text{ (in the presence of water)}$$

Since a positive value indicates thermodynamic stability at the interface and a negative value instability, it is clear that water may disturb the chemical bonds at the adherend/adhesive interface.

It is generally recognized that the moisture transport will occur dominantly through the adhesive. The moisture preferentially diffuses towards the oxide layer because both the oxide and the water is more or less polar (ref. 24). In this respect, the resin boundary layer near the interface may play an important role in the diffusion behaviour. It is certain that the physical and mechanical properties of this resin boundary layer will differ from those of the bulk material. However, on this topic there is an interesting discrepancy in the literature. Kinloch (ref. 24) states that this resin boundary layer is more susceptible to hydrolysis than the bulk adhesive because of its lower cross-link density, whereas Brockmann (ref. 29) considers the boundary layer as a diffusion barrier because of its tighter cross-linking.
ad 2: In the past ten years, interesting work has been performed on the hydrolysis of oxide layers as the result of penetrating moisture. It was shown by several authors (e.g. ref. 24, 30) that the oxide layer resulting from P.P.L.-etching rapidly hydrates into pseudo-boehmite in the presence of water creating a weak boundary layer at the interface. Anodising pretreatments such as chromic or phosphoric anodising demonstrated a stable oxide layer (e.g. ref. 31), most probably resulting from the presence of ions (e.g. PO₄ for the phosphoric anodising process) at the surface which prevent oxide hydration (e.g. ref. 32, 33). Another reason for an improved durability of the anodised oxide layers may be the absence of certain elements (e.g. magnesium) in the oxide layer (e.g. ref. 34, 35).

Nowadays, the durability of the adherend/adhesive interface is largely improved by the application of corrosion inhibiting primers on the oxide layer. These primers have a chemical structure related to the adhesive (e.g. an epoxy primer for an epoxy adhesive). The primers mostly contain chromate inhibitors which limit the moisture diffusion rate through the primer. Except for hampering the moisture diffusion, the primers also have some other functions, e.g.:

- assure chemical, water-stable bonding between oxide layer and adhesive
- fill up the cavities of the oxide layer and displace water which could be trapped in the oxide layer
- stabilize the oxide layer to prevent corrosion processes (ref.36)

An excellent survey of oxide layers and protective systems for oxide layers is presented by W. Moonen (ref. 37).
Chapter 3: Moisture absorption of ARALL

3.1: Introduction

One of the actual problem areas of composites, or more general, of fibre reinforced materials, is that most currently used resins or adhesives (epoxy, phenol) and some type of fibres (aramid) do absorb moisture in a wet environment. Depending on the chemical and/or physical stability of these organic materials, the absorbed moisture may cause serious degradation of mechanical properties, mostly as a result of a decrease in glass transition temperature $T_g$ (plasticising effect). Since possible degradation is a function of the amount of absorbed moisture and the distribution of the moisture in the material, knowledge of the diffusion properties of any new material is indispensable. Therefore, a large test series has been executed to examine the diffusion process in ARALL for several relative humidities and temperature levels (section 3.4 and 3.5). As a second step, the moisture absorption of ARALL is compared to the absorption of both aramid and carbon fibre composites (section 3.6). Further, the influence of diffusion barriers (e.g. coatings) on the diffusion process is examined, both experimentally and by a numerical analysis (section 3.7). Some attention is paid to a more accurate description of moisture profiles in ARALL (section 3.8).

3.2: Theoretical aspects, a literature survey

Using the resemblance between moisture diffusion and heat transfer, Fick described a one-dimensional form of the diffusion process as:

$$\frac{\delta C}{\delta t} = D_x \frac{\delta^2 C}{\delta x^2}$$  \hspace{1cm} (9)

where $C$: concentration

$t$: time

$x$: coordinate

$D_x$: diffusion coefficient in $x$-direction
In ref. (38) it is shown that the diffusivity is almost independent of the moisture content. As a consequence, eq.(9) may be simplified to:

\[
\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2}
\]  

(10)

An appropriate set of boundary conditions is necessary to solve this equation. For the one dimensional problem it is often proposed that the initial moisture content in the material is constant (c=c_i at t<0). At the start of the environmental exposure (t=0), the specimen edges reach immediately the saturated (equilibrium) condition:

\[
t<0: \quad c(x) = c_i \\
\quad t>0: \quad c(0) = c(\hat{h}) = c_m
\]

(11)

where \( c_i \): initial concentration  
\( c_m \): equilibrium concentration

With the boundary conditions in eq.(11), eq.(10) can be solved (e.g. Jost, ref.39) which results in:

\[
\frac{c - c_i}{c_m - c_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \frac{\sin(2j+1)\pi x}{h} \cdot e^{-(2j+1)^2 \pi^2 D_x t/h^2}
\]

(12)

The total weight of absorbed moisture per unit area can be found by integration of eq.(12):

\[
m = \int_{0}^{h} c \, dx
\]

which results in:

\[
G = \frac{m - m_i}{m_m - m_i} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \cdot e^{-(2j+1)^2 \pi^2 D_x t/h^2}
\]

(13)

Eq.(13) is often approximated by:

\[
G = 1 - e^{-7.3(D_x t/h^2)^{0.75}}
\]

(14)

With a Laplace-Transform solution technique and the same set of boundary conditions, another solution can be found for eq.(10):

\[
G = \frac{4D_x t^{\frac{1}{2}}}{h^2} \cdot \left( \frac{1}{\pi^2} + 2 \sum_{n=0}^{\infty} \frac{(-1)^n \text{erfc} \left( \frac{nh}{2(2D_x t)^{\frac{1}{2}}} \right)}{n^2} \right)
\]

(15)

For short-term absorption, it was shown that eq.(15) will provide a more rapid convergence if compared to solution (13).
The one-dimensional solution, presented above, is appropriate for several applications, e.g. almost all thin skin composite structures. For anisotropic materials, Shen and Springer (ref.42) derived the relation between the diffusion coefficient perpendicular to the specimen surface ($D_x$) and the diffusion coefficients parallel and perpendicular to the fibre direction (U.D. composites, $D_{11}$ and $D_{22}$ resp.):

$$D_x = D_{11} \cos^2 \alpha + D_{22} \sin^2 \alpha$$  \hspace{1cm} (16)

In the same reference, the relation is shown between $D_x$ and the diffusion coefficient of the matrix $D_r$ (fibres do not absorb moisture):

$$D_x = D_r \cdot (1 - v_f \cos^2 \alpha + (1 - 2(v_f/\pi)^{1/2}) \sin^2 \alpha)$$  \hspace{1cm} (17)

where $v_f$: fibre volume fraction

$\alpha$: angle between x-axis and fibre direction

In most cases $\alpha = 90^0$ which reduces eq.(17) to:

$$D_x = D_r \cdot 1 - 2(v_f/\pi)^{1/2}$$

Since the one-dimensional solution does not cover all diffusion conditions, several extensions of this solution have been proposed in the literature. For specimens with a significant thickness compared to length and width, Shen and Springer (ref.42) proposed a correction term for edge effects:

$$D = D_x \left( 1 + \frac{h}{D_{\frac{1}{2}}} + \frac{h}{D_{\frac{1}{2}}} \right)^2$$

where $D_x$, $D_y$, $D_z$: diffusion coefficients in x, y, z direction respectively.

---

**Diagram Description:**

- The diagram shows a cross-sectional view of a composite material with moisture entering from the top and fibre direction in the x-y plane.
- The diffusion coefficient $D_x$ is expressed in terms of $D_{11}$ and $D_{22}$.
- The angle $\alpha$ between the x-axis and fibre direction is shown.
- The correction term for edge effects includes terms involving $h$, $D_{1/2}$, and $D_{2/2}$.
For isotropic materials, eq.(18) reduces to:

\[ D = D_x \left( 1 + \frac{h}{l} + \frac{h}{n} \right)^2 \]  

(19)

Instead of using edge corrections, some authors (e.g. ref.43) used two or three-dimensional derivations of Fick's second law:

\[ \frac{\delta c}{\delta t} = D_x \frac{\delta^2 c}{\delta x^2} + D_y \frac{\delta^2 c}{\delta y^2} + D_z \frac{\delta^2 c}{\delta z^2} \]  

(20)

With the appropriate set of boundary conditions, the differential equation (20) can be solved:

\[ G = 1 - \frac{512}{\pi} \sum_{k=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} A^2 e^{-B^2 \pi^2 (D_x/h^2 + D_y/l^2 + D_z/n^2)} t \]

(21)

where \( A = (2k+1)(2n+1)(2p+1) \) \(^{-1} \)

\[ B = 1/A \]

The above solutions are applicable only if the diffusion coefficients and the boundary conditions are both independent of time and temperature. This assumption is reasonable for well-controlled laboratory experiments, but it can hardly be expected to be valid for a realistic environment. Among others, Weitsman (ref.44) proposed a time-dependent diffusion coefficient (temperature and therefore diffusion rate varies with time):

\[ D = D_0 \cdot h(t) \]

where \( h(t) = e^{-c/T(t)} \)

\[ T: \text{absolute temperature} \]

For this case, the eqs.(13) and (15) have to be modified:

\[ \frac{D_x \cdot t}{h^2} \quad \rightarrow \quad \frac{D_0}{h^2} \int_0^t h(s) \, ds \]

E.C. Edge (ref.45) proposed a solution for a time-dependent surface concentration. Using the earlier mentioned one-dimensional differential equation (9) in its time-dependent diffusivity configuration:

\[ \frac{\delta c}{\delta t'} = \frac{\delta^2 c}{\delta x^2} \]

(22a)

where \( t' = D(t) \delta t \)
The boundary condition eq.(11) is replaced by:

$$c_s = \sum_{i=0}^{N} c_i H(T-T_i)$$  \hspace{1cm} (22b)

where \( H \): Heaviside step function

For a one-dimensional solution, this results in:

$$c(x,T) = \sum_{i=0}^{N} f_i(x,T) H(T-T_i)$$  \hspace{1cm} (23)

where:

$$f_i(x,T) = c_i (1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-(2n+1)^2 \pi^2 (T-T_i)/h^2} \cos(2n+1) \pi x)}$$  \hspace{1cm} (24)

Although an extension of the basic equations towards time varying diffusion coefficients and/or surface concentrations looks very attractive, it is not a feasible solution to describe a continuously varying temperature and relative humidity condition as encountered in realistic environments. To avoid analytical limitations, finite difference approximations (ref.46,47) have been introduced in which the concentration distribution is calculated, step by step, as a function of the momentary temperature and the relative humidity. Since such a finite difference approach is not always possible, G.S. Springer (ref.48) examined possible similarities between realistic aircraft environments and laboratory tests performed in a constant relative humidity and temperature. He concluded that:

- A simple simulation of transient conditions by laboratory testing is not possible although the "steady state" moisture content (only attained after 10 to 20 years in a realistic environment) can be predicted within certain limits by laboratory tests.

Heaviside (1850-1925) introduced an 'operator' \( p \) to replace \( d/dt \) in a differential equation:

$$a_0 \frac{d^n x}{dx^n} + a_1 \frac{d^{n-1} x}{dx^{n-1}} + \cdots + a_{n-1} \frac{dx}{dt} + a_n x = 1 \quad (t>0)$$

becomes

$$a_0 p^n + a_1 p^{n-1} + \cdots + a_{n-1} p + a_n = 1$$

The solution of the above differential equation is:

$$x = 1/F(p) \cdot H(t)$$

where \( H(t) = 0 \quad (t<0) \)

$$= 1 \quad (t>0)$$
- Steady state condition is attained after 10 to 20 years in a realistic environment. After that, moisture distribution variations will be limited to a narrow layer near the exposed surface.

It should be noted that besides analytical and numerical solutions based on Fick's second law, also empirical relationships between absorption and both temperature and relative humidity have been developed, e.g. the hyperbolic tangent approximation by a.o. Mc. Kague (ref.49):

\[ M_t = M_i + (A \cdot RH - M_i) \cdot \tanh \left( \frac{4}{\pi} \left( \frac{D_t}{\pi} \right)^{\frac{1}{2}} \right) \]  

(25)

where \( M_t \): moisture content at time \( t \)
\( A \): absorption coefficient
\( RH \): relative humidity
\( D \): diffusion coefficient

In ref.(56), the hyperbolic tangent approximation (eq.25) is compared with the infinite series solution (eq.12) and a finite difference approximation. The authors found a very satisfactory similarity between the three methods in predicting the moisture content with increasing exposure time.

3.3: Moisture absorption of ARALL

Because of its specific built-up, an investigation of the moisture absorption of ARALL requires a different approach compared to composites:

- The aluminium sheets on the outer parts of the material act as diffusion barriers. Moisture absorption is only possible through the edges of the specimen.

- Different from carbon and glass fibres, the moisture absorption of aramid fibres is significant. Since the fibres are oriented unidirectionally there will be a difference in absorption rate parallel and perpendicular to the fibre direction.

These aspects require a two-dimensional solution of Fick's second law:

\[ \frac{\delta c}{\delta t} = D_y \frac{\delta^2 c}{\delta y^2} + D_z \frac{\delta^2 c}{\delta z^2} \]  

(26)

where \( D_y \): diffusion coefficient in fibre direction
\( D_z \): diffusion coefficient perpendicular to the fibre direction
\[ c_0: \text{initial condition} \]
\[ c_m: \text{equilibrium condition} \]

The boundary conditions \( c(y,z,t) \) for the prepreg layer between the two aluminium sheets are:

\[
\begin{align*}
c(y, z, 0) &= c_0 \\
c(0, z, t) &= c_m \\
c(1, z, t) &= c_m \\
c(y, 0, t) &= c_m \\
c(y, b, t) &= c_m \\
c(y, z, \infty) &= c_m \\
\end{align*}
\]

In ref.(50) the author solved eq.(26) which resulted in:

\[
\frac{c_m - c}{c_m - c_0} = \frac{16}{\pi^2} \sum_{n=0}^{\infty} A^2 \sin(2m+1)\pi y \sin(2n+1)\pi z \frac{1}{b} e^{-B^2 \pi^2 (D_y/1^2 + D_z/b^2) t} \\
\text{where } A = (2n+1) \cdot (2m+1)^{-1} \\
B = 1/A
\]

(28)

or, written in moisture content:

\[
\frac{M_m - M}{M_m - M_0} = \frac{64}{\pi^4} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} A^2 e^{-B^2 (D_y/1^2 + D_z/b^2) \pi^2 t} \\
\text{where } l: \text{length of the specimen in fibre direction} \\
b: \text{length of the specimen perpendicular to the fibre direction} \\
A = (2n+1) \cdot (2m+1)^{-1}
\]

(29)

In both eqs.(28) and (29), the diffusion coefficients parallel \( (D_y) \) and perpendicular \( (D_z) \) to the fibre direction have to be available before moisture profiles \( (c=f(y,z,t)) \) or moisture contents \( (M=f(t)) \) can be calculated. According to the Arrhenius equation, the diffusion coefficients are a function of the environmental temperature:

\[
D = D_0 e^{-A/RT}
\]

where \( D_0, A \): constants

\( T \): absolute temperature

\( R \): universal gas constant

Since the maximum weight gain of a specimen is directly related to the environmental relative humidity (chapter 3.4), an experimental programme to obtain the whole range of diffusion coefficients has to include both
variations on temperature and relative humidity.

3.4: Experiments

The diffusion coefficients, necessary to calculate moisture profiles or moisture contents, are mostly obtained by carrying out weight gain tests at different temperatures and relative humidities. Because of the necessity of a two-dimensional approach, the relation between diffusion coefficients ($D_y$ and $D_z$) and moisture pick-up is deviating from the one normally used for composites. This problem was analysed in ref.(50) which led to:

$$\frac{(D_y)^{\frac{1}{2}}}{1} + \frac{(D_z)^{\frac{1}{2}}}{b} = \pi^{\frac{1}{2}} \cdot \frac{M}{4 M_m} \cdot \frac{M}{(t)^{\frac{1}{2}}}$$

(30)

where $M_m$: maximum moisture content

For each combination of temperature and relative humidity, an $M/t^{1/2}$ curve can be experimentally obtained. However from eq.(30) it will be clear that a single $M/t^{1/2}$ result is not sufficient to solve the equation (2 unknowns: $D_y$ and $D_z$). This problem is solved by introducing two specimen configurations for each set of temperature and relative humidity. The two configurations (different l and b) result in two weight gain curves and as a result, eq.(30) can be solved.

In eq.(30), the presence of the maximum moisture content $M_m$ is a complicating factor since theoretically it can be obtained only after an infinite exposure period ($t = \infty$). Fortunately, $M_m$ is a function of the relative humidity only, independent of the test temperature. In ref.(51) the following relation between $M_m$ an relative humidity was introduced:

$$M_m = a \cdot RH^b$$

(31)

where $RH$: relative humidity

$a, b$: constants

Again, the constants a and b have to be experimentally determined. Most investigators (e.g. ref.52) found b to be approximately unity.

The test programme performed to obtain the diffusion properties of ARALL included the following combinations of relative humidity and temperature:
<table>
<thead>
<tr>
<th>Test series A</th>
<th>Test series B</th>
</tr>
</thead>
<tbody>
<tr>
<td>in distilled water</td>
<td>in humid air</td>
</tr>
<tr>
<td>T(°C)</td>
<td>RH (%)</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>60</td>
<td>20 and 50</td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

The specimens of test series A were simply submerged in distilled water at the specified temperature. The specimens of test series B were exposed above a saturated salt solution in a closed chamber. The salt solutions used in the test programme are shown in table 1 (ref.53). The specimens of test series A were wiped dry before weighing, carried out on a Mettler balance (accuracy of 10^-4 gr). The specimen dimensions are shown in fig.(3). Two fibre orientations (fibres in length and width direction) have been introduced to obtain two different specimen configurations. As mentioned before, this is necessary to solve eq.(30). To avoid corrosion problems during exposure, the specimens were thoroughly pretreated including degreasing, pickling and chromic acid anodising. To assure a stabilized dry weight (before starting the experiment) all specimens were dried in an oven. For every variable (combination of temperature, relative humidity and fibre orientation), six specimens were used.

Since a large amount of data had to be compiled and stored during the experiments, data collection was fully computerised (ref.53). The computer programme offered the following possibilities:

- monitoring the weight gain of each individual specimen and/or groups of specimens (6 specimens per variable)

- prediction of the diffusion coefficients after each weight gain measurement

- plotting of weight gain curves and/or moisture profiles after each weight gain measurement
3.5: Results of the experimental programme

3.5.1: Weight gain curves

A survey of the weight gain curves is shown in figs. 4 and 5 and table 2. Several observations can be made:

- The linearity of the $M-t^{1/2}$ curves is highly satisfactory for all temperatures and relative humidities (see correlation coefficients in table 2). It proves that the weighing accuracy was sufficient.

- For all temperatures and relative humidities, the absorption rate of specimens with fibres in the length direction is systematically smaller than for specimens with fibres in the width direction. This difference can be explained by the absorption behaviour of aramid fibres and the orientation of these fibres in the specimens. For specimens with the fibres in the width direction, the number of fibre ends, exposed to the environment, is 5 times larger than for specimens with fibres in the length direction (fig.3). Because moisture diffusion in the fibres occurs more rapidly** than in the matrix material (epoxy) the trend observed should be expected. The effect of the smaller absorption rate of specimens with fibres in the length direction (as compared with specimens with fibres in the width direction) is even more pronounced if the moisture gain of aramid fibres perpendicular to the fibre axis is examined***. Perpendicular to the fibre direction, the moisture gain is hampered by the presence of the fibres. This effect is more pronounced for specimens with fibres in the length direction. This phenomenon will be further discussed in chapter 3.8.

- The expected influence of the temperature is present for all environments (increasing diffusion rate with increasing temperature).

- The following maximum moisture contents were found:

  $$M_m = 1.58\% \text{ (distilled water)}$$
  $$0.47\% \text{ (80\% relative humidity)}$$
  $$0.28\% \text{ (50\% relative humidity)}$$
  $$0.27\% \text{ (30\% relative humidity)}$$

As mentioned before, the maximum moisture content should be independent of the test temperature. The difference between the maximum moisture content at 80% relative humidity and after distilled water exposure is unexpectedly large. However, it should be noticed that the 1.5% is found for a $100^\circ\text{C}$ distilled water exposure ***. It is well possible that, because of the high temperature, chemical changes in the matrix (or at the fibre/matrix interface) did occur which can highly

** footnotes on page 20
affect the maximum moisture content. It is therefore expected that the 1.5% maximum moisture content, found for a distilled water exposure is too high. In ref.(51) a relation was shown between $M_m$ and the relative humidity:

$$M_m = a \cdot RH^b$$  (31)

where RH: relative humidity

As mentioned before, some authors (e.g. ref.52) found $b$ to be approximately unity. If the ARALL data are examined (fig.6), there is definitely no linear relationship between $M_m$ and RH. However, a more extensive experimental programme is necessary to obtain a reliable relation between $M_m$ and RH for ARALL.

- All the results are presented as the weight gain of ARALL itself although only the prepreg absorbs moisture. For the calculation of the diffusion coefficients the two possible approaches (measuring weight gain ARALL (Al.+prepreg) or weight gain prepreg only) lead to identical results because $M/M_m$ in eq.(30) has the same value in both cases. If the maximum moisture content is calculated in relation to the prepreg itself, the following data are obtained:

$$M_m = 11.6\% \text{ (distilled water exposure)}$$
$$3.6\% \text{ (80\% relative humidity)}$$
$$2.2\% \text{ (50\% relative humidity)}$$
$$2.1\% \text{ (30\% relative humidity)}$$

As mentioned previously, the maximum moisture content after distilled water exposure is much higher than could be expected from literature data; the three other results are in agreement with literature data (e.g. ref.51).

- The weight gain tests were duplicated for the exposure of 100°C distilled water (series A). As can be seen in table 2, the test results are quite reproducible (deviation <10% for both fibre orientations).

- The large influence of the environmental temperature on the diffusion process was, by accident, clearly demonstrated in the 100°C exposure of test series A (fig.7). Because of accidental damage to the heating system, for two days the temperature dropped to 20°C. This low temperature period could be easily detected in the weight gain curve (fig.7). After restoring the initial temperature level of 100°C, the diffusion rate again increased up to its original level.

- The influence of cracks on the weight gain is clearly shown in fig.8. After 30 days a steep increase of the weight gain was observed which was accompanied by the
occurrence of small cracks at the adherend/adhesive interface. The cracks occurred most probably because of the presence of an improper oxide layer.

** Different from both glass and carbon fibres, the moisture gain of aramid fibres is significant and mostly exceeds the moisture gain of presently used epoxy systems. In ref.(54), the diffusion coefficient of aramid fibres in longitudinal direction was found to be approximately $9.8 \times 10^{-7} \text{ cm}^2/\text{sec}$ (96% RH, 20°C) which is approximately 1000x larger than found for common epoxy systems.

**2 In ref.(54), for diffusion normal to the fibre, a diffusion coefficient of $4.2 \times 10^{-13} \text{ cm}^2/\text{sec}$ (96% RH, 20°C) was found which is about 1000x smaller than similar diffusion coefficients for epoxies.

**3 The number of data on $M_m$ is very much limited because the time to reach saturation (approximated by $M=0.99M_m$) is extremely long at lower temperature levels. In ref.(50) an equation for the saturation period is presented:

$$t_s = \frac{1}{\pi^2} \left( \frac{D}{V^2} + \frac{D}{Z^2} \right) \left( 0.42 + \ln(1 - M/M_m) \right)$$  \hfill (32)

In ref.(50) it was shown that for the specimen configuration used in the experiments (aramid fibres in width direction, $l=10\text{mm}$, $b=50\text{mm}$) and exposed to distilled water:

- saturation at 100°C will take 115 days
- 60°C will take 1490 days
- 40°C will take 4650 days

For this reason the measurements on $M_m$ had to be limited to higher temperature exposures.
3.5.2: diffusion coefficients and moisture profiles

The diffusion coefficients parallel \( (D_Y) \) and perpendicular \( (D_Z) \) to the fibre direction have been calculated for the different fibre orientations (fibres in width or length direction), temperature levels and relative humidities. The results obtained with eq.(30) are shown in table 3. Some remarks can be made:

1: There is a significant difference in diffusion rate parallel and perpendicular to the fibre orientation \( (2.15 < D_Y/D_Z < 3.60) \). These results emphasize the important role of the fibres in the diffusion process.

2: Distilled water exposure results in relatively low diffusion rates, both parallel and perpendicular to the fibre direction. In the literature it was already recognized that, compared to a 100% relative humidity environment, the moisture pick-up of specimens exposed to distilled water is considerably lower. Also the most probably overestimated \( M_m \) value of distilled water exposure results in lower diffusion coefficients. If, as a comparison, a linear relation is used between \( M_m \) and relative humidity, 100% RH should result in a maximum moisture content of about 0.57% (4.46% if only the prepreg is considered). Using this more realistic value of \( M_m \) results in:

<table>
<thead>
<tr>
<th>temperature (^{0}\text{C})</th>
<th>(D_Y) (cm(^2)/sec)</th>
<th>(D_Z) (cm(^2)/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\times 10^{-9})</td>
<td>(\times 10^{-9})</td>
</tr>
<tr>
<td>20</td>
<td>167.0</td>
<td>58.0</td>
</tr>
<tr>
<td>40</td>
<td>722.0</td>
<td>296.0</td>
</tr>
<tr>
<td>60</td>
<td>2255.0</td>
<td>656.0</td>
</tr>
</tbody>
</table>

Compared with the results of table 3, it is clear that these diffusion coefficients fit much better with the different relative humidity results.

3: For test series A (distilled water exposure) and B (humid air exposure), the validity of the Arrhenius equation is examined for the different temperature levels:

\[
D = D_0 \cdot e^{-A/RT}
\]

or \( \ln D = \ln D_0 - A/RT \)

In fig. 9 the diffusion coefficients are plotted on a temperature scale \((\ln D - 1/T)\). The following features
are remarkable:

- the linearity obtained for both $D_y$ and $D_z$ is striking
- the activation energy $A$ (slope of the curves) seems to be independent of the type of environment (distilled water or humid air)
- the difference between $D_y$ and $D_z$ is almost identical for the two environments

**moisture profiles**

Moisture profiles can be calculated by using eq. (28):

$$\frac{c_m - c}{c_m - c_0} = \frac{16}{\pi^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{A^2 \sin((2n+1)\pi y) \sin((2m+1)\pi z) \cdot e^{-B^2 \pi^2 (D_y/1^2 + D_z/b^2) t}}{b}$$

where $A = \{(2n+1)(2m+1)\}^{-1}$

$$B = 1/A$$

(28)

In a computer programme, a sufficient convergence was achieved for $n=m=8$ (eq.28). Some moisture profiles calculated as a function of specimen geometry (fibre orientation), exposure period and temperature are shown in the figures 10a to 10d. As an example, the weight gain after increasing exposure periods is shown in these figures for a 50% relative humidity, 50°C environment. As mentioned for the boundary conditions (eq.27), the edges of the specimen have, immediately after exposure, the maximum moisture content. With increasing exposure period, the whole specimen is gradually reaching the same equilibrium level.
3.6: A theoretical comparison between the moisture absorption of ARALL and carbon and aramid composites

The moisture absorption of ARALL, as a function of temperature and relative humidity has been discussed in the previous section. In this section a theoretical comparison will be made between the moisture absorption in ARALL and two composite materials:

CFRP: carbon fibre reinforced plastic
AFRP: aramid fibre reinforced plastic

Because through-the-thickness diffusion is possible in the composites, the 3-dimensional version of Fick's second law (eq.20) and the solution eq.(21) have to be used. In view of the theoretical nature of the comparison some simplifying assumptions are made:

1: The same matrix system (i.e. the ARALL matrix system) applies to all three materials**. Moreover the composites are supposed to be unidirectional. As a result, the diffusion coefficients $D_y$ and $D_z$ as found for ARALL (table 3) have some meaning for the composites also:

ARALL: $D_x = 0$ because the aluminium sheets are perfect diffusion barriers.

AFRP: The same $D_y$ and $D_z$ of ARALL are applicable. However, $D_x \neq 0$. Because the x-direction is also perpendicular to the fibres $D_x = D_z$.

CFRP: In contrast with the aramid fibres, carbon fibres do not absorb moisture. As a first approximation all three diffusion coefficients are supposed to be equal to $D_z$ of ARALL ($D_x = D_y = D_z$).

2: Calculations are made for (arbitrarily) selected dimensions of the specimen:
   a (length in fibre direction): 50mm
   b (length perpendicular to the fibre direction): 50mm
   h (thickness of the specimen): two values 1mm, 10mm

For the ARALL specimens, the aluminium sheets are supposed to be infinitely thin in order to have the same amount of matrix material as for the composites.

3: The infinite series $\sum_{n=0}^\infty \sum_{m=0}^\infty \sum_{k=0}^\infty$ in eq.(21) are limited to: $\sum_{n=0}^{10} \sum_{m=0}^{10} \sum_{k=0}^{10}$

** footnote on next page
(which explains small deviations from zero of \((M-M_0)/(M_m-M_0)\) at \(t=0\) in fig. 11).

**Results**

In figs. 11 and 12, some comparisons between ARALL, CFRP and AFRP are shown for an environmental temperature of 60\(^\circ\)C and for a specimen thickness of 1 and 10 mm respectively. The diffusion coefficients \(D_x, D_y\) and \(D_z\) used in the calculations are presented in Table 4. As mentioned in assumption 1, these coefficients are directly related to the diffusion coefficients obtained in chapter 3.5.

The following remarks can be made:

- For thin specimens (\(h<<b\) and \(h<<l\); see fig. 11), the absorption rate of ARALL is negligible compared to the absorption rate of CFRP and AFRP. At 60\(^\circ\)C, saturation of the composites is reached within a limited exposure period (70 days); no differences can be found between the two composite systems. It is obvious and clearly demonstrated by fig. 11 that for thin specimens the absorption process is totally dominated by the diffusion in \(x\)-direction, a diffusion direction which is absent for the ARALL material. Since absorption through the edges has only a very limited effect on the total moisture pick-up, no influence can be found of the absorption properties of the fibres.

- For thicker specimens (\(h=10\) mm, fig. 12) diffusion through the edges becomes significant. This increased influence on the absorption process of the edges has two major effects:

1: A small difference in absorption rate between CFRP and AFRP; the moisture absorption rate of CFRP is slightly lower than the absorption rate of AFRP, due to the absence of moisture absorption by the carbon fibres.

2: The advantage of ARALL of having a diffusion barrier in \(x\)-direction becomes less important. Still the absorption rate of ARALL is superior compared to AFRP and CFRP.

**The ARALL matrix system is much more expensive than the resins used for composites. Some exploratory adhesion tests indicated excellent results for a composite of aramid or carbon fibres with the ARALL matrix system.**
3.7: Influence of diffusion retardation by protective coatings

In the previous sections it has been shown that the moisture absorption of ARALL is very limited compared to composite materials. Still it may be attractive to further decrease the absorption rate by introducing a protective coating with a very low diffusion coefficient. For ARALL, in contrast to composites, only the edges have to be protected. First the beneficial influence of a coating will be examined theoretically. Experiments are carried out also.

3.7.1: Finite difference method

The following model will be adopted:

The specimen dimension is infinite in z-direction. Because no moisture gradients will occur in the y-direction, the problem is purely 1-dimensional.

The analytical solutions presented in the previous sections do not apply in this case (two different materials with different diffusion coefficients). Therefore a numerical approach is used, in ref.(55) presented as the finite difference method. The differential equation:

$$\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2}$$

is replaced by the finite difference expression:

$$\frac{c_{n}^{i+1} - c_{n}^{i}}{dt} = D \frac{c_{n+1}^{i} - 2c_{n}^{i} + c_{n-1}^{i}}{(dx)^2}$$  \hspace{1cm} (36)

where superscripts \(i\) and \(i+1\) designate time steps

subscripts \(n\), \(n-1\), \(n+1\) designate grid point locations

The finite difference method is demonstrated in fig.13 for an illustrative model with a low-diffusion layer (material II) between a surface layer (material I) and a substrate of the same material. Locations of grid
Eq. (36) is rewritten as:

\[
\frac{c_{n+1}^i}{c_n^i} = \frac{D}{(dx)^2} \cdot (c_{n+1}^i - 2c_n^i + c_{n-1}^i) \quad (37)
\]

or in matrix notation:

\[
c(i+1,j) = c(i,j) + \frac{D}{(dx)^2} \cdot \{c(i,j+1) - 2c(i,j) + c(i,j-1)\}
\]

where:
- \(i\): time coordinate
- \(j\): length coordinate
- \(dt\): time step
- \(dx\): length step (distance between two grid points)

According to eq. (38) the new concentration of grid point \(j\) (at time \(i+1\)) is found by examining the concentration of the grid points \(j-1, j, j+1\) at time \(i\). As for the analytical solution it is assumed that:

at \(t=0\) (\(i=1\)): edge of the specimen (\(j=1\)) has the equilibrium concentration \((c_{\text{edge}} = c_m)\)

With increasing time periods, more grid points get a concentration unequal to zero and continuously the concentration of every grid point will increase until full moisture saturation has been reached. In fig. 13 two solutions are presented, one for the model with a low-diffusion layer (material II with \(D_2 = D_1/10\)) and a second one for a homogeneous material (\(D_2 = D_1\)). For the model with the two materials, eq. (38) is subdivided in two equations having different diffusion coefficients:

\[
c(i+1,j) = c(i,j) + \frac{D_1}{(dx)^2} \cdot \{c(i,j+1) - 2c(i,j) + c(i,j-1)\} \quad (39a)
\]

\(1 < j < (L_1/dx) + 1\) (see fig. 13')

\[
(L_2/dx) + 2 < j < (L_1/dx) + 1 \quad (\text{see fig. 13})
\]

\[
c(i+1,j) = c(i,j) + \frac{D_2}{(dx)^2} \cdot \{c(i,j+1) - 2c(i,j) + c(i,j-1)\} \quad (39b)
\]

\(L_1/dx) + 2 < j < (L_2/dx) + 1 \quad (\text{see fig. 13'})

Depending on the grid point location, eq. (39a) or (39b) has to be used to calculate at a time \(i+1\) the concentration \(c(i+1,j)\). For the two-material case it results in lower concentrations compared with the single material solution (dotted lines in fig. 13').
3.7.2: Results

Before the finite difference method was used for a combination of two dissimilar materials, the validity of the method was checked for a single material. The results obtained with the finite difference method (eq.38) should be identical with the analytical solution of eq.(12) for a single material.

Using the stability requirement as proposed in ref.(55),

\[ dt < \frac{dx^2}{4D} \]  \hspace{1cm} (40)

the agreement between the numerical and analytical results (fig.14a to d) is excellent for smaller exposure periods \( t < 11.5 \) days but starts to deviate at larger exposure periods. The deviation from the analytical solution at larger exposure periods is due to a numerical problem at the other edge of the specimen opposite to the free edge.

In eq.(38), also for the last grid point \( x = 1 \text{mm}, j=11 \), \( c(i,j+1) \) has to be inserted, which concentration is always zero (grid point \( j+1 \) is at that location outside the specimen thickness). At every time step, the concentration gradient will diminish, but since \( c(i,j+1) \) remains zero, the maximum concentration content in the specimen will correspond to a constant gradient and thus become a straight line between \( c/c_m \) at the free edge and \( c/c_m \) at the grid point just outside the opposite edge. It can be checked in eq.(38) that for a straight line:

\[ c(i,j+1) + c(i,j-1) = 2c(i,j) \]

and therefore \( c(i+1,j) = c(i,j) \)

This is of course an inaccurate approximation of the maximum moisture content. The numerical problem can be solved by assuming symmetry at the opposite edge (grid point \( n+1 \) has the same concentration as grid point \( n-1 \)).
For the moisture profiles, this numerical adjustment has been introduced. In fig.14d the results obtained with this adjusted solution are also plotted (dotted lines). The agreement with the analytical solution is excellent, also for longer exposure periods.

The beneficial effect of a coating will now be demonstrated by considering a base material (material 1) with a thickness of 4.5mm with a surface coating (material 2) with a thickness of 0.5mm (total thickness: 5mm). The diffusion coefficient of the base material is $D_m$ ($D_m = 1.0 \times 10^{-7}$ mm²/sec), while for the coating two values will be adopted, $D_C = D_m/10$ and $D_C = D_m/100$ respectively. Calculations are also made for $D_C = D_m$, i.e. for a homogeneous material without a coating. In fig.15, the moisture absorption of the coated material and the uncoated material are compared for four different exposure periods. The beneficial effect of the coating is significant, especially when $D_C = D_m/100$. By summing the areas under the curves, the total moisture content in the base material can be calculated and compared for the coated and the uncoated case. The results are shown in table 5. It is clear that the retardation of the moisture absorption due to a coating can be important.

3.7.3: Experiments

The effect of a coating on the moisture absorption of ARALL will be tested by means of weight gain tests. A comparison will be made between the absorption behaviour of an uncoated ARALL specimen and specimens covered with different kinds of coatings. A first initial test was not very successful. Some weight gain experiments were performed on coated (polyurethaaen coating Aerodur Finish C21/100) and uncoated specimens using a distilled water environment at 50°C and 80°C respectively. As for the initial weight gain tests, 2 fibre orientations were chosen to obtain the diffusion coefficient parallel and perpendicular to the fibre orientation. Before applying the coating, two different pretreatments of the free edges were introduced:

- a simple degreasing process (room temperature)
- a degreasing ($80^\circ C$ for 30 min) and pickling ($60^\circ C$ for 20 min) process

The number of variables is therefore three:

- uncoated specimen
- coated specimen, pretreatment 1
- coated specimen, pretreatment 2

For every variable and every environment, 6 specimens were used. A survey of the weight gain results is shown in fig.16. These results are not too encouraging. The specimens with a protective coating absorbed as much as, or even more moisture than the uncoated specimens, independent of the pretreatment used before coating. A closer examination of the coated surfaces showed on localised spots moisture bubbles in the coating (fig.17) which caused the higher moisture pick-up. Most probably, the curing of the coating was incomplete which resulted in the porous structure. Since possible retardation of the moisture pick-up can be extremely large (section 7.2) because of the use of protective coatings, it is certainly worthwhile to examine other coatings and/or improve the coating process itself to obtain the theoretical gains shown in section 3.7.2.
3.8: Moisture profile of ARALL

In a previous section (3.5) the diffusion coefficients $D_y$ (parallel to the fibre direction) and $D_z$ (perpendicular to the fibre direction) were introduced. If absorption by fibres and matrix are considered separately, it is obvious that one diffusion coefficient parallel and another one perpendicular to the fibre direction is incorrect, especially if the moisture distribution (profile) is considered. For more accurate moisture profiles on a microscopic level the different absorption rates of fibres and matrix materials have to be considered. This will be done in the sections below.

3.8.1: Diffusion parallel to the fibre direction

In chapter 3.3 the diffusion coefficient in the fibre direction was called $D_y$. Since aramid fibres absorb moisture, $D_y$ will be a combination of two diffusion coefficients:

- $D_m$: diffusion coefficient of the matrix
- $D_{f1}$: diffusion coefficient of the fibre in longitudinal direction

![Diagram](image)

The relation between $D_y$, $D_m$, and $D_{f1}$ can be found using the rule of mixtures for the moisture contents of the matrix and fibres respectively. The following relation is always valid:

$$M_{t1} = \frac{M_{f1} \cdot W_f + M_{m1} \cdot W_m}{W_f + W_m}$$  \hspace{1cm} (41)

where $M_{t1}$: weight gain of prepreg (fibres+matrix) at time $t_1$

- $M_{f1}$: weight gain of the fibres at time $t_1$
- $M_{m1}$: weight gain of the matrix at time $t_1$
- $W_f$: dry weight of the fibres
- $W_m$: dry weight of the matrix

For the prepreg used in ARALL, the density of matrix and aramid fibres is almost identical and therefore eq.(41) can be written as:
\[ M_{t1} = \nu_f M_{f1} + \nu_m M_{m1} \]  

(42)

where \( \nu_f \): fibre volume content  
\( \nu_m \): matrix volume content

In chapter 3.4 the relation between the diffusion coefficients and the moisture content for a one-dimensional model was shown to be:

\[ \frac{D^N}{h} = \frac{\pi^{3/2}}{4M} \cdot \frac{M}{t^N} \]  

(43a)

or

\[ M = \left( \frac{D \cdot t}{\pi} \right)^{3/2} \cdot \frac{4M}{h} \]  

(43b)

Eq. (42) thus becomes:

\[ \frac{D_{P}^N \cdot t}{\pi}^{3/2} \cdot \frac{4M_{MP}}{h} = \nu_f \left( \frac{D_{f}^N \cdot t}{\pi} \right)^{3/2} \cdot \frac{4M_{MF}}{h} + \nu_m \left( \frac{D_{m}^N \cdot t}{\pi} \right)^{3/2} \cdot \frac{4M_{MM}}{h} \]  

(44)

where
\( D_P \): diffusion coefficient of prepreg (=\( D_y \))  
\( D_f \): diffusion coefficient of fibres  
\( D_m \): diffusion coefficient of matrix  
\( M_{MP} \): maximum moisture content of prepreg  
\( M_{MF} \): maximum moisture content of fibres  
\( M_{MM} \): maximum moisture content of matrix

For the maximum moisture content, eq. (42) is also valid:

\[ M_{MP} = \nu_f M_{MF} + \nu_m M_{MM} \]

For ARALL, the fibre volume content is 50% (\( \nu_f = \nu_m = 0.5 \)) and eq. (44) reduces to:

\[ D_y^{1/2} \cdot (M_{MF} + M_{MM}) = D_f^{1/2} \cdot M_{MF} + D_m^{1/2} \cdot M_{MM} \]  

(45)

In the literature some data are available concerning \( D_m \), \( M_{MF} \) and \( M_{MM} \) (e.g. ref. 54):

\[ D_m = 5.0 \cdot 10^{-8} \text{ mm}^2/\text{sec} (20^0 \text{C}, 75\% \text{ RH}) \]

\[ M_{MM} = 2.0\% (20^0 \text{C}, 75\% \text{ RH}) \]

\[ M_{MF} = 4.0\% (20^0 \text{C}, 75\% \text{ RH}) \]

Using eq. (45) and the data obtained for \( D_y \) (table 3), an estimation is possible of the diffusion coefficient of
the aramid fibres in longitudinal direction (D_{f1}):

\[ D_y = 19.5 \times 10^{-8} \text{ mm}^2/\text{sec} \ (20^0\text{C}, 80\% \text{ RH}) \]

the result is: \( D_{f1} = 30.3 \times 10^{-8} \text{ mm}^2/\text{sec} \ (20^0\text{C}, 80\% \text{ RH}) \)

Compared with the diffusion coefficient of the matrix, the diffusion rate along the fibres is approximately 6x faster, which is a much smaller difference than expected from ref.(54) \((D_{f1} = 1000xD_m).\)

The above discussion assumes that diffusion between the fibre and the surrounding matrix does not occur. In ref.(54) it was indeed found that the diffusion rate through the fibre surface is about 1000x smaller than the diffusion rate in a typical matrix. Disregarding the diffusion through the fibre surface, the moisture profile in the matrix and fibre can be compared by using the finite difference method (eq.38) or the analytical solution (eq.12). In fig.18 the moisture profiles of matrix and fibre (longitudinal direction) are compared for two exposure periods. As could be expected from the difference in diffusion coefficients, the amount of absorbed moisture is significantly larger for the fibres than for the matrix. It should also be recognized that the moisture profiles are plotted as a function of \( c/c_m \) and not as a function of the concentration \( c \) itself. Since the maximum concentration of the fibres is larger than the one of the matrix \((M_{mf} = 2M_{mm})\), the differences in concentration gradients as shown in fig.18 will be larger if plotted as a function of the concentration itself.

3.8.2: diffusion perpendicular to the fibre direction

The diffusion coefficient perpendicular to the fibre direction \( D_z \), defined and calculated in chapter 3.3 is, just like \( D_y \), a kind of an average parameter for the diffusion rate perpendicular to the fibres. On a microscale, the concentration distribution will be significantly affected by the positioning of the fibres in the matrix and by the difference in diffusion coefficients of fibres and matrix.

First, as an example, the influence of a single fibre on the moisture profile will be shown. In this case, two diffusion coefficients are of interest:

- \( D_m \): diffusion coefficient of the matrix
- \( D_{fp} \): diffusion coefficient of the fibres perpendicular to the fibre length
As mentioned in ref. (54), £fr is considerably smaller than £m (as a first approach £fp = £m/1000). For this situation no straightforward analytical solution is available. Therefore, again the finite difference approach is used. Because of the presence of the fibre (and its different diffusion coefficient), the diffusion orientation will be two-dimensional. As a consequence eq. (37) has to be extended to a 2-dimensional solution:

\[
\frac{\delta c}{\delta t} = D \left( \frac{\delta^2 c}{\delta x^2} + \frac{\delta^2 c}{\delta z^2} \right)
\]

![Diagram showing moisture absorption and grid points](image)

The finite difference expression of this 2-dimensional problem is:

\[
\frac{c_{i+1,j,k} - c_{i,j,k}}{dt} = D \left( \frac{c_{i,j+1,k} - 2c_{i,j,k} + c_{i,j-1,k}}{(dx)^2} + \frac{c_{i,j,k+1} - 2c_{i,j,k} + c_{i,j,k-1}}{(dz)^2} \right)
\]

where
- \(dt\): time interval
- \(dx\): length interval in x-direction
- \(dz\): length interval in z-direction
- \(D\): diffusion coefficient
- superscript \(i\): time step
- subscript \(j,k\): grid point location in \(x\) and \(z\) directions respectively

In matrix notation eq. (46) becomes:

\[
c(i+1,j,k) = c(i,j,k) + D\cdot dt \cdot (A + B)
\]

\[
A = \frac{(c(i,j+1,k) - 2c(i,j,k) + c(i,j-1,k))}{(dx)^2}
\]

\[
B = \frac{(c(i,j,k+1) - 2c(i,j,k) + c(i,j,k-1))}{(dz)^2}
\]

As for the finite difference approach used in chapter 3.7 the computer programme for every grid point location \((j,k)\) checks whether or not the point is situated in the matrix or in the fibre. It must be noticed that the fibre/matrix interface is circular while square grid elements are used. However, if the elements are sufficiently small compared to the fibre radius, the deviations near the boundary will be limited. The
distinction between fibre and matrix is based on:

For a fibre $i$, situated arbitrary in the matrix, the fibre/matrix boundary can be easily described using the local coordinates $K_i, L_i$:

![Diagram](image)

To the interior of the fibre belong all grid points with:

$$K_i^2 + L_i^2 < R_i^2$$  \hspace{1cm} (48)

with $K_i = x - L_{1i}$

$L_i = z - L_{2i}$

eq.(48) can be written in the global coordinate system which results in:

$$x(x-2L_{1i}) + z(z-2L_{2i}) < R_i^2 - L_{1i}^2 - L_{2i}^2$$  \hspace{1cm} (49)

For every fibre the right part of eq.(49) is a constant. For each grid point $(x,z)$, eq.(49) is checked, and depending on the result, the diffusion coefficient of the matrix or the fibre is used in eq.(47). In the calculations the grid point distance is equal for the $x$ and $z$ direction ($dx = dz$).

As an example, the influence of one single fibre on the moisture profile is shown with varying exposure periods in the fig.19. The fibre is situated in the centre of the specimen and has a small diffusion coefficient compared to the matrix ($D_m = 1000xD_{fp}$). As can be seen in this figure, the distortion of the moisture profile due to the presence of the fibre increases with increasing exposure period.

A more realistic impression of the influence of the fibre positioning and radial fibre diffusion coefficient $D_{fp}$ can be obtained by introducing more fibres in the matrix. To emphasize the effect of fibre positioning, two extreme cases will be examined:
The diffusion coefficient of the matrix is chosen to be the same through all calculations. A representative value for the matrix diffusion at average environmental temperatures is adopted: $D_m = 2.5 \times 10^{-8}$ mm$^2$/sec. Since a reliable diffusion coefficient in radial fibre direction is not known for aramid fibres (only one, rough approximation is known from the literature by the author: $D_{fp} = D_m/1000$, ref.54), three different radial fibre diffusion coefficients are considered for both fibre positionings:

$$D_{fp} = \frac{D_m}{10}$$
$$= \frac{D_m}{100}$$
$$= \frac{D_m}{1012} \quad (D_{fp} = 0)$$

For an exposure period of 116 days, the results for the two fibre positionings (case I and II) and the three different radial fibre diffusion coefficients are shown in the figs. 21 and 22. In fig. 20, the concentration gradients are shown for a single matrix (no fibres) using the same specimen dimensions, matrix diffusion coefficient and exposure period. As for the previous series of moisture profiles, the fibre positionings in the matrix are shown by their grid points. It is clear that the influence of the first fibre on the moisture profiles is large, especially if the radial fibre
The diffusion coefficient is low. For $D_{fp} = 0$, the moisture is almost not able to pass the first fibre. Because of the decisive influence of the radial fibre diffusion coefficient on the moisture profiles, the differences in moisture gradients because of fibre positioning are limited (compare fig. 21 with fig. 22). The influence of the fibre positioning is shown in greater detail in the figures 23 and 34 by presenting the moisture distribution along two cross-sections just behind the fibres. The $c/c_m$ scale in these figures is amplified as compared to the preceding figures.

Although the total amount of moisture present at these cross-sections is small, the general impression is valid, also for much larger amounts of absorbed moisture at longer exposure periods (a numerical evaluation of longer exposure periods is perfectly possible, but it consumes a lot of computer time without resulting in different trends as observed for an exposure period of 116 days; the evaluation is therefore limited to that exposure period). In fig. 23, the influence of fibre positioning on the concentration distribution is very clear. For case I, the highest concentration level is present near the edges while for case II the highest concentration is situated in the centre of the specimen. The differences for the three radial fibre diffusion coefficients are increasing with decreasing $D_{fp}$. At cross-section BB (behind the third fibre, fig. 24), the concentration distribution of case I and II looks similar, which could be expected from the identical positioning of the third fibre for both cases. The influence of the fibre positioning on the amount of absorbed moisture at those cross-sections can be found by integrating the areas under the curves of figs. 23 and 24. These results are shown in table 6. Only if a large difference between matrix and radial fibre diffusion coefficient is present, case II will result in a significantly lower moisture content. For $D_{fp} = D_m/10$, the differences between case I and case II remain limited.

If one observes the large influence of the radial fibre diffusion coefficient on the moisture content (compare the figs. 20, 21 and 22) it should be clear that, for obtaining the experimentally determined $D_z = D_m/3$, $D_{fp}$ must be larger as stated in ref. (54) (for $D_{fp} = V_m/1000$, $D_z$ should be much smaller than $D_m$). It is therefore expected that:

$$D_m/100 < D_{fp} < D_m/10$$

will be a much more realistic difference between the radial fibre diffusion coefficient and the matrix diffusion coefficient.
3.9: Discussion

3.9.1: The finite difference method vs the analytical method

Before discussing the diffusion results obtained for ARALL, it is interesting to examine the usefulness of the two approaches introduced in the previous chapters, namely an analytical and a finite difference solution method. It has been demonstrated that for a single material (with a known diffusion coefficient) both approaches result in identical results. However, where the analytical solution is straightforward and always accurate, the accuracy of the numerical method is strongly depending on the relation between time periods, grid distances and the diffusion coefficient. A further disadvantage of the numerical method is the possible inaccuracy near edges of the specimen where numerical adjustments are necessary to assure reliable results.

The large power of the numerical method is its wide range of possible applications. Especially when two (or more) different materials are present, the numerical solution method is still powerful. An other advantage of the numerical approach is that it can be easily translated into a computer programme which can solve a wide variety of problems, whereas the analytical approach demands an analytical solution for every single problem, which sometimes is hard to obtain.

In conclusion, for simple straightforward problems the analytical approach is preferable to the numerical one. However, if a numerical programme is available it is, certainly for complicated problems, a rapid and reliable method for solving diffusion problems. For problems with two or more different materials, the numerical approach may be the only one available.

3.9.2: Moisture pick-up of ARALL

In the previous chapters it is clearly demonstrated that the moisture pick-up behaviour of ARALL is highly superior to the behaviour of pure composite materials, in spite of the fact that the diffusion coefficients are comparable. This result is due to the barrier function of the aluminium sheets on the outer sides of the ARALL material. The barriers are limiting the moisture pick-up to the edges of the material. The beneficial absorption behaviour is not resulting from lower diffusion coefficients (which should be very surprising since ordinary matrix and fibre systems are used) but is totally due to the limited diffusion possibilities in ARALL. As a very simple but clarifying example: in the
exposure period to reach full saturation of a composite specimen of 1000x1000x1 mm, only approximately 1 mm near the edges of the ARALL specimen will be affected. This is the main reason why, throughout all environmental experiments performed on ARALL, never dramatic or even significant losses of mechanical properties were found. The affected area is just too small. Some moisture pick-up at the edges of ARALL may even be beneficial for mechanical properties, because of local stress redistribution as a result of plasticizing processes.

In our experimental test series it was shown that at higher environmental temperatures (> 60°C) interface cracks may appear, which somewhat increases the absorption and maximum moisture content. However, as published in the literature and proven in our test series, water present in these micro-cracks does not affect the physical and/or mechanical properties.

The different diffusion rates for absorption parallel and perpendicular to the fibre direction emphasize the important role of the aramid fibres in the absorption process of ARALL (and more general but to a smaller extent, of all aramid composites). Although the difference in diffusion data between matrix and aramid fibres is most probably overestimated in the present literature (1000x difference seems far too high) still the difference is significant:

\[ D_{f1} = 10D_m \]
\[ D_{fp} = \frac{D_m}{10} \text{ to } \frac{D_m}{100} \]

where \( D_m \): diffusion coefficient of the matrix
\( D_{f1} \): diffusion coefficient of the fibre in length direction
\( D_{fp} \): diffusion coefficient of the fibre in radial direction

It was shown that absorption perpendicular to the fibre direction is not, as often mentioned in the literature, totally matrix controlled. Surely, the diffusion occurs predominantly through the matrix, but the positioning and/or radial fibre diffusion coefficient play an important role in hampering the moisture to enter the material. This hampering can be very thorough as clearly shown in figs. 21 and 22. Especially for ARALL, a high fibre volume content near free edges may limit the moisture presence to the first few layers of fibres.

Although the absorption behaviour of ARALL is much better compared to composites and mostly limited to the specimen edges, further improvements can be achieved by introducing protective coatings with low diffusion coefficients. Theoretically, possible improvements
could be clearly demonstrated; practically, the control of the process variables of a coating system (e.g. thickness, curing) on the edges of the ARALL specimens is still not solved but will be further examined in the near future.

3.9.3: The use of Fick's second law to describe the moisture absorption of composite materials

The diffusion coefficients $D_x$ and $D_z$, calculated with eq.(30), are derived from experimental data on $M/t^{1/2}$ (weight gain slope) and $M_m$ (maximum moisture content). The derivation of eq.(30) is based on the assumption that the prepeg material is homogeneous, but anisotropic. In other words $D_x$ and $D_z$ are constant through the prepeg thickness (independent of $x$), but $D_x \neq D_z$. As a consequence the $D_x$ and $D_z$ values obtained from the experiments are a kind of an average result for moisture adsorption by the fibres and matrix materials. For ARALL and other composites this approximation might be debatable because of the inhomogeneity of the material. For ARALL in the $y$-direction (fibre direction) the moisture diffusion in the fibres occurs much faster than in the matrix which implies that in the prepeg thickness $D_y = f(x,z)$. In the $z$-direction the diffusion is hampered by the fibres, because of the low diffusion coefficient of the fibres in the radial direction. Also then $D_z = f(x,y)$.

The reason for using an equation for homogeneous materials for composites is that there is no feasible alternative. The distribution of fibres in the matrix is more or less random and the number of fibres is too large to even attempt a coordinate description of each single fibre. The results shown in section 3.5 and 3.6 must therefore be considered as a rough prediction of the absorption behaviour of the material. In chapter 3.8 a more realistic approach is presented for the diffusion parallel and perpendicular to the unidirectional fibre orientation. The models presented in chapter 3.8 might be a first step to a more accurate description of the absorption behaviour of composite materials.
Conclusions

1: The numerical (finite difference) and analytical approach can be used to describe the absorption behaviour of ARALL. Both approaches are based on Fick's second law of absorption.

2: As could be expected from the literature, the moisture pick-up of ARALL was shown to be strongly dependent on the environmental temperature, while the maximum moisture content is mainly a function of the environmental relative humidity.

3: The diffusion coefficients of ARALL obtained for different temperature and relative humidity levels are comparable with similar data found in the literature for composites. Within the studied temperature range, a linear relationship between temperature and diffusion coefficient was found.

4: Because of the unidirectional orientation of the aramid fibres in the prepreg layer, the diffusion rates parallel and perpendicular to the fibre direction are highly different (by a factor 3). It was shown that for ARALL, the diffusion coefficient of the aramid fibres themselves (in the longitudinal direction) is about 10x higher than the diffusion coefficient of the surrounding matrix.

5: The favourable absorption behaviour of ARALL as compared to composites is due to the diffusion barrier function of the outer aluminium sheets. For ARALL, the presence of moisture will, for realistic environments, be limited to narrow edges of the specimens. Hence, it can be expected that the moisture pick-up of the prepreg perpendicular to the fibre orientation will be significantly lower.

6: It is shown that perpendicular to the fibre direction, the positioning and radial fibre diffusion coefficient of the aramid fibres will highly influence the moisture pick-up of the prepreg perpendicular to the fibre orientation.

7: A protection of ARALL's sheet edges by protective coatings can further decrease the moisture pick-up. Experimental work has to be performed to confirm the theoretical predicted improvements.
Chapter 4: Influence of absorbed moisture on the aramid fibre/matrix adhesion

4.1: Introduction

Similar to the characterization of fibre/matrix adhesion, treated in the first part of this investigation, the characterization of the influence of absorbed moisture is performed by means of standardized test specimens such as:

1: Bell-peel specimen (dominantly mode I fracture mechanism)
2: Width tapered double cantilever beam specimen (dominantly mode I fracture mechanism)
3: Wedge-edge specimen (dominantly mode I fracture mechanism)
4: Inter laminar shear specimen (dominantly mode II fracture mechanism)
5: Thick adherend specimen (dominantly mode II fracture mechanism)
6: Delamination specimen (combined mode I and mode II fracture mechanism)
7: Relaxation specimen

Specimen types (1,2,4,5), already introduced in the first part of the dissertation, will not be described in detail in this second part; the results obtained with "new" specimen types will be preceded by a detailed introduction of the specimen.

Before the results of the different test series are presented and discussed (section 4.5 to 4.11), some general information is given concerning the standard intermediate materials used (section 4.2). For convenience possible delamination paths are defined again for both an adhesive and prepreg layer (section 4.3). In section 4.4, some attention is paid to the problem of choosing adequate environments for durability tests and the difficulty of translating results obtained from durability tests to the behaviour of realistic structures in realistic environments. Chapter 4 will be completed with an overall evaluation of the durability results.
4.2: Standard materials

In the environmental test series, three different intermediate layers have been tested:

1: A polyether toughened metal epoxy adhesive (amine-cured bisphenol A) with the tradename AF 163-2K (3M). The adhesive, known for its toughness properties, is used by the aircraft industry (e.g. Airbus Industries). The adhesive is cured under vacuum in an autoclave (60 min. at 125°C and 3 atm.).

2: A unidirectional aramid prepreg consisting of:
   - metal epoxy adhesive (AF 163-2, see above)
   - high modulus aramid fibres (TWARON - ENKA)
The aramid prepreg is standardized with a fibre volume content of 50%. An identical curing cycle is used as for the adhesive.

3: A unidirectional carbon prepreg consisting of:
   - metal epoxy adhesive (AF 163-2, see above)
   - high strength carbon fibres (T 300 HS, Toray)
The carbon prepreg is also used with a fibre volume content of 50%. An identical curing cycle is used as for the adhesive.

The specimens consist of two (or more) aluminium adherends and one (or more) intermediate layers. Except where noted, 7075-T6 (bare) sheet is used for the adherends because of its high yield strength (for most experiments, plastic deformation of the adherends is not allowed). Before curing, the adherends were carefully pretreated according to Fokker specifications which include:
   - alcalic degreasing (30 min. at 70°C)
   - pickling in a chromic-sulfuric solution (20 min. at 60°C)
   - chromic acid anodizing
   - priming (EC 3980 ot BR 127 primer from 3M and Ciba Geigy respectively)

4.3: Definition of the possible delamination paths in an adhesive or prepreg intermediate layer

In this section, the different possible fracture (delamination) paths are described for both an adhesive and a prepreg layer. The nomenclature introduced in this section will be used throughout the test series. The definitions were already given in the first part of the present study. They are repeated here for convenience.

adhesive layer: except for the nylon carrier, the adhesive can be regarded as an isotropic and homogeneous
layer. The following delamination paths can occur:

- prepreg layer: the number of possible delamination paths is larger for the prepreg because of its inhomogeneous composition. Microscopic examination of a prepreg cross-section showed:
  - a relatively thin (1/10 of total prepreg thickness) resin-rich layer near the adherends
  - a relatively thick (8/10 of total prepreg thickness) fibre-rich layer in the centre of the prepreg.

The following delamination paths can occur:

4.4: Environmental testing

If one considers the actual service life of a civil airplane (> 15 years) it is clear that for the sake of safety and economy, the durability (long-term behaviour) of materials is a point of major concern. It is
therefore obvious that the introduction of a new material demands major efforts of testing to prove its durability behaviour. Unfortunately, there is no universal testing procedure, which is relevant to all practical conditions. Aspects to be considered are:

- Materials used in primary structures should be tested more severely and extensively than materials used for secondary structures.
- Different parts of an aircraft structure will be subjected to highly different environments, which demands different types of tests.
- Different types of materials (metals, composites, ARALL) will demand specific ways of environmental testing in view of the sensitivity to a variety of environments.
- The ease of inspection and repair may influence the gradation of durability testing.

An optimum durability test should simulate, as far as possible, realistic environments and loading conditions. However, a realistic simulation offers some problems:

- The long service life of an airplane should demand an extremely long testing period, which is a rather difficult condition for the introduction of new materials.
- Unfortunately, there is not one single climate on earth (e.g. there are hot-wet, hot-dry, cold-wet climates) and even more problematic, in most places the climate itself is continuously changing which makes a realistic simulation hardly possible.
- The simulation of the environmental and load history is so complicated that testing of large numbers of specimens is in practice not possible.

To avoid the limitations mentioned above, the necessity for a realistic reproduction of the environmental condition is often abandoned to allow testing of large numbers of specimens in laboratory conditions. However, then a major question is how to translate the laboratory results into the behaviour of the material under realistic conditions. A few problem areas will be mentioned:

- It is common knowledge that the environmental degradation of materials can be accelerated by introducing environments with a higher severity (e.g. for composites, increasing the environmental temperature will speed up the moisture absorption or, for metals, the usage of a salt spray cabinet will accelerate possible corrosion processes). One should however be aware of the fact that a more severe environment may induce degradation processes which may not occur in realistic environments. In such a case, the durability
of the material will be severely underestimated. Still, it is interesting to cover severe environmental conditions to determine the environmental limits of a material (e.g. determination of the temperature level above which it is not tolerated to perform accelerated testing).

- A test set up for environmental exposure, including static or fatigue loading, is more complicated than environmental testing in the absence of external loading. As an example, the performance of environmental fatigue tests is rather time and money consuming. However, it is generally recognized that the combination of stress and environment can induce degradation processes (e.g. stress corrosion of metals) which do not occur in simple environmental tests.

- For the sake of economy, there is a strong tendency to apply durability specimens as small and simple as possible. It is obvious that smaller specimens will show accelerated degradation (e.g. in the case of composites sensitive to moisture absorption) but it can be very difficult to translate the experimental results to realistic geometry conditions.

- Service experience has learned that the lack of durability of a structural part need not primarily be due to inferior properties of the applied materials. It can also result from a poor structural design. It is clear that durability tests by means of standardized specimens will never account for design mistakes.

- If the approach of a strict simulation of the realistic environment is left, still the question remains which environment one has to choose for environmental testing. First it is necessary to recognize the nature of the realistic environment which may be quite different from an outdoor climate (e.g. hydraulic fluids). Depending on the realistic environment, it is than possible to choose some accelerating environments although it is obvious that one environment will not be accelerating for all materials (e.g. salt spray is very aggressive for metals but not necessarily for composites; the opposite is true for a hot-wet environment; some thermoplastics will degrade rapidly in hydraulic fluids while thermosets are not or only slightly affected). In general it demands a lot of experience to be able to define a reliable set of environments for the durability testing of a new material.

ARALL is, because of its composition, a complex material for durability testing since it contains a metal part (corrosion!), an adhesive bonded part (bondline corrosion!) and a composite part (moisture absorption!). It is clear that the durability testing has to cover the three possible problem areas. In that respect, different environmental conditions have been applied in the test series:
- corrosion sensitive environments: saltspray or salt water
- moisture sensitive environments: distilled water or humid air
4.5: The influence of absorbed moisture by means of the Bell-peel test

4.5.1: Introduction

The background of the Bell-peel test has been discussed in the first report on the investigation concerning the fibre/matrix adhesion characterization. To cover the worst possible case, the prepreg is oriented in the width direction of the specimen to ensure maximum moisture absorption (as demonstrated in chapter 3, for moisture absorption of ARALL, the diffusion process is largely governed by the aramid fibres). In the test series the following environments have been introduced:

<table>
<thead>
<tr>
<th>environment</th>
<th>details</th>
<th>exposure period</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. outdoors</td>
<td>roof of the main building of the aerospace department (ref.57)</td>
<td>up to 3.5 years</td>
</tr>
<tr>
<td>2. salt spray</td>
<td>salt spray cabinet, according to standardized procedures (ref.58 and 60)</td>
<td>27, 42, 87, 143, 365 and 519 days</td>
</tr>
<tr>
<td>3. distilled water</td>
<td>100°C (ref.61)</td>
<td>up to 31 days</td>
</tr>
<tr>
<td>4. salt water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 5. humid air   | 80%RH, 20°C  
                 | 30%RH  
                 | 50%RH, 50°C  
                 | 80%RH (ref.59)   | up to 160 days |
while outdoor exposure of 3.5 years did not result in any observable degradation. As could be expected from the aggressiveness of the environment, distilled and salt water exposure at 100°C rapidly resulted in a catastrophic loss of the peelstrength.

The fractured surfaces after exposure are also of great interest. The following observations were made:

1: For all environments and exposure periods, the fracture path was situated at the interface between the fibre-rich and the resin-rich layer (type 5 delamination, see chapter 4.3). Except for the longest saltspray exposure period (519 days), the adherend/adhesive interface remained undamaged, which points to a very adequate pretreatment process used for the ARALL production.

2: Distilled water exposure or exposure at different humidity levels did not result in significant corrosion processes (also not on the free untreated edges), but the environments may, as the result of the absorbed moisture, effect the fibre/matrix adhesion. This is clearly demonstrated for the distilled water exposure at 100°C. The fractured surfaces of the exposed specimens showed a larger quantity of individual fibres peeled out of the fractured surface (in comparison with the non-exposed specimens) which points to a largely degraded fibre/matrix adhesion (fig.25).

3: In spite of full pretreatments, saltspray exposure results in severe corrosion processes on the aluminium adherends (the free specimen edges corrode very quickly, the pretreated surfaces only after long exposure periods, > 365 days). However, the laminated composition of ARALL proves, also when corrosion processes are involved, its damage tolerance. Corrosion is always limited to one sheet and will stop on the aramid prepreg intermediate layer (through-the-thickness corrosion is not possible) which proved to be an excellent corrosion "barrier". Even more important, the experimental results indicate that no rapid delamination will propagate from a corroded spot which reaches the aramid prepreg layer. The lower peelstrengths, observed after 519 days of exposure were not primarily the consequence of a decreased fibre/matrix adhesion, but resulted from the degraded thin aluminium layer (in one case, the thin aluminium layer even fractured).

4: It is very reassuring that 3.5 years of outdoor exposure did not result in any degraded fractured surfaces.

4.5.3: Conclusions

The results obtained with the Bell-peel test show that ARALL has a sufficient durability, mainly because of its laminated built-up. Moisture pick-up is limited because
of the presence of aluminium layers on the outer surfaces. It can therefore occur through the edges only. Corrosion will stop on the aramid prepreg which acts as a corrosion barrier (the aluminium layers act as diffusion barrier).
4.6: The influence of absorbed moisture by means of the thick adherend specimen

4.6.1: Introduction

A theoretical background of the thick adherend specimen has been presented in the first part of this investigation. It will not be repeated here. In the test series, the environmental degradation of the aramid fibre/matrix interface is examined for both a unidirectional aramid prepreg and a prepreg with an aramid 50-50 weave. Two different environmental conditions were applied:
- saltspray; exposure periods: 1 and 3 months
- distilled water (60°C)
  exposure periods: 1 and 3 months

The environmental tests were carried out on identical specimens (fig.26). The standard critical shear stress equation (see first part of this investigation) is used:

\[ \tau_{cr} = \frac{P_{cr}}{bL} \]  \hspace{1cm} (50)

where \( \tau_{cr} \): critical shear stress (N/mm^2)
\( P_{cr} \): critical load level (N)
\( b \): specimen width (mm)
\( L \): overlap length (mm)

In the first part of the present study it is stated that eq.(50) can only be used for a qualitative comparison (as in this section between non-exposed and exposed specimens).

4.6.2: Results

The results of the environmental test series are shown in fig.27 (average values of 4 to 6 specimens). The two environments have a significant influence on the critical shear stress of the aramid prepreg; especially the deterioration as the result of distilled water exposure is remarkable. The decrease of the critical shear stress as the result of environmental exposure is summarized in the table below:

<table>
<thead>
<tr>
<th>Condition and Exposure Period</th>
<th>Loss of Critical Shear Strength % (Average Results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aramid prepreg</td>
<td>aramid weave</td>
</tr>
<tr>
<td>saltspray (1 month)</td>
<td>11</td>
</tr>
<tr>
<td>saltspray (3 months)</td>
<td>20</td>
</tr>
<tr>
<td>distilled water (1 month)</td>
<td>25</td>
</tr>
<tr>
<td>distilled water (3 months)</td>
<td>47</td>
</tr>
</tbody>
</table>
From the above results it is clear that absorbed moisture will weaken the critical fibre/matrix interface of an aramid prepreg, which results in lower critical shear stress levels. Although the critical shear stress loss seems to be rather dramatic, it should be recognized that the decreases are strongly related to the limited bonded area (200 mm²). Even when moisture can only diffuse through the edges of the specimen, rapid saturation will occur for the chosen specimen geometry. Therefore the thick adherend specimen is a typical example of accelerated testing (see chapter 4.4) for which it is difficult to translate the results obtained to more realistic circumstances. The statement that a thick adherend specimen resembles a border case for the edges of a realistic structural geometry is doubtful, because at the border area of an ARALL sheet, saturation will never occur. Moreover, the local shear stress distribution will be significantly different. The thick adherend specimen should therefore only be used to recognize possible deteriorative processes as the result of environmental testing.

In chapter 4.5, it was shown that the affected fibre/matrix adhesion could also be observed on the fractured surface, because of an increased number of individual fibres peeled out of the fractured surface. However, for the thick adherend specimens the fibres were oriented in the width direction of the specimen, which resulted in a rather irregular fractured surface (fig.28), also for non-exposed specimens. Therefore possible differences between non-exposed and exposed specimens could not be observed.

4.6.3: Conclusions

Because of the limited bonded area, the decrease of the critical shear stress as the result of environmental exposure is significantly augmented. Since a direct relation with a realistic ARALL geometry is absent, the thick adherend specimen should only be used to recognize possible deteriorative processes as the result of environmental testing.
4.7: The influence of moisture absorption by means of the interlaminar shear test

4.7.1: Introduction

In the first part of this investigation, a theoretical background was presented for the interlaminar shear (ILS-) specimen. It was demonstrated that the ILS-test cannot be used for a quantitative evaluation of fibre/matrix adhesion, because large scale yielding of the adherends is preceding delamination. Since the available ILS-equations (see first part of the present investigation) do not account for yielding of the adherend, in this section only the critical load levels are used as a qualitative indication for determining the influence of environmental exposure. A standard specimen geometry (fig.29) has been applied throughout the environmental test series (to allow direct comparison of data).

In the test series, the degradation of fibre/matrix adhesion as the result of environmental exposure has been determined using the following set of environmental conditions:

<table>
<thead>
<tr>
<th>environment</th>
<th>temperature (^\circ\text{C})</th>
<th>exposure period</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. salt spray</td>
<td>35</td>
<td>1 month</td>
</tr>
<tr>
<td>2. distilled water</td>
<td>20, 40, 60, 80, 100</td>
<td>4 months, 1 month</td>
</tr>
<tr>
<td>3. salt water</td>
<td>100</td>
<td>1, 2 months</td>
</tr>
<tr>
<td>4. humid air</td>
<td>20 and 80%RH, 30, 50 and 80%RH</td>
<td>6 months, 6 months</td>
</tr>
</tbody>
</table>

Saltspray is used to determine the possible occurrence of bondline corrosion. Salt water has been applied to examine the environmental limits of the material. The tests in humid air and distilled water were part of the moisture absorption programme performed on the ARALL material.

4.7.2: Results

The results are summarized in table 8, fig. 37. All results are the average of at least six specimens.
Exposure at different relative humidities (160 days) has no significant influence on the critical load. Also the environmental exposure to distilled water does not result in any degradation up to a temperature of 60°C. As could be expected from previous experiments, the very severe environmental exposures (salt water and distilled water at 100°C) indeed strongly deteriorate the fibre/matrix adhesion which results in lower data. The recovery of the fibre/matrix adhesion after a drying period is remarkable. For all environments and exposure periods, the fractured surfaces were identical showing fracture at the fibre-rich/resin-rich layer interface.

A comparison between results for specimens with the prepreg orientation in length or width direction can easily be made in figure 30. It is remarkable that specimens with fibres in the width direction show a faster degradation at more severe environmental exposures. This should be expected because specimens with fibres in the width direction will exhibit in the region of the high critical shear stresses (area between the spans) fast moisture absorption through the fibres. For specimens with fibres in the length direction moisture transport to the critical shear stress areas will take much longer exposure periods (water preferentially diffuses through the fibres, see chapter 3). On the other hand, in the first part of the present study it was argued that the behaviour of ILS specimens with fibres in the width direction is strongly governed by the plastic deformation of the adherends, which could result in an insensitivity for degradation processes in the intermediate layers. The test series proved that this insensitivity is no longer present after a severe environmental exposure.

4.7.3: Conclusions

The ILS-test does not show any degradation of the fibre/matrix interface strength after a long-term exposure to "mild" environments. However, in an environment with a temperature exceeding 60°C (distilled water or salt water exposure) significant deterioration did occur after relatively short exposure periods.

Specimens with fibres in the width direction are more sensitive to moisture than specimens with fibres in the length direction due to a faster moisture transport.
4.8: Influence of environmental exposure by means of the width tapered double cantilever beam test

4.8.1: Introduction

The theoretical background of the width tapered double cantilever beam (WTDCB-) specimen has been presented in the first part of this investigation and will therefore not be repeated in this section. The specimen geometry is shown in fig.31. In the test series, which includes static and dynamic (fatigue) experiments, the degradation of an aramid prepreg due to environmental exposure is compared with the environmental behaviour of an adhesive and a carbon prepreg (a description of these three layers was presented in section 4.2). First the test programme will be presented (section 4.8.2), followed by a survey of the results (section 4.8.3) and some conclusions (section 4.8.4).

4.8.2: Test programme

As mentioned above, a static and a fatigue test programme have been performed. Each test series will be discussed separately.

Static environmental test programme

The test procedure for static testing of a WTDCB-specimen was extensively discussed in the first part of the present investigation. It will not be repeated here, but it should be recalled that the tests are performed with a constant displacement rate (5 mm/h). During testing, the load is continuously recorded. The strain energy release rate $G_{IC}$ can be calculated with eq.(51):

$$G_{IC} = P_C^2 \cdot Q$$  (51)

where $P_C$: load level at which delamination propagates

$Q$: constant depending on geometry parameters

Contrary to the non-environmental test series (first part of the investigation) it was now observed that the load increased with increasing delamination length. This was unexpected, because the purpose of the tapering of the specimen is to have a constant $K$-value and thus a constant $P_C$ value, assuming that $G_{IC}$ is constant. In view of this phenomenon it was necessary to continuously measure the load and the delamination length. This length was measured with an optical microscope.
Two test procedures were adopted:

1: Environmental exposure in distilled water at $90^\circ C$, followed by $G_{IC}$ testing in laboratory air.

   exposure periods: 55 days
   160 days

2: $G_{IC}$-tests under environmental exposure in an environmental cell, but without pre-exposure.

   environment: distilled water
   temperature levels: 20$^\circ C$
   50$^\circ C$

For the latter type of tests a transparent environmental cell was built with the walls parallel to the specimen edges (see fig.32). For both types of environmental tests, specimens with a carbon an an aramid prepreg layer were examined. The fibres were oriented in the length direction of the specimen. For the second type of tests the pure adhesive system was investigated also. Distilled water was used in both types of tests but the environmental exposure is essentially different:

Tests of type 1
- During the pre-exposure, moisture can enter through the edges of the specimen only.
- Water absorption is controlled by the diffusion properties of the prepreg layer.
- The moisture affected width of the specimen will be limited because in the proposed exposure periods saturation of the specimen is not expected. Due to the tapered geometry, the influence of the affected width is decreasing for larger crack lengths (fig.33).
- In the pre-exposure periods, corrosion processes on the adherends can be expected, especially for the carbon prepreg (galvanic corrosion).
- During the $G_{IC}$ tests, there is no water in the delaminating area.

Tests of type 2
- Water is present at the crack tip over the entire width of the specimen.
- The effect of moisture diffusion through the edges is negligible due to the short testing period (about 5 hours).
- The crack growth rate is much higher than the diffusion rate of the moisture.
- In the short testing period ($\approx 5$ hours), no significant corrosion processes have to be expected (Therefore, for this part
of the test series, the adherends were only subjected to the limited pretreatments: degreasing, etching).

Fatigue environmental test programme

A detailed description of the fatigue test procedure was presented in the first part of the investigation. Environmental fatigue testing (distilled water at 20°C) is performed in the environmental cell shown in fig.32. For the fatigue programme it is necessary to monitor the delamination size. This is done with an optical microscope. For the aramid prepreg, an accurate determination of the delamination tip is extremely difficult (see first part of the investigation). Therefore the results obtained for the aramid prepreg should be considered as being approximative only. To allow a comparison between the non-exposed and the exposed test series, the load and frequency parameters used in the environmental test series are largely identical with the parameters used for the non-environmental testing. A survey of the environmental fatigue test series is presented in table 9.

4.8.3: Results

4.8.3.1: Static environmental test programme

As mentioned before two different test procedures were adopted for the static environmental tests. The results will be presented separately.

Environmental exposure followed by static testing

In fig. 34 the $G_{IC}$-results obtained after exposure periods of 55 and 160 days are shown and compared with result for unexposed specimens. As said earlier, the load on the environmentally exposed specimens is not constant, but it increases with the delamination length. It implies that $G_{IC}$ is increasing with increasing crack length. The reason for this phenomenon should be expected to be moisture, which has a deteriorating effect on both carbon and aramid prepreg layers. Moisture can only diffuse through the edges of the specimen, with a rate controlled by the environmental temperature. Because of the tapered geometry, the deteriorated proportion of the width of the specimen relatively decreases with increasing delamination length (fig.46). It should result in an increasing $G_{IC}$-value, because $G_{IC}$ is an average crack growth resistance over the full width of the specimen.

For the aramid prepreg after 55 days of exposure, there is a small increase of $G_{IC}$, but after 160 days of
exposure a strong decrease was observed. The fractured surface of the aramid prepreg after environmental exposure is shown in fig.35. The presence of single fibres is more pronounced than for the unexposed specimens; no corrosion is visible at the adherend surface (aramid is an organic material which is electrically non-conductive). Microscopic examination of the single fibres shows a perfectly smooth fibre surface. It seems that moisture again decreases the already poor strength of the aramid/adhesive interface.

For the carbon prepreg, the decrease of $G_{IC}$ due to environmental exposure is dramatic. For this system, the influence of the environment is a result of two contributing factors:
- severe galvanic corrosion of the aluminium alloy adherend
- moisture causes a change in the fracture mode from cohesive failure in the resin-rich layer (type 1, section 4.3) to failure between the fibre-rich and resin-rich interface (type 5, section 4.3)

The fractured surface of the carbon prepreg is shown in fig.37. The influence of the corrosion process is somewhat decreasing with increasing delamination length (due to the tapered geometry). It is well-known that aluminium and carbon form a galvanic cell which will, because of the large potential difference, lead to rapid corrosion of the aluminium part. As a result of the corrosion process, the fracture path at some localised spots is situated at the adherend/resin-rich layer interface (type 2, see section 4.3). In other areas, more single fibres are present at the fractured surface. Microscopic examination of these fibres shows a more interface dominated failure (fibre/adhesive interface) which was fully absent for the non-exposed specimens. The corroded area at the edges of the specimen facilitates the moisture to enter the specimen after which the moisture creates a galvanic cell. This deterioration process seems to propagate at a very high rate, which results in poor $G_{IC}$-data.

Combined $G_{IC}$-test and environmental exposure

The results of the $G_{IC}$-test series performed in a distilled water environment (2 temperature levels) are compared in fig.38 with data of unexposed specimens. As for the first type of environmental tests, $G_{IC}$ increases with increasing delamination length (except for one carbon prepreg case, for which a decrease was observed). The explanation for the first type of tests cannot be applicable in this case (no edge-controlled deterioration process). For the adhesive, the $G_{IC}$ increase with increasing delamination length is large, especially at the higher test temperature. The fracture
surface of the adhesive (fig. 39) points to some possible reasons for the $G_{IC}$-increase during delamination extension:

- Increased plastic deformation of the adhesive due to a combination of temperature and distilled water exposure. In a WTDCB test with a constant displacement rate, increased plastic deformation should result in an increased critical load level. However, it is questionable whether this load level can continuously increase or remain constant at a higher level (as compared to unexposed specimens) with increasing crack (delamination) length.

The linearly increasing $G_{IC}$-level cannot be the result of increasing specimen width because the energy is measured per unit of crack length. Therefore the only possible explanation for the $G_{IC}$ increase might be a continuous increase of the plastic energy dissipation per unit of crack length. However, it is not clear why and how such an increasing plastic energy dissipation should take place.

- Increasing irregularity of the fracture surface with increasing crack length. With increasing delamination length, the number of irregularities in the fracture surface (zone B and C in fig. 39B) are increasing, but no more than proportional to the specimen width. Locally irregular crack fronts did also occur due to fracture at the adherend/adhesive interface. It might cause a sudden increase of $P_C$ (or $G_{IC}$) but by no means a kind of a continuous increase as it is encountered in the experiments.

The fracture surface of the adhesive after environmental testing is shown in fig. 39. Three typical area's, corresponding to two different fracture modes can be observed:

area A: Cohesive fracture in the adhesive near the carrier interface, see fig. 40 (type 3, section 4.3). For the 20°C exposure, the surface is identical with the unexposed fracture surface (yielded character). For the 50°C exposure, a discolouring of the adhesive is visible which can point to an activated chemical process. The yielding for this test temperature is even more pronounced than for the 20°C, distilled water exposure.

area B: adhesive side, see fig. 41
area C: aluminium side, see fig. 42
Interfacial fracture at the adhesive/aluminium interface (type 2, section 4.3). This fracture
mode, absent for the unexposed specimens, is characterized by a very brittle fracture surface. It will ask significantly less energy for delamination growth than cohesive fracture in the adhesive. If this fracture mode occurs only at small localised spots, the influence on the total required energy for crack growth will be small. However, it introduces a staggered fracture path, which can increase $G_{IC}$, as observed at $20^\circ C$. For the $50^\circ C$ distilled water exposure, this fracture mode occurred much more abundantly which results in lower $G_{IC}$-values. An improved pretreatment of the adherends (specimens were only degreased and pickled) will most probably prevent this fracture mode.

For the prepregs, the presence of moisture at the crack tip results in a somewhat lower $G_{IC}$-level and a temperature effect is present (increased deterioration with increasing temperature). The increase of $G_{IC}$ with increasing delamination length is less pronounced than for the adhesive which is understandable considering the hampered plastic deformation capability of the matrix (presence of the fibres in the matrix) and the absence of partial adherend/matrix failure (irregular fracture path). In fig.41, a microscopic view of an aramid fibre surface is shown after testing. The fibre surface is completely smooth which points to a very low interfacial strength. A carbon fibre surface after a $50^\circ C$, distilled water exposure is shown in fig.44. It has an interface dominated fracture (carbon fibre/matrix interface). This change in fracture mode results in much lower $G_{IC}$-data, as shown by the results in fig.38.

4.8.3.2: Fatigue environmental test programme

Before evaluating the results, it is necessary to discuss the validity of the test procedure. In the first part of the investigation considerable attention was already paid to this subject. In the presence of distilled water, another problem may arise, especially at lower load levels. Because of the low test frequencies, a specimen may be submerged in the distilled water environment for several hours. Because moisture diffusion is a time-dependent process, the effect of moisture may be different between measurements performed at smaller and larger crack lengths. The interference with the moisture may be twofold:

- Moisture, present at the crack tip, may diffuse in the organic material surrounding the crack tip:
Subsequent fatigue crack growth is then occurring in an affected zone. It is not certain whether the crack growth rate will be retarded or accelerated in this zone because moisture can have a beneficial or a detrimental effect. However, this problem can only occur if the crack growth rate is lower than or comparable with the diffusion rate. A typical diffusion coefficient of an adhesive exposed to distilled water (room temperature) is $5.0 \times 10^{-8}$ mm$^2$/sec. The crack growth rates present in the test series are:

\[
10^{-2}\text{ mm/cycle} < \frac{da}{dn} < 10^{-4}\text{ mm/cycle}
\]

or, with $f = 0.1$ Hz

\[
10^{-3}\text{ mm/sec} < \frac{da}{dn} < 10^{-5}\text{ mm/sec}
\]

These values are considerably higher than the diffusion rates. Consequently the effect of moisture diffusion into the crack tip zone is expected to be insignificant.

- During submersion in distilled water, moisture will continuously diffuse into the intermediate layer through the edges of the specimen. Considering the reasons mentioned above, it is not expected that this edge diffusion will cause any interference, also not at larger crack lengths (longer exposure periods).

Results

The results of the fatigue environmental testing are summarized in Table 9. An evaluation of the influence of environmental exposure should include a comparison with crack (delamination) growth data for non-exposed specimens. A comparison is made in Figs. 45 (adhesive) and 46 (aramid prepreg), where the crack growth rates are plotted as a function of $P_{\text{max}}$ ($R=0$). For both interfacial layers, the influence of distilled water implies:

1: a decrease of $P_{\text{cr}}$ (load level at which unstable crack growth occurs)
2: a decrease of $P_{\text{thr}}$ (load level below which no crack growth occurs)
3: an increased crack growth rate in the overlapping load range between $P_{\text{cr}}$ and $P_{\text{thr}}$
The environmental influence is summarized in the table below:

<table>
<thead>
<tr>
<th></th>
<th>adhesive</th>
<th>aramid prepreg</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduction of $P_{cr}$</td>
<td>17%</td>
<td>25%</td>
</tr>
<tr>
<td>reduction of $P_{thr}$</td>
<td>25%</td>
<td>50%</td>
</tr>
<tr>
<td>fatigue crack growth rate increased by:</td>
<td>$4.2 \times (P_{max}=800N)$</td>
<td>$10.3 \times (P_{max}=500N)$</td>
</tr>
<tr>
<td></td>
<td>$5.8 \times (P_{max}=600N)$</td>
<td></td>
</tr>
</tbody>
</table>

Especially in the case of the aramid prepreg, the decrease of $P_{cr}$ and $P_{thr}$ is remarkable. Also, the influence of distilled water on the crack growth rate is larger for the prepreg than for the adhesive. For the adhesive, the environmental effect on crack growth rate decreases with increasing $P_{max}$. This appears to agree with a smaller effect on $P_{cr}$ (high $P$-values) than on $P_{thr}$ (low $P$-values).

The fractured surfaces examined after the environmental testing strongly resembled the fracture paths observed after the non-environmental testing (see first part of the investigation). Fatigue delamination in the adhesive was characterized by a rather "brittle" fracture surface near the carrier interface. The difference in "toughness" level between the static and the fatigue delamination path was less pronounced than for the non-environmental test series. For the aramid prepreg, no fracture surface difference could be observed between the environmental and non-environmental test series although the observed crack growth rates were strongly different.

4.8.4: Conclusions

1: Moisture, introduced by pre-exposure or during testing decreases the strain energy release rate ($G_{IC}$) of the three tested intermediate layers (adhesive, aramid prepreg, and carbon prepreg). The decrease is especially significant if the moisture induces a change in fracture path:

- from cohesive failure in the resin-rich layer to failure at the fibre-rich/resin-rich interface (carbon prepreg)
- from failure at the carrier/adhesive interface to
failure at the adherend/adhesive interface (adhesive)

The fracture path in the aramid prepreg is situated at the resin-rich/fibre-rich layer interface. It is not affected by the moisture, but the energy level ($G_{IC}$) at which delamination propagates at this path is decreased by the moisture.

2: A distilled water exposure has a detrimental effect on the fatigue delamination behaviour of the aramid prepreg and the adhesive. The effect is larger for the aramid prepreg. The environmental influence is threefold:

- decrease of the load at which unstable crack extension occurs ($P_{cr}$)
- decrease of the threshold fatigue load below which no crack growth occurs ($R=0$, reduced $P_{thr}$)
- for the same set of fatigue parameters ($P_{max}$, $R$, frequency) an increased crack growth rate
4.9: The influence of absorbed moisture by means of the wedge-edge test

4.9.1: Introduction

In the previous section 4.8 (and in the first part of the investigation) the width tapered double cantilever beam test proved to be very useful to determine the strain energy release rate $G_{1c}$ of different intermediate layers and to examine the influence of environmental exposure on $G_{1c}$. Although the WTDCB-specimen is a very useful specimen, it is too expensive for usage in comprehensive durability test programmes. Further, the test requires a tensile testing machine for long periods. For these reasons, some years ago a more simplified specimen was introduced: the wedge-edge specimen (fig.47). Similar to the WTDCB-specimen it consists of two adherends bonded together by an intermediate layer. In contrast with the WTDCB-specimen, an external load is not applied, but a wedge is inserted in between the adherends which causes a displacement controlled delamination extension in the intermediate layer. For this condition, a similar equation as for the WTDCB-specimen can be derived. The strain energy release rate of a double cantilever beam specimen was derived a.o. by Ripling and Mostovoy (ref.63):

$$G_I = \frac{P^2}{3bEI} \cdot \left(3(a+0.6h)^2 + h^2\right)$$  \hspace{1cm} (52)

where $P$: critical load level  
$b$: specimen width  
$E$: Young's modulus adherend  
$I$: moment of inertia ($I = bh^3/12$)  
h: beam height  
a: crack length

The same authors also derived an expression for the strain energy release rate as a function of the displacement of the load fixture (ref.64):

$$G_I = \frac{y^2 E h^3}{16} \cdot \frac{3(a+0.6h)^2 + h^2}{\{a+0.6h\}^3 + ah^2}$$  \hspace{1cm} (53)

where $y$: displacement of the load $P$ at the load fixture

For a wedge-edge specimen, the displacement $y$ is a
constant (thickness of the wedge) (ref.65, 66):

\[
G_1 = \frac{d^2 E h^3}{16} \cdot \frac{3(a+0.6h)^2 + h^2}{(a+0.6h)^3 + ah^2}^2
\]

where \( d \): thickness of the wedge

The test procedure and the test programme are presented below (section 4.9.2), followed by an evaluation of the results (section 4.9.3) and some conclusions (section 4.9.4).

4.9.2: Test procedure and programme

The test procedure for a wedge-edge specimen is rather simple. The wedge is inserted into the specimen by means of a bench-vice. It will cause some delamination. For unexposed specimens the corresponding crack length "a" can be measured directly after inserting the wedge. However, to assure a reliable determination of \( G_{ic} \), the crack lengths are measured a few hours later. The threshold strain energy release rate level after environmental exposure is determined in a similar way. The specimen is regularly removed from the environment to measure the crack length. With increasing exposure period, the crack propagation rate is decreasing until a threshold level is reached (fig 48). Depending on the severity of the environmental condition, the time to reach the threshold limit may vary from a few hours ("mild" environments) to a few days ("severe" environments).

The test programme includes specimens with fibres oriented in the length and the width direction of the specimen, and the following environmental conditions (L: fibres in length direction; W: fibres in width direction):

<table>
<thead>
<tr>
<th>environment</th>
<th>temperature(°C)</th>
<th>fibre direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. salt spray</td>
<td>35</td>
<td>L</td>
</tr>
<tr>
<td>2. distilled water</td>
<td>20, 50, 60, 70, 100</td>
<td>L, W, L, W</td>
</tr>
<tr>
<td>3. salt water (5% NaCl)</td>
<td>50, 100</td>
<td>W, W</td>
</tr>
<tr>
<td>4. humid air 30% RH</td>
<td>20</td>
<td>L</td>
</tr>
<tr>
<td>50% RH</td>
<td>and</td>
<td></td>
</tr>
<tr>
<td>80% RH</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
4.9.3: Results

The results are presented in fig. 49. The results are the average data of at least six specimens, while for each specimen, two crack lengths (each side of the specimen) are measured. As mentioned in section 4.8 on the WTDCB-tests, an accurate measurement of the crack length is extremely difficult for the aramid prepreg specimens. For the wedge-edge specimen, a small deviation in crack length results in significant deviations for $G_I$. For realistic crack lengths (50 to 60 mm) a crack length deviation of 1 mm results in a deviation of $G_I$ of about 50 N/m. Therefore, the results shown in fig. 49 should be considered as trends only.

The following trends can be observed:

- Specimens with fibres in the width direction exhibit a higher initial strain energy release rate (no exposure) than specimens with fibres in the length direction. This result is in contradiction with the data obtained for the more accurate WTDCB-test series (see first part of the investigation). However, the differences encountered for the wedge-edge test most probably resulted from an inaccuracy in the crack length measurements. Instead of measuring crack length from the end of the rectangular part of the wedge (see fig. 47), the crack length was measured from the beginning of the prepreg layer. For the specimens with fibres in the length direction, these two points were almost identical. However, because of a production mismatch, the specimens with fibres in the width direction showed a distance of approximately 7 mm between the two points (unbonded length 27 mm), which explains the higher $G_{IC}$ values obtained for specimens with fibres in the width direction. A further cause for the deviation could be the usage of different adherend thicknesses for the two prepreg orientations. According to eq. (54), different adherent thicknesses should not result in a different strain energy release rate, but the relation between the crack length "a" and the adherend thickness h shown in eq. (54) has not been experimentally verified (and, as mentioned before, small deviations in crack length but also in adherend thickness will cause large variations of $G_I$).

The influence of different relative humidities (30%, 50%, 80%) on the strain energy release rate in humid air is very small. The small differences may well be a matter of scatter.

Exposure in distilled water, salt water or saltspray results in a significant decrease of the strain energy release rate. The absence of an environmental temperature influence up to 70°C is remarkable.
However, it is clear that for a wedge-edge specimen temperature-controlled-diffusion is less important since in all cases moisture will be present at the crack tip. In agreement with earlier experiments, saltspray exposure proved, in comparison with distilled water exposure, to be less aggressive for the delamination propagation in a prepreg intermediate layer.

Exposure at 100°C (distilled water or salt water) rapidly decreases the strain energy release rate to a very low level. This result is in agreement with previous experiments.

After the tests were completed, the specimens were opened to allow an examination of the fracture surfaces. In all cases, the typical fracture at the fibre-rich/resin-rich layer interface was present. Even for the saltspray or the salt water exposure, no degradation at the adherend/resin-rich layer was visible (no bondline corrosion). As observed in earlier experiments, exposure to a 100°C distilled or salt water environment resulted in a more irregular fracture surface with more individual fibres peeled out of the fracture surface.

4.9.4: Conclusions

The wedge-edge test is a fast, cheap and reliable method to determine the occurrence of deteriorative processes as the result of environmental testing. Due to the problematic measurement of the precise crack length for the aramid prepreg, the results obtained with the wedge-edge specimen should be considered as trends only. The trends observed in the wedge-edge test series correlated quite well with observations in other environmental experiments:

- Saltspray exposure is less deteriorative than distilled or salt water exposure.

- High temperature (100°C) distilled or salt water exposure results in a catastrophic decrease of the strain energy release rate.

- The humidity effect on the strain energy release rate is very small.
4.10: Influence of absorbed moisture by means of the delamination specimen

4.10.1: Introduction

In section 4.4, the importance of a combined load/environment condition to perform reliable durability tests was recognized. However, it was also argued that such a kind of testing will be expensive, since it requires static or fatigue testing facilities for long periods. One of the easier ways of performing combined load/environment experiments is offered by sustained load test series in simple dead-weight load fixtures. A specimen is subjected to a certain constant load and exposed to a specific environment. The time until failure is measured. If a certain load range is experimentally covered, it is possible to obtain for each environment a so-called sustained load curve (for a schematic example, see fig.50).

In this test series, a new specimen type has been used: the delamination specimen (fig.51). Four pieces of an Al-alloy sheet are bonded together with an aramid prepreg layer to obtain the specimen shown in fig.51. The specimen is loaded in tension and because of the discontinuity in the middle of the specimen, full load transfer has to occur through the prepreg. It implies a very severe loading condition for the fibre-rich layer and the resin-rich layer, at a location which is directly exposed to the environment.

In ref.67, the present author adopted a shear lag analysis to evaluate the shear stress distribution in the resin-rich layer as the result of the stress transfer at the centre of the specimen. The following relation was obtained for the shear stress distribution:

\[
\frac{\tau}{P} = \frac{\alpha}{\lambda} \frac{\sinh(\lambda l - \lambda x)}{\cosh \lambda l}
\]

where:
- \( P \): applied sustained load level
- \( b \): specimen width
- \( \alpha = \frac{2G}{t_{rr}\cdot t_{fr}\cdot E_{fr}} \)
- \( \lambda^2 = \frac{(G/t_{rr})}{(1/t_{ad}\cdot E_{ad}) + (2/t_{fr}\cdot E_{fr})} \)
- \( t_{rr} \): thickness of the resin-rich layer
- \( t_{fr} \): thickness of the fibre-rich layer
- \( t_{ad} \): thickness of the adherend layer
- \( G \): shear modulus of the resin-rich layer
- \( E_{fr} \): Young's modulus of the fibre-rich layer
- \( E_{ad} \): Young's modulus of the adherend layer
- \( l \): half of the specimen length
For the specimen in fig. 51, the shear stress distribution as the result of stress transfer is shown in fig. 52. The high shear stress peak occurs at the centre of the specimen, where the resin-rich layer is directly exposed to the environment.

Because of the limited number of eight available sustained load test machines, up to now only a few load/environment conditions could be tested. A survey is presented in the table below:

<table>
<thead>
<tr>
<th>Salt Water Environment 5% NaCl</th>
<th>Sustained Load Level (% Ultimate Load)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tests at 25°C</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

* Ultimate load: static failure load of the specimen without environmental exposure (for this case: $P_{ult} = 11750$ N)

4.10.2: Results

The results are summarized in fig. 53 and table 11. Most of the specimens did not fail after an exposure period of more than 3 years. At that moment, the tests were stopped and the specimens were examined to detect possible delamination.

Because of the limited number of available test results, it is clear that results should be considered as preliminary indications. Still, the environmental stability of the fibre-rich and resin-rich layer is remarkable in view of the long exposure periods and the aggressive environment. In all cases except one (clamping failure), specimen failure resulted from fracture of the fibre-rich layer in the centre of the specimen. After the specified exposure period ($\pm$ 1200 days), the unfailed specimens were also examined to determine possible delamination. Specimens exposed to lower sustained load levels (20% and 40% $P_{ult}$, 25°C) did not show any delamination. Specimens tested at 40% $P_{ult}$ (65°C) and 60% $P_{ult}$ (25°C) indeed showed delamination: 5mm in the case of 25°C salt water exposure, 10 to 20 mm in the case of 65°C salt water exposure. In all cases delamination did occur between the fibre-rich and resin-rich layer, and not at the adherend/resin-rich layer interface.

4.10.3: Conclusions
The first results of sustained load tests on delamination specimens prove the environmental stability of the aramid fibres and the epoxy matrix system. In view of the aggressive nature of the environment (salt water at 25 and 65°C), the time to failure (as a function of the applied load level) of the specimens is remarkably high. Specimens with a sustained load level at or below 60% (25°C salt water) or 40% (65°C salt water) of the ultimate failure load ($P_{ult}$) did not fail at all after an exposure period of more than three years. Specimens exposed at 40% $P_{ult}$ (65°C salt water) and 60% $P_{ult}$ (25°C salt water) showed a delaminated area after 3 years exposure. Specimens exposed to lower sustained load levels did not show any delamination.
4.11: Influence of the environment on relaxation of the residual stress

4.11.1: Introduction

This section deals with the question whether environmental exposure may result in relaxation processes in the ARALL material. In the first part of the investigation it was argued that the superior fatigue behaviour of the ARALL material is partially due to its favourable internal stress distribution (compression in the aluminium layers, tension in the fibre-rich layer). To assure the long-term fatigue behaviour of ARALL it is necessary to examine possible relaxation of the internal stress system as the result of different environmental exposures. A very simple specimen has been adopted for measuring internal stresses. It consists of two thin aluminium layers bonded together by a unidirectional aramid prepreg layer (fibres in the length direction of the specimen, see fig. 54). To cover a wide range of environmental conditions, the number of environments and exposure periods applied in the test series is rather comprehensive. A survey of the test conditions is shown in table 12. The test procedure is discussed below (section 4.11.2) followed by a presentation of the results (section 4.11.3) and some conclusions (section 4.11.4).

4.11.2: Test procedure

The internal stress distribution is introduced by means of a prestrain procedure after curing. The specimens were cut from some larger prestrained ARALL sheets. An overall prestrain level of 0.5% was chosen but, because of adjustment problems, it varied between 0.48% and 0.54%.

The internal stress distribution in the relaxation specimen was experimentally determined by using a chemical milling process. By this process one of the two aluminium strips is removed, while the second one is protected by a non-dissolving coating. The prepreg is not affected by the chemical milling process. After removing one strip the originally symmetric internal stress system is no longer present. As a result, the second strip with the prepreg layer still attached to it, will be curved. The radius of curvature is measured and from the radius the original internal stress system can be calculated. This method was originally developed for measuring residual stress distributions in monolithic sheet material. It has been extended for application to the (inhomogeneous) ARALL material.
(ref.69). The radius of the resulting curved specimen is calculated using a computer programme (ref.68). The internal stress distributions are simple functions of the radius of curvature (ref.69). For this specimen geometry:

$$S_{al} = -\frac{11666}{R} \quad (N/mm^2)$$
$$S_{fr} = \frac{26514}{R} \quad (N/mm^2)$$

where $S_{al}$: internal stress in the aluminium sheet

$S_{fr}$: internal stress in the fibre-rich layer

$R$: radius of curved specimen after chemical milling (mm)

The environmental conditions and exposure periods, as shown in table 12, cover two environments (distilled water and dry air) and three temperature levels ($20^\circ C, 40^\circ C, 70^\circ C$).

4.11.3: Results

As indicated in table 12, three external load levels were adopted. It turned out that any effect of this level on the remaining internal compressive stress could not be detected. It will be ignored in the following discussion. The results are summarized in figures 55 and 56. In both figures, the remaining internal compressive stress in the aluminium sheet after environmental exposure is plotted as a function of the exposure period. Results of non-exposed specimens are used as baseline data for comparisons. For this purpose the internal stresses of ten specimens were measured immediately after prestraining. The average result and scatterband of these specimens is also shown in the figures.

The results of the non-exposed and the exposed specimens exhibit quite a bit of scatter. Some sources for scatter have to be considered. As said before the prestrain level varied from 0.48 to 0.54%. According to calculation (ref.69) the corresponding variation of the internal stress would be from $-47.9$ to $-56.5$ N/mm². For the non-exposed specimens the range is from $-51.3$ to $-66$ N/mm². It should be expected that there are other sources for scatter as well, such as:

- variations of the internal stress in one ARALL sheet
- specimen production effects

It is difficult to quantify the first source, but some comments can be made on the second one. Cutting the 10 mm wide specimens from an ARALL sheet can have some unknown effect on the internal stress system, although
the effect is assumed to be small. However, with respect to chemical milling of the specimens (to obtain a curved specimen) some problems occurred in the beginning of the test series. Because of insufficient protection by the coating system the edges of the remaining strip were also affected by the milling process. As a result the radius of curvature and the calculated internal stress is lower which should result in an opposite deviation as mentioned above (lower experimental results as compared to theoretically calculated values). This points to a larger influence of the first source for deviations (variation of internal stress in one ARALL sheet). The shortcomings in the milling process could be avoided later in the programme.

The specimens, exposed to a 20°C, dry air environment (fig.55a) do not show any significant relaxation after 56 weeks of exposure. Some lower data, obtained in the first ten weeks were not confirmed after longer exposure periods. Consequently, they can not be related to relaxation processes, but are due to the not yet optimized chemical milling process.

Also the relaxation specimens, exposed to a distilled water environment at 20°C or 40°C (fig.55b and c) do not show any systematic relaxation over an exposure period of 56 weeks. Again the scatter of the data is considerable.

For an exposure at 70°C in distilled water (fig.56) a systematic relaxation seems to be present for increasing exposure periods. After 20 weeks of exposure, all data fall below the lower boundary of the scatter band of the non-exposed specimens. The same trend is not observed for the 70°C dry air exposure. Moisture therefore seems to be essential for the relaxation process. Moisture absorption of ARALL was examined in a previous chapter (chapter 3), where it was shown to be strongly dominated by the aramid fibres. If moisture is an important factor in the relaxation process, two influences should be present:

- a strong influence of the environmental temperature (exponential relation in Fick's second law between moisture absorption and temperature). Because relaxation only occurred at 70°C and not at lower temperatures, this temperature effect is evident.
- a continuous decrease of the internal stress (increase of the radius) along the length direction of the specimen. Moisture absorption occurs much faster in the fibre direction. Consequently it will predominantly start at the ends of the specimen and continue later towards the centre of the specimen. Considering the geometry of relaxation specimen,
a significant difference should be visible between the curvature at the ends and at the centre of the specimen. In fig. 57 it is shown that this feature is present indeed (specimen exposed at 70°C, distilled water environment): the ends have an almost infinite radius (no remaining internal stresses!) where the centre of the specimen is not influenced. Because the computer programme calculates the average radius along the total length of the specimen, this aspect of the relaxation process is not directly shown in fig.56.

4.11.4: Conclusions

After an exposure period of 56 weeks, no significant relaxation was encountered for specimens exposed to dry air or to distilled water at either 20°C or 40°C. Even at 70°C a systematic relaxation was absent in dry air. However, specimens exposed to distilled water of 70°C did show relaxation after an exposure period of 56 weeks.

Any effect of an external tensile load (up to 260N/mm²) on internal stress relaxation turned out to be absent.
4.12: Evaluation of the environmental test series

In the previous chapters (4.5 to 4.11) results of the test series on seven different types of specimens were reported and analysed. The primary issue was the durability behaviour of ARALL under severe environmental conditions in view of application of the material in aircraft structures. For this type of questions a major problem is concerned with the time scale. A laboratory test with a limited duration should give relevant information about the behaviour in service after 10 to 20 years. Accelerated test are unavoidable then. The duration of tests in the present investigation in many cases was in the order of weeks and months, and sometimes even 1 to 3 years. Nevertheless, the tests by nature are accelerated tests. Such tests are usually carried out under more severe environments and a range of temperatures. The more severe test conditions should compensate for the shorter duration. This is one problematic aspect of the evaluation of the test results.

A second aspect of simulating service durability problems is related to the specimen configuration, which has to be representative for the relevant details of the structure. In principal, it should be solved by adopting specimens with relevant stress systems (tension, shear) and opening modes (modes I and II).

It will now be tried to evaluate the information gained from the experimental programmes, keeping in mind the above problem definitions. The fracture phenomena, as they occurred in the various test series, were also studied in order to find the weakest link of the hybrid material, and to see which fracture mechanism was prevalent. Such information, together with theoretical and empirical knowledge about diffusion in ARALL, should lead to a phenomenological understanding of the observed delamination failures under severe environmental conditions. The understanding is essential for considering the relevance of the test series for practical problems. The evaluation is presented below as a number of summarizing conclusions.

It should be recalled that ARALL is built up from two or more thin Al-alloy sheets (adherends), bonded together with intermediate prepreg layers. A prepreg layer consists of an adhesive matrix and unidirectional aramid fibres. The structure of the prepreg shows two relatively thin resin-rich layers with a fibre-rich layer in between. All results apply to ARALL unless indicated otherwise.
Corrosion aspects

1) Under severe corrosive environments corrosion along the adherend/resin-rich layer interface did not occur, provided an adequate pretreatment was applied to the Al-alloy sheets. The weakest link apparently is the matrix/fibre interface. The interface strength is sensitive to environmental exposure, depending on the type of environment and exposure period.

2) Corrosion of the outer Al-alloy sheets of ARALL is hard to prevent under severe corrosion conditions. However, through-the-thickness corrosion cannot occur, since the prepreg layer acts as a corrosion barrier.

Interface strength and delamination

3) The strength of the fibre/matrix interface is already poor without environmental effects. It is further decreased by the presence of moisture. The moisture sensitivity applies to both peel (mode I) and shear (mode II) fracture mechanisms. Under cyclic mode I loading the degradation of the interface strength due to environmental exposure is technically significant. This was not studied for mode II loading, which should still be recommended.

4) The deteriorating effect of moisture on the fibre/matrix interface strength is clearly supported by the fractured surfaces, which show an almost perfectly smooth aramid fibre surface under the electron microscope.

5) Moisture will result in a significant decrease of the energy required for delamination extension if it provokes a new weakest fracture path. This phenomenon was observed for experiments with a carbon prepreg (delamination path from cohesive in matrix to interfacial at fibre/matrix interface) and an adhesive (delamination path from cohesive in the matrix to interfacial at adherend/adhesive interface) intermediate layer.

6) The degradation of the fibre/matrix interface strength is more significant if the environment can enter the delamination. In this case it is not depending on moisture diffusion to the critical location, which otherwise would occur rather slowly (thanks to the diffusion barrier function of the outer aluminium sheets).

7) For distilled water exposure, 70°C seems to be a critical threshold temperature above which strong degradation processes do occur in relatively short exposure periods. For dry or humid air environments
this temperature level is far less critical. Still, it may be considered as the upper test temperature for accelerated testing.

8) If the delamination is exposed to the environment, distilled water proved to have a larger deteriorating effect on the fibre/resin interface than a salt spray exposure. Salt water had an intermediate effect. The effect of humid air with a relative humidity up to 80% was negligible.

9) If the Al-alloy sheets of ARALL (loaded in tension) have completely failed, full load transmission occurs through the fibres. Under these circumstances the delamination resistance under high sustained loads and severe environmental conditions was remarkably good.

Relaxation of internal stresses in ARALL

10) The internal stress system introduced by prestraining of ARALL turned out to be stable at temperature levels of 20 and 40°C, even in distilled water. After 56 weeks exposure at a distilled water environment of 70°C, some relaxation occurred. An external tensile load did not have any effect on relaxation of the internal stress.

Usefulness of different types of specimens

11) For mode I (peel) loading the width tapered double cantilever beam specimen gives well defined loading conditions. It can be used for both static and cyclic loading. However, the experiments are fairly laborious.

12) For mode II (shear) loading the delamination specimen gives a well defined loading condition also. Again the experiments are fairly laborious. For sustained load testing the specimen is very suitable.

13) The wedge-edge specimen is a simple and cheap specimen for delamination tests under mode I loading. However, reproducibility of results (scatter) may be a problem. The specimen can be used for screening tests to indicate qualitative trends.

14) In the thick-adherend specimen the prepreg layer is subjected to a well defined shear load. However, due to the small dimensions moisture saturation of the prepreg will rapidly occur. Adverse effects will thus show up in short testing times, but the indications obtained may be unrealistic for structural application of ARALL.

15) Poorly defined test conditions occur in the Bell peel test and the inter-laminar shear test. Both type
of specimens and the testing procedures are rather simple, which could make it attractive for comprehensive test series. Another advantage of the inter-laminar shear specimen is the small size. Both specimens can be used for indicating qualitative trends. The interpretation should be done with great care.

**Durability aspects of ARALL in view of structural application**

16) The moisture absorption in ARALL sheet material occurs extremely slowly, as compared to the absorption in the classical composite materials. The explanation is that the Al-alloy sheets act as an impermeable shielding for the prepreg. Moisture absorption along the edges of ARALL sheets occurs so slowly that detrimental effects in general should be insignificant.

17) Delamination of ARALL is sensitive to the environment and the temperature. Under static shear dominated loading the delamination resistance appears to be quite good, even under severe environments. Also the temperature stability seems to be acceptable. The shear dominated delamination under cyclic loading and its environmental sensitivity should still be investigated. Under tensile dominated loading, delamination of ARALL is sensitive to the environment. The fibre/adhesive interface is the weakest link. Designers should keep in mind the limitations of the peel strength. However, it should be pointed out that tests on specimens, more representative for structural application of ARALL, may well indicate that the restrictions are rather unimportant.

18) The understanding of environmental effects on ARALL, obtained by analysis and fractography, greatly supports the evaluation of the durability properties of ARALL.
Chapter 5: Summary

The experimental and theoretical work, presented in this investigation, is performed on ARALL (Aramid Aluminium Laminate) which is a new structural material for aircraft applications. The material is built up of alternately thin aluminium alloy sheets and thin intermediate layers, consisting of unidirectional aramid fibres embedded in a metal adhesive matrix. Its most striking property (fatigue insensitivity) is the result of a crack opening restraint mechanism exerted by unbroken fibres in the wake of a fatigue crack.

Part I: fibre/matrix adhesion and delamination

The first part of the investigation is dealing with delamination, a phenomenon which was recognized to be very important for obtaining the superior fatigue behaviour of the material. The investigation on delamination is subdivided in an experimental part (characterisation of delamination) and a theoretical part (prediction of the direction of delamination growth). Part I is concluded with a general discussion on the influence of delamination on the fracture toughness and fatigue properties of ARALL.

In the experimental test series, seven types of specimens were applied to cover, as complete as possible, the different loading conditions (mode I, mode II, mode I+II) which can result in delamination. Because most of the test methods were originally developed for the testing of adhesives, the more complex built-up of an aramid prepreg as used in ARALL required an analytical evaluation of the stress distribution in the different specimens.

A comparison between several test methods and an analysis of the results obtained, indicated the usefulness of the width tapered double cantilever beam (WTDCB-) specimen for the characterisation of delamination phenomena, both for static and fatigue loading (mode I). The Bell-peel test (mode I) should only be used for rapid qualitative evaluations. However, differences between the results for intermediate layers, as observed with this test method, might be out of realistic proportion. Three well-known test methods for evaluating delamination under a mode II loading condition were found to have some major limitations: the critical delamination parameter of the interlaminar shear (ILS-) specimen is strongly depending on plastic deformation of the metal adherends. The same parameter of the thick adherend (TA-) specimen is very sensitive for specimen geometry. An inherent disadvantage of the
fibre pull-out (FPO-) test is the small bonded area between fibre and matrix, which in general also implies large scatter bands. Two relatively recent specimen types (the edge notched flexure specimen, mode II, and the central notched delamination specimen, mode I+II) showed some promising results. These specimens should be used more in the future. The first one is a mode II counterpart of the mode I WTDCB-specimen. The second specimen type is useful because of its resemblance with realistic composite structures.

In the experimental test series it was observed that delamination of ARALL will occur in the aramid prepreg at the interface between a resin-rich and fibre-rich region. This delamination path is the consequence of poor adhesion at the aramid fibre/matrix interface which is clearly demonstrated by scanning electron microscopy pictures. It is important to notice that this delamination path is independent of the loading condition, i.e. the fibre-rich/resin-rich region interface is critical for mode I, mode II or combinations of the two loading modes. Compared to adhesives, and because of its poor fibre/matrix adhesion, the aramid prepreg as used in the ARALL material proved to be rather sensitive for fatigue loading. On the other hand, the threshold fatigue load level of the aramid prepreg and an adhesive is found to be comparable.

Starting from the delamination behaviour as observed in the various test series, a calculation model was developed to analyse the direction of delamination extension under different loading conditions. The stress analysis performed on an interface crack between an isotropic (resin-rich region) and an anisotropic (fibre-rich region) material was first checked on two well-known cases: a homogeneous isotropic and a homogeneous anisotropic material with a crack. The correspondence between the numerical data and the exact or fracture mechanics solutions was found to be excellent. One of the most interesting results from the stress analysis is that the main stress components ($\sigma_y$ in the case of mode I loading, $\tau_{xy}$ in the case of mode II loading) at the interface, are independent of the stiffness properties of the materials. In order to predict the direction of delamination extension, the stress components are considered in relation to fracture criteria. The maximum stress, the Tsai-Hill and the strain energy release rate criterion showed similar trends:

- Delamination extension is governed by both peel and shear stresses.
- The resistance against delamination growth is lower for mode I loading \( (G_{IC}) \) as compared to the resistance for a mode II loading \( (G_{IIC}) \).

- Delamination growth in the resin-rich layer should not be expected.

- For a mode I loading case, the stress distribution points to the possible occurrence of a step-wise delamination growth in the fibre-rich region.

- For a mode II loading case, delamination will propagate at the fibre-rich/resin-rich region interface.

The effect of fibre/matrix adhesion on the fracture toughness and the fatigue behaviour of ARALL was examined qualitatively by considering an ARALL sheet specimen with a central through crack. The influence of poor fibre/matrix adhesion is twofold:

- Early delamination will occur in the fibre-rich region between the interrupted and the non-interrupted fibres. This delamination will relieve the stress concentration effect of the initial through crack in the fibre-rich region.

- Delamination will occur between the fibre-rich and resin-rich region in the fibre-bridging area.

The delamination will diminish the stress peak in the fibres at the end of the through crack but on the other hand, crack bridging will be less effective. Therefore a "controlled" delamination behaviour is necessary to obtain an optimum fracture toughness and fatigue performance. Such a controlled behaviour does occur in ARALL.
Part II: Influence of absorbed moisture on fibre/matrix adhesion

The second part of the investigation deals with the influence of moisture on the fibre/matrix adhesion. As for part I, the investigation is subdivided in an experimental test series (evaluation of the influence of absorbed moisture on adhesion) and a primarily theoretical study concerning the moisture absorption of ARALL.

In the theoretical part of the investigation both a finite difference and an analytical approach were used to describe the absorption behaviour of ARALL. Both approaches were based on Fick's second law. It is noteworthy that for ARALL but also for composites in general, the assumption that the diffusion coefficient can be considered as constant might be valid on a macroscopic level, but by no means on a microscopic level where it is strongly depending on e.g. fibre positioning in the matrix material. The latter phenomenon was examined in two separate sections concerning moisture diffusion parallel and perpendicular to the fibre direction.

On a macroscopic level, the moisture absorption of ARALL was examined using a two-dimensional derivation of Fick's second law. The two dimensional approach is necessary because of the presence of unidirectional aramid fibres in the moisture absorbing region (aramid prepreg). A weight gain test series, performed in different environments (humid air and distilled water at different temperature levels) indeed proved the significant influence of the aramid fibres on the diffusion process: the diffusion coefficient in fibre direction is about three times higher than the diffusion coefficient perpendicular to the fibre direction. On a microscopic level it is found that:

\[
D_{fl} = 10 \ D_m \\
D_{fp} = D_m/10 \ to \ D_m/100
\]

where \( D_{fl} \): diffusion coefficient of the aramid fibre parallel to the fibre length direction

\( D_{fp} \): diffusion coefficient of the aramid fibre perpendicular to the fibre length direction

\( D_m \): diffusion coefficient of the matrix

The observed differences showed the same trend as mentioned in the literature, but their magnitude is a factor 10 to 100 smaller.
In spite of the comparable diffusion coefficients of ARALL and composites, a three dimensional absorption model showed that the moisture pick-up of ARALL is negligible as compared to composites. The latter phenomenon is due to the diffusion barrier function of the aluminium sheets.

In another theoretical study it was shown that the absorption behaviour of ARALL can be further improved by introducing protective coatings with low diffusion coefficients.

Considering the general usefulness of the two approaches used (finite difference versus analytical method), it was argued that, if possible, analytical solutions should be aimed at. Finite difference methods have to be used carefully because of potential free boundary and/or stability problems. The power of the finite difference method is its wide range of possible applications, especially when more than one material is involved.

The influence of moisture on the fibre/matrix adhesion was examined in an experimental test series using six different types of specimens. The width tapered double cantilever beam (WTDCB-, mode I) and the delamination (mode II) specimen proved to be very useful for evaluating environmental effects on fibre/matrix adhesion. The wedge-edge (mode I) and the thick adherend (mode II) specimen can be used to rapidly obtain qualitative trends. Poorly defined test conditions occur in the Bell-peel (mode I) and the inter laminar shear (ILS-, mode II) test.

The test series proved that the aramid fibre/matrix adhesion is further decreased in the presence of moisture. The moisture sensitivity applies to both peel (mode I) and shear (mode II) fracture mechanisms. Under cyclic mode I loading, the degradation of the interface strength is technically significant. Because of the limited moisture pick-up of the ARALL material, the degradation will only be present if the environment can directly enter the delamination tip (as e.g. in the WTDCB and the wedge-edge specimen).

A comparison of the different environments showed that the adhesion is sensitive for distilled or salt water environments. In this respect 70°C seems to be a threshold temperature above which fast degradation will occur. Humid air environments (RH up to 80%) turned out to be far less aggressive.
Part of the environmental test series dealt with possible corrosion aspects in severe corrosive environments (e.g. salt spray). However, in the test series bondline corrosion could never be observed. Corrosion pits on the outer Al.- alloy sheets do not penetrate the prepreg layer which acts as a corrosion barrier.

As a summary, the present investigation has revealed new insights into several questions, such as:

(1) phenomenological details of the delamination mechanisms in ARALL,

(2) environmental effects on the delamination,

(3) usefulness and limitations of different types of specimens to study delamination in a prepreg intermediate layer under mode I, mode II or combined modes of loading,

(4) the application of fracture mechanics to understand the delamination behaviour, and

(5) the application of diffusion models to analyse the moisture absorption behaviour of ARALL.
Chapter 6: Samenvatting

Het onderzoek uitgevoerd in het kader van dit promotiewerk, is gericht op een nieuw materiaal voor de vliegtuigindustrie: ARALL (Aramid Aluminium Laminate). ARALL is opgebouwd uit opeenvolgende laagjes van een aluminium legering en een unidirectioneel komposietmateriaal. Het grote voordeel van ARALL ten opzichte van de huidige Al-legeringen is, naast het lagere soortelijke gewicht, de vermoeingsongevoligheid van het materiaal. Ten opzichte van volledige komposieten vertoont ARALL betere breuktaaiheids-, bewerkings- en vochtopname-eigenschappen. Toepassing van ARALL in vliegtuigconstructies kan leiden tot gewichtswinsten van 20 tot 30%.

Deel I: vezel/matrix hechting en delaminatie

De vermoeingsongevoligheid van ARALL is mede te danken aan het onstaan van een "gecontroleerd" delaminatie gebied rond de vermoeingsscheur. Een onderzoek naar deze delaminaties is het onderwerp van deel I. Het onderzoek is gesplitst in twee delen:

1) Een experimenteel gedeelte waarin aan de hand van verschillende proefstuktypen de ontwikkeling en de groei van delaminaties wordt bestudeerd. Getracht wordt de resultaten vast te leggen in karakteristieke grootheden uit de breukmechanica (K, G).
2) Een theoretisch gedeelte waarin aandacht besteed wordt aan de richting van delaminatie-uitbreiding.

Deel I wordt afgesloten met een beschouwing rond de invloed van delaminaties op de breuktaaiheids- en vermoeingseigenschappen van ARALL.

Om een zo volledig mogelijk overzicht te krijgen van mogelijke belastingsomstandigheden (mode I, mode II, mode I+II), zijn er in het experimentele programma zeven verschillende proefstuk geometriëén opgenomen. De meeste van deze proefstukken zijn ontwikkeld voor het onderzoek van lijmverbindingen. Omwille van de complexe opbouw van ARALL (metaal+vezels+lijm) was het noodzakelijk de spanningsverdeling in de proefstukken nader te onderzoeken. Deze studies zijn opgenomen in appendix, gebundeld aan het eind van deel I.

Niet alle proefstukken zijn even bruikbaar voor het karakteriseren van delaminaties in ARALL. Het WTDCB (width tapered double cantilever beam) proefstuk bleek uitermate geschikt te zijn voor dit doel. Het kan zowel voor statische als voor vermoeingsproeven worden toegepast. De Bell-peel proef is alleen geschikt voor het verkrijgen van kwalitatieve indicaties. De peel-
sterkte zelf heeft echter geen reële betekenis voor de grootte van de delaminatie weerstand. Een drietal veel gebruikte beproevingsmethoden voor het evalueren van delaminatie onder een afschuijbelaasting (mode II) vertonen voor een ARALL configuratie ernstige tekortkomingen:
1: De afschuifsterkte van een ILS (interlaminar shear) proefstuk wordt in hoge mate beïnvloed door plastische deformatie van de metaallagen.
2: De afschuifsterkte van het TA (thick adherend) proefstuk bleek bij een spanningsanalyse sterk afhankelijk te zijn van de proefstukgeometrie.
3: Inherent aan een FPO (fibre pull-out) proefstuk is de relatief korte lijm/vezel verbinding. Dit leidt meestal tot grote spreiding in resultaten als gevolg van lokale verontreinigingen.

Interessante resultaten werden bereikt met twee relatief onbekende proefstuk geometrieën: het ENF (edge notched flexure) proefstuk, dat beschouwd kan worden als de mode II tegenpool van het WTDCB proefstuk, en het CND (central notched delamination) proefstuk dat veel gelijkenis vertoont met een reële komposiet opbouw.

Bij ARALL onstaat een delaminatie in de aramide-prepreg laag op het grensvlak tussen een vezel-rijk en een lijm-rijk gedeelte. De situering van de delaminatie op deze plaats is het gevolg van de beperkte hechting tussen aramide vezels en het epoxy lijmsysteem. Onderzoek toonde aan dat deze delaminatie zone altijd kritiek is ongeacht de aard van de lokale belasting (mode I of II). Ook blijkt de aramide preprep als gevolg van de beperkte hechting zeer gevoelig te zijn voor een vermoeiingsbelasting (WTDCB proefstuk, mode I).

Aansluitend op het experimentele gedeelte is een berekeningsmethode ontwikkeld voor het evalueren van het delaminatiegedrag in ARALL. Hierbij is voornamelijk aandacht besteed aan het bepalen van de richting van delaminatie-uitbreiding. In een rekenmodel worden de spanningen bepaald rond een scheur gesitueerd op het grensvlak tussen een isotroop (lijm-rijk gebied) en een anisotroop (vezel-rijk gebied) materiaal. Het model is eerst getoetst aan de hand van twee gevallen met bekende oplossingen: een scheur in een homogeen isotroop materiaal en een scheur in een homogeen anisotroop materiaal. De overeenkomst tussen de numerieke resultaten en de exacte en/of breukmechanica-oplossingen bleek uitstekend. Een verrassend resultaat is dat het rekenmodel aantoonde dat, voor een scheur gesitueerd op een grensvlak tussen een isotroop en een anisotroop materiaal, de voornaamste spanningscomponent in het grensvlak (\(\theta=0^\circ\), \(\sigma_y\) voor mode I, \(\tau_{xy}\) voor mode II) onafhankelijk is van de stijfheidseigenschappen van de materialen aan het grensvlak. Om een voorspelling te
maken van de richting waarin delaminatie zich zal uitbreiden, is het noodzakelijk om, via een breukkriterium, de berekende spanningen te koppelen aan kritische grenswaarden. Drie onderzochte breukcriteria gaven dezelfde trends aan:
- delaminatie uitbreiding wordt bepaald door peel- en afschuifspanningen
- delaminatie uitbreiding zal eerder plaatsvinden onder een mode I dan onder een mode II belasting
- delaminatie uitbreiding vindt niet plaats in de richting van het lijm-rijke gebied
- voor een mode I belasting ligt een staps-gewijze delaminatie uitbreiding in het vezel-rijke gebied in de lijn der verwachting

- bij een mode II belasting zal delaminatie uitbreiding plaatsvinden op het grensvlak tussen de twee materialen

De invloed van de beperkte vezel/matrix hechting op het breuktaaiheids- en vermoeiingsgedrag van ARALL is tweevoudig:

1. Delaminatie zal optreden in de vezel-rijke laag op het grensvlak tussen de onderbroken en de ongestoorde vezels.

De delaminatie zal het effect van de spanningsconcentratie in de vezel-rijke laag als gevolg van de scheur in de aramide prepreg gevoelig verminderen.
2: Delaminatie zal ook optreden in het grensvlak tussen de lijm-rijke en de vezel-rijke laag in het gebied waar de vezels de scheur overbruggen. Deze delaminatie zal de spanningspiek in de vezels naast de initiële scheur verminderen en dus breuk van deze vezels uitstellen. Een nadeel van de delaminatie is echter dat ook het "crack-bridging effect" vermindert. Tijdens het optimalisatie proces uitgevoerd aan ARALL is daarom ook gezocht naar een middenweg.

Deel II: Invloed van vocht op delaminatie

In het tweede gedeelte van het onderzoek is de invloed onderzocht van vocht op de hechting tussen vezel en matrix. Zoals in deel 1 is het onderzoek gesplitst in een experimenteel deel (evaluatie invloed vocht op hechting) en een overwegend theoretisch deel, waarin de vochtopname van ARALL is bestudeerd.

Voor het beschrijven van de vochtopname van ARALL is gebruik gemaakt van analytische en van finite-difference rekenmethoden gebaseerd op de 2e wet van Fick. Hierbij moet worden opgemerkt dat het invoeren van een of meer constante diffusiecoëfficiënten (zoals gebruikelijk bij de 2e wet van Fick) alleen op macroschaal reëel is omdat dan de coëfficiënten beschouwd kunnen worden als een soort van gemiddelde waarde. Op microschaal spelen de diffusiecoëfficiënten van vezel en matrix en de positie van de vezels in de matrix een belangrijke rol. Berekeningen voor de micro-schaal zijn uitgevoerd voor diffusie respectievelijk parallel en loodrecht op de vezelrichting.

De vochtopname van ARALL op macroschaal is berekend met een 2-dimensionele afleiding van de 2e wet van Fick. Een 2-dimensionele afleiding is noodzakelijk omwille van de aanwezigheid van unidirectioneel aangebrachte aramide vezels (in tegenstelling tot koolstof en glas neemt aramide vocht op). Een experimenteel programma uitgevoerd met verschillende milieu omstandigheden (vochtige lucht en gedistilleerd water bij verschillende temperaturen) toonde inderdaad aan dat de invloed van de aramide vezels in het vochtopname proces belangrijk is. De diffusie coëfficiënt van de aramide prepreg in vezelrichting is ongeveer 3x groter dan de diffusie coëfficiënt loodrecht op de vezelrichting. Met behulp van deze gegevens kon ook voor diffusie op microschaal een schatting worden gemaakt van de diffusiecoëfficiënten van de vezel zelf. In vezelrichting is deze ongeveer 10x hoger, loodrecht op de vezelrichting een factor 10 tot 100 kleiner dan de diffusie coëfficiënt van het omringende matrix materiaal. Een soortgelijke trend was reeds eerder vermeld in de literatuur, waarbij echter veel grotere
verschillen werden gevonden tussen de diffusiecoëfficiënten van vezel en matrix.

Met een 3-dimensionaal model is de vochttopname van ARALL vergeleken met de vochttopname van twee gemodelleerde composiet materialen (met aramide, resp. koolstof). Dankzij de aanwezigheid van de metaalplaatjes is de vochttopname van ARALL verwaarloosbaar klein ten opzichte van de composieten alhoewel de diffusie coëfficiënten vergelijkbaar zijn. De metaallaagjes werken namelijk als diffusie barrières.

Van de twee gebruikte oplossingsmethoden voor vochttopname problemen (analytisch, resp. finite-difference) geniet de eerstgenoemde methode de voorkeur. De finite-difference methode moet zeer zorgvuldig gebruikt worden in verband met mogelijke vrije randen/of stabiliteitsproblemen. Verder vraagt de methode veel rekentijd. De kracht van de finite-difference methode ligt in de brede toepasbaarheid. Dat is vooral interessant bij samengestelde materialen.

De invloed van vocht op de vezel/matrix hechting is onderzocht met zes verschillende proefstuk vormen. Het WTDCB (mode I) en het delaminatie (mode II) proefstuk zijn zeer geschikt voor dit doel. Het wedge-edge (mode I) en het thick adherend (mode II) proefstuk zijn bruikbaar voor het snel bepalen van kwalitatieve trends. Slecht gedefinieerde proefomstandigheden zijn aanwezig bij het Bell-peel (mode I) en het interlaminar shear (mode II) proefstuk.

De proevenserie toonde aan dat de aramide vezel/matrix hechting verder verzwaakt wordt door de invloed van vocht. De vochtgevoeligheid van het vezel/matrix grensvlak is aanwezig bij zowel mode I als mode II belastingomstandigheden. De groeisnelheid van een delaminatie onder een combinatie van vocht en een mode I vermoeiingsbelasting is aanzienlijk. Als gevolg van de langzame vochttopname van ARALL treedt de verzakking alleen op als het vocht direct aan de delaminatie tip aanwezig is (bijv. b het wedge-edge en het WTDCB proefstuk) of bij kleine proefstuk afmetingen na relatief lange expositieperioden (ILS, TA proefstuk). De vezel/matrix hechting is veel gevoeliger voor gedistilleerd en voor zout water dan voor vochtige lucht. Voor het water is 70°C een kritieke temperatuur waarboven snel een sterke terugval optreedt. Onderzoek in een "salspray" milieu toonde aan dat bij ARALL "bondline corrosie" niet voorkomt als het materiaal goed is voorbehendeld bij het lijmen. Corrosieputten die ontstaan aan het aluminium oppervlak, gaan niet verder dan de prepreg laag. Deze laag werkt als een corrosie-barrière (het aluminium werkt ook als een vocht-barrière).
Résumerend mag worden gesteld, dat het onderzoek heeft bijgedragen tot nieuwe inzichten met betrekking tot:
(1) fenomenologische details in verband met delaminatie-ontwikkeling in ARALL,
(2) milieu-invloeden op de delaminatie-uitbreiding,
(3) bruikbaarheid van verschillende proefstuktypes voor het bestuderen van delaminaties in ARALL onder een mode I, mode II- of een gekombineerde belastingsconditie,
(4) het gebruik van breukmechanica voor het bestuderen van het delaminatiegedrag van ARALL, en
(5) het gebruik van diffusiemodellen voor het bepalen van de vochtopname van ARALL.
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<tr>
<td>temperature °C</td>
<td>relative humidity %</td>
<td>saturated salt solution</td>
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<td>-------------------------</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>magnesium chloride</td>
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<tr>
<td></td>
<td>50</td>
<td>sodium nitrate</td>
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<tr>
<td></td>
<td>80</td>
<td>ammonium sulfate</td>
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<td>50</td>
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<td>ammonium sulfate</td>
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Table 1: Saturated salt solutions for the different kinds of environments.
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<tr>
<th>temperature °C</th>
<th>relative humidity %</th>
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<th>width M/t (×10^5) (% sec^{-1/2})</th>
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<td>30</td>
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<td>2.928 (.98)</td>
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<td></td>
<td>50</td>
<td>2.549 (.97)</td>
<td>3.283 (.98)</td>
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<td></td>
<td>80</td>
<td>3.852 (.98)</td>
<td>5.269 (.99)</td>
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<td>30</td>
<td>6.065 (.99)</td>
<td>8.881 (.99)</td>
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<td>50</td>
<td>6.675 (.98)</td>
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<tr>
<td></td>
<td>80</td>
<td>8.325 (.99)</td>
<td>11.199 (.99)</td>
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<tr>
<td>5</td>
<td>distilled water</td>
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<td>3.712 (.93)</td>
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<td>79.110 (.99)</td>
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Table 2: Moisture pick-up of the specimens in the different environments. Values between brackets are the correlation coefficients of the linear parts of the weight gain curves.
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<tr>
<th>Temperature °C</th>
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<th>$D_z (x10^9)$ mm$^2$/sec</th>
<th>$D_y/D_z$</th>
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<td>179.85</td>
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<td>Distilled water</td>
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<td>100</td>
<td></td>
<td>4219.00</td>
<td>1281.00</td>
<td>3.30</td>
</tr>
</tbody>
</table>

Table 3: Diffusion coefficients parallel and perpendicular to the fibre direction for different kinds of environments. 

$D_y$: diffusion coefficient parallel to the fibre direction. 

$D_z$: diffusion coefficient perpendicular to the fibre direction.
<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>$D_x (x\times10^9)$</th>
<th>$D_y (x\times10^9)$</th>
<th>$D_z (x\times10^9)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARALL</td>
<td>60°C</td>
<td>0.00</td>
<td>325.50</td>
<td>94.85</td>
</tr>
<tr>
<td>CFRP</td>
<td>60°C</td>
<td>94.85</td>
<td>94.85</td>
<td>94.85</td>
</tr>
<tr>
<td>AFRP</td>
<td>60°C</td>
<td>94.85</td>
<td>325.50</td>
<td>94.85</td>
</tr>
</tbody>
</table>

Table 4: Diffusion coefficients used for the comparison of the moisture absorption rates of ARALL, AFRP and CFRP.

<table>
<thead>
<tr>
<th>M/M_m (uncoated)</th>
<th>115.5</th>
<th>578.5</th>
<th>868</th>
<th>1157</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>25.3%</td>
<td>56.0%</td>
<td>67.6%</td>
<td>76.1%</td>
</tr>
<tr>
<td>M/M_m (coating 1)</td>
<td>5.4%</td>
<td>32.8%</td>
<td>45.9%</td>
<td>56.4%</td>
</tr>
<tr>
<td>%</td>
<td>0.7%</td>
<td>6.7%</td>
<td>11.6%</td>
<td>16.9%</td>
</tr>
</tbody>
</table>

Table 5: Influence of a coating on the moisture content at different exposure periods.

- coating 1: $D_{coating} = 1/10 \ D_m$
- coating 2: $D_{coating} = 1/100 \ D_m$

$D_m = 1.10^{-7} \ mm^2/sec$
<table>
<thead>
<tr>
<th>( \frac{M}{M_m} \times 10^3 )</th>
<th>case I</th>
<th>case II</th>
<th>case I/case II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{fp} = \frac{1}{10} D_m )</td>
<td>7.49</td>
<td>7.75</td>
<td>0.97</td>
</tr>
<tr>
<td>( D_{fp} = \frac{1}{100} D_m )</td>
<td>0.24</td>
<td>0.11</td>
<td>2.18</td>
</tr>
<tr>
<td>( D_{fp} = 10^{12} D_m )</td>
<td>0.03</td>
<td>0.01</td>
<td>3.00</td>
</tr>
</tbody>
</table>

**cross-section AA (after second fibre)**

<table>
<thead>
<tr>
<th>( \frac{M}{M_m} \times 10^4 )</th>
<th>case I</th>
<th>case II</th>
<th>case I/case II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{fp} = \frac{1}{10} D_m )</td>
<td>3.66</td>
<td>2.76</td>
<td>1.33</td>
</tr>
<tr>
<td>( D_{fp} = \frac{1}{100} D_m )</td>
<td>0.05</td>
<td>0.00</td>
<td>----</td>
</tr>
<tr>
<td>( D_{fp} = 10^{12} D_m )</td>
<td>0.00</td>
<td>0.00</td>
<td>----</td>
</tr>
</tbody>
</table>

**cross-section BB (after third fibre)**

Table 6: Moisture contents of the cross-sections AA (after second fibre) and BB (after third fibre) for an exposure period of 116 days.

- \( D_m \): diffusion coefficient of the matrix
- \( D_{fp} \): diffusion coefficient of the fibre in radial direction
- \( M_m \): maximum moisture content
<table>
<thead>
<tr>
<th>environment</th>
<th>exposure period days</th>
<th>$P_0$ (N/mm)</th>
<th>$P$ (N/mm)</th>
<th>degradation $\Delta P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>saltspray</td>
<td>27</td>
<td>2.75</td>
<td>2.75</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>2.75</td>
<td>2.75</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>87</td>
<td>2.35</td>
<td>2.35</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>143</td>
<td>2.35</td>
<td>2.35</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>365</td>
<td>2.35</td>
<td>1.57</td>
<td>42.9</td>
</tr>
<tr>
<td></td>
<td>519</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>outdoor</td>
<td>1275</td>
<td>2.75</td>
<td>3.01</td>
<td>-9.5</td>
</tr>
<tr>
<td>humid air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RH(%) T(°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 20</td>
<td>160</td>
<td>2.70</td>
<td>2.70</td>
<td>0</td>
</tr>
<tr>
<td>30 50</td>
<td>160</td>
<td>2.80</td>
<td>2.60</td>
<td>-3.7</td>
</tr>
<tr>
<td>80 50</td>
<td>160</td>
<td>2.70</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>distilled water (100°C)</td>
<td>31</td>
<td>2.94</td>
<td>1.02</td>
<td>65.3</td>
</tr>
<tr>
<td>salt water (100°C)</td>
<td>31</td>
<td>2.94</td>
<td>1.12</td>
<td>61.9</td>
</tr>
</tbody>
</table>

Table 7: Influence of various environments on the Bell-peel strength.
Average values of four to six specimens
$P_0$: initial peel strength (no exposure)
$P$: peel strength after exposure
$\Delta P = (P_0 - P)/P_0$
<table>
<thead>
<tr>
<th>Prepreg orientation</th>
<th>Environment</th>
<th>Temperature (°C)</th>
<th>Exposure period (days)</th>
<th>critical load level (N)</th>
<th>degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length direction</td>
<td>no exposure</td>
<td>----</td>
<td>----</td>
<td>1567</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>humid air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RH(%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>20</td>
<td>160</td>
<td>1586</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td>1579</td>
<td>-0.8</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>50</td>
<td></td>
<td>1599</td>
<td>-2.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td>1583</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td>1586</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td>distilled</td>
<td>20</td>
<td>110</td>
<td>1555</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40</td>
<td>110</td>
<td>1535</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>31</td>
<td>1520</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>93</td>
<td>1480</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>110</td>
<td>1480</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>110</td>
<td>1250</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>salt spray</td>
<td>35</td>
<td>31</td>
<td>1540</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93</td>
<td></td>
<td>1515</td>
<td>3.3</td>
</tr>
<tr>
<td>Width direction</td>
<td>no exposure</td>
<td>----</td>
<td>----</td>
<td>1364</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>humid air</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RH(%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>20</td>
<td>160</td>
<td>1430</td>
<td>-4.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td>1385</td>
<td>-1.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>50</td>
<td></td>
<td>1380</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td>1370</td>
<td>-0.4</td>
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<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td>1300</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>distilled</td>
<td>20</td>
<td>110</td>
<td>1420</td>
<td>-4.1</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40</td>
<td></td>
<td>1335</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td></td>
<td>1200</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td></td>
<td>930</td>
<td>31.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>31</td>
<td></td>
<td>1005</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>salt water</td>
<td>100</td>
<td>31</td>
<td>995</td>
<td>27.1</td>
</tr>
<tr>
<td></td>
<td>(5%NaCl)</td>
<td>60</td>
<td></td>
<td>970</td>
<td>28.9</td>
</tr>
<tr>
<td></td>
<td>ditto-drying</td>
<td>60</td>
<td></td>
<td>1190</td>
<td>12.8</td>
</tr>
</tbody>
</table>

Table 8: Influence of environmental exposure on the critical load ILS-specimen.
<table>
<thead>
<tr>
<th>intermediate layer</th>
<th>R</th>
<th>$P_{\text{max}}$ (N)</th>
<th>test frequencies (Hz)</th>
<th>test results $\frac{da}{dn}$ (x10$^{-6}$)</th>
<th>0.10Hz</th>
<th>0.20Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>adhesive</td>
<td>0</td>
<td>1000</td>
<td>0.10</td>
<td>unstable</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.10, 0.20</td>
<td>156.0</td>
<td>86.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>0.10, 0.20</td>
<td>32.5</td>
<td>26.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.10</td>
<td>3.1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.10</td>
<td>no growth</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>800</td>
<td>0.10</td>
<td>117.0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>800</td>
<td>0.10</td>
<td>35.0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>800</td>
<td>0.10</td>
<td>1.2</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>aramid prepreg</td>
<td>0</td>
<td>600</td>
<td>0.10</td>
<td>unstable</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>0.10, 0.20</td>
<td>350.0</td>
<td>115.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.10, 0.20</td>
<td>40.0</td>
<td>24.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.10, 0.20</td>
<td>1.3</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>0.10, 0.20</td>
<td>1.2</td>
<td>no growth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>500</td>
<td>0.10</td>
<td>385.0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>500</td>
<td>0.10</td>
<td>92.5</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 9: Survey of the environmental fatigue test series on WTDCB-specimens
Tests performed in distilled water (20°C)

<table>
<thead>
<tr>
<th>Sustained load (N)</th>
<th>% of ultimate load</th>
<th>Test results: Time to failure in salt water (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11750 (static strength)</td>
<td>100</td>
<td>$T=25^\circ C$</td>
</tr>
<tr>
<td>9400</td>
<td>80</td>
<td>1.5</td>
</tr>
<tr>
<td>7050</td>
<td>60</td>
<td>&gt;1200</td>
</tr>
<tr>
<td>4700</td>
<td>40</td>
<td>&gt;1200</td>
</tr>
<tr>
<td>2350</td>
<td>20</td>
<td>&gt;1200</td>
</tr>
</tbody>
</table>

Table 10: Survey of results of the sustained load tests on delamination specimens
<table>
<thead>
<tr>
<th>environment</th>
<th>temperature (°C)</th>
<th>external loading (N/mm²)</th>
<th>exposure periods in weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>dry air</td>
<td>20</td>
<td>---</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>---</td>
<td>-</td>
</tr>
<tr>
<td>distilled water</td>
<td>20</td>
<td>---</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>---</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>---</td>
<td>x</td>
</tr>
</tbody>
</table>

Table 11: Survey of the environmental conditions for the residual stress relaxation test series. In all cases two specimens were tested, except for the period of 56 weeks (2 to 6 specimens, in most cases 6 specimens).
dry yarn data shown by solid line
wet yarn data shown by points

Figure 1: Effect of temperature on the tensile strength and the tensile modulus of dry and wet yarns of aramid fibres after exposure for 21 days at 80°C and 95% R.H. (data from ref. 4).

Figure 2: Room temperature break strength retention after air aging of yarn of Kevlar 49 at various temperatures (data from ref. 4).

Figure 3: Specimen used for weight gain experiments (moisture absorption).
Figure 4: Survey of the weight gain results. Test series A: distilled water exposure of six environmental temperatures.
Figure 5: Survey of the weight gain results. Test series B: different relative humidity and temperature levels.

(1): 30% rel. humidity
(2): 50% rel. humidity
(3): 80% rel. humidity
Figure 6; Relation between the maximum moisture content and relative humidity (ARALL specimen).
Figure 7: Weight gain curves of ARALL specimens (fibres in length or width direction) for a 100°C, distilled water environment.

Figure 8: Weight gain curve of ARALL specimens (fibres in width direction) for a 80°C, distilled water environment.
Figure 9: Relation between diffusion coefficient and temperature (ARALL specimens, distilled water exposure).
Figure 10: Two dimensional moisture profiles of an ARALL specimen for a $50^\circ$C, 50% relative humidity environment. Four different exposure periods.
Figure 10c: Period 100 days.

Figure 10d: Infinite period, full saturation.

Figure 10 (continued)
Figure 11: Comparison between the calculated moisture absorption of ARALL and AFRP (aramid fibre reinforced plastic) and CFRP (carbon fibre reinforced plastic) for a 60°C distilled water environment.

Specimen dimensions: length = width = 50 mm

thickness = 1 mm
Figure 12: Comparison between the calculated moisture absorption of ARALL and AFRP (aramid fibre reinforced plastic) and CFRP (carbon fibre reinforced plastic) for a 60°C distilled water environment.
Specimen dimensions: length = width = 50 mm
thickness = 10 mm
Fig. 13: Finite difference method

--- : single material

-- -- : two materials (see upper drawing) $D_{II} = 1/10 \ D_I$
Fig. 14: Comparison between a numerical (finite difference) and analytical solution method (single material; \( D = 5 \times 10^{-8} \text{ mm}^2/\text{s} \))

- *: analytical solution
- ○: numerical solution
- □: adjusted numerical solution
Fig. 15: Influence of a protective coating on the concentration distribution in ARALL (theoretical model)
Fig. 16: Survey of the weight gain results of the coated and uncoated specimens:  
(1): no coating  
(2): degreasing and coating  
(3): degr. + etching and coating
moisture bubbles

Fig. 17 : The presence of moisture bubbles in a coating on the edges of an ARALL specimen
Fig. 18: Comparison between the moisture absorption of aramid fibres and an epoxy matrix (20° C, 76 % relative humidity)
Fig. 19: Concentration distribution in a matrix with a single central fibre after different exposure periods
Fig. 20: Concentration distribution in a single matrix specimen (no fibres): exposure period: 116 days
diffusion coefficient matrix: $2.5 \times 10^{-8}$ mm$^2$/s
$D_m = \text{matrix diffusion coefficient} = 2.5 \times 10^{-8} \text{ mm}^2/\text{sec}$

$D_{f/p} = \text{fibre diffusion coefficient} : \text{3 values}$

Fig. 21: Concentration distribution for a matrix with three fibres (case I):
exposure period: 116 days
$D_m$ = matrix diffusion coefficient = 2.5 $10^{-8}$ mm$^2$/sec
$D_{fp}$ = fibre diffusion coefficient : 3 values.

Fig. 22: Concentration distribution for a matrix with three fibres (case II): exposure period: 116 days.
Fig. 23: Concentration distribution for case I and II at cross-section AA (behind second fibre).
Exposure period: 116 days
$D_{fp}$: radial fibre diffusion coefficient
$D_m$: matrix diffusion coefficient
Fig. 24: Concentration distribution for case I and II at cross-section BB (behind third fibre)
Exposure period: 116 days

$D_{fp} = D_m / 10$

$D_{fp} = D_m / 100$

$D_{fp} \approx 0$

no moisture

case I

case II

$D_{fp}$: radial fibre diffusion coefficient
$D_m$: matrix diffusion coefficient
Figure 25: Influence of high temperature (100°C), distilled water exposure on the fractured surface of an aramid prepreg (Bell-peel test).
Magnification: x
Figure 26: Thick adherend specimen for the environmental tests.

Figure 27: Influence of environmental exposure on the critical shear stress. Thick adherend specimen (fig. 37).
Figure 28: Fracture surface of the aramid prepreg (fibres in width direction in a thick adherend specimen. Magnification: x5.

Figure 29: Interlaminar shear (ILS) specimen for environmental tests.
Figure 30: Effect of environment, temperature, humidity and fibre orientation on failure load in interlaminar shear tests (ILS).
Figure 31: Width tapered double cantilever beam (WTDCB) specimen.

Figure 32: $G_{IC}$-test performed on a WTDCB specimen in an environmental cell.
Figure 33: The decrease of the influence of the deteriorated part with increasing crack length (deterioration of the specimen edges due to environmental pre-exposure).

Figure 34: Influence of distilled water exposure (90°C) on the energy release rate of a carbon and aramid prepreg. Because for the exposed specimens, $G_{1c}$ increased with crack length, the crack lengths at the beginning and the end of the measurement period are noted.
Figure 35: Fracture surface of the aramid prepreg after environmental exposure (160 days distilled water at 90°C) followed by $G_{1c}$ testing. Magnification: 5x.

Figure 36: Comparison of the fracture surfaces of an aramid prepreg with and without environmental exposure. Magnification: x.
Figure 37: Fracture surface of the carbon prepreg after environmental exposure (160 days distilled water at 90°C) followed by $G_{1c}$ testing. Magnification: 5x.
Figure 38: The influence of environmental exposure on the energy release rate of two prepreg and an adhesive (in the prepreg, the adhesive is used as matrix system).
- Test performed in a distilled water environment at two different temperature levels (20°C and 50°C).
- Because for the exposed specimens, $G_{IC}$ is a function of the crack length, the crack lengths at the beginning and end of the measurement period are noted.
Figure 39a: Fracture surface of the adhesive after $G_{lc}$ testing in an environmental cell (distilled water exposure-temperature 20°C). Magnification: 25x.

Figure 39b: Three typical fracture zones on the surface of the adhesive after $G_{lc}$ testing in an environmental cell (see Fig. 50a). Magnification: 20x.
Figure 40: Magnification of zone A in Fig. 39b, cohesive failure in the adhesive. Magnification: 85x.

Figure 41: Magnification of zone C in Fig. 39b, interfacial failure at the adhesive/adherend interface (adhesive side). Magnification: 300x.
Figure 42: Magnification of zone B in Fig. 39b, interfacial failure at the adhesive/adherend interface (adherend side). Magnification: 300x.

Figure 43: Aramid fibre surfaces after $G_{1c}$ testing in an environmental cell (distilled water exposure, temperature 20°C). Magnification: 1360x.
Figure 44: Carbon fibre surfaces after $G_{lc}$ testing in an environmental cell (distilled water exposure, temperature $20^\circ C$). Magnification: 2020x.
Figure 45: Influence of distilled water exposure on the crack growth rate of an adhesive. 

R = 0.

UCG: unstable crack growth.

$P_{\text{thr}, dw}$: threshold fatigue load level in distilled water.

$P_{\text{thr}, la}$: threshold fatigue load level in laboratory air.
Figure 46: Influence of distilled water exposure on the crack growth rate of a prepreg.

R = 0.

UCG: unstable crack growth.

$P_{\text{thr, dw}}$: threshold fatigue load level in distilled water.

$P_{\text{thr, la}}$: threshold fatigue load level in laboratory air.
Figure 47: Wedge-edge specimen.
Figure 48: Increasing crack length and the corresponding decreasing $G_I$ during a wedge-edge test (schematic picture).
Figure 49:
Threshold $G_{IC}$ values for different environmental exposures. Results of wedge-edge tests.
Figure 50: Schematic picture of sustained load curves.
Figure 51: Delamination specimen used in the sustained load test series.
calculated with:
\( E_{ad} = 72500 \), \( E_{fr} = 62500 \), \( G = 580 \) (N/mm²)
\( t_{ad} = 0.5 \), \( t_{fr} = 0.184 \), \( t_{rr} = 0.046 \) (mm)
\( L = 150 \), \( b = 50 \) (mm)

Figure 52: Calculated shear stress distribution in the resin-rich layer of a delamination specimen.
Figure 53: Preliminary sustained load test results (delamination specimen).
Figure 54: Specimen used for measuring possible relaxation of residual stresses.
Figure 55a: Exposure to a 20°C dry air environment.

Figure 55b: Exposure to 20°C distilled water.

Figure 55c: Exposure to 40°C distilled water.

Figure 55: Effect on environmental exposure on the internal stress in the Al-sheets of ARALL.
Figure 56: Remaining residual stress in the aluminium sheet of specimens exposed to a dry air environment and a distilled water environment, both 70°C.
Figure 57: Varying radius along the length direction of the specimen due to moisture absorption.