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A Review Of Mechanisms And Fracture Mechanics Of Moisture Ingress In Composite Systems

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A REVIEW OF MECHANISMS AND FRACTURE MECHANICS OF MOISTURE INGRESS IN COMPOSITE SYSTEMS

By

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A project report presented to Ryerson University

in fulfillment of the requirements
for the degree of
Master of Engineering
In the program of
Aerospace Engineering

Toronto, Ontario, Canada, 2012
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Abstract

Composite materials help realize high strength to weight ratio requirements of the Aerospace Industry. Composite structures and sandwich composite structures are susceptible to moisture ingress. Moisture ingress causes degradation of thermo-mechanical properties of the composite panels. Water accumulation in sandwich composite structures causes rapid degradation of face to core bondline, damage of cells frozen water and even blow off skins owing to sudden pressure build up in the cells of the honeycomb structure. Mechanisms of moisture ingress can be broadly classified into direct and indirect mechanisms. Direct ingress occurs through pre-existing pathways formed by defects in the composite system. Indirect mechanisms are diffusion, Capillary actions, Wicking actions, and Osmosis. The first form of damage in FRP materials is microcracking. The rate of microcracking increases with moisture ingress. Microcracking fracture toughness is a material property for the susceptibility of a composite system to the formation of microcracks. This work implores the mechanisms and the fracture mechanics dominating the formation of microcracks.

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*To my loving parents and husband.
I hope to make you proud.*

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List of symbols

J – Diffusive flux

D – Diffusion coefficient

Φ – Concentration

T – Temperature

T_s – Saturation time

$M(\infty)$ – Equilibrium moisture content

RH – Relative humidity

PEEK – Polyether ether ketone

M_e – Equilibrium weight uptake

M_t – Weight increase at time t

G_{mc} – Microcracking fracture toughness

G_m – Energy release rate

CHAPTER 1

INTRODUCTION

A combination of materials, with different characteristics put together in ingenious methods, resulting in superior products is the philosophy of composite materials. Some common examples are steel reinforcements with concrete for stronger building support structures, straw reinforced mud for making roofs of huts etc. The emergence of boron filaments in the early 1960s ushered in a new generation of composites. The composite materials that utilize high modulus continuous filaments such as boron and carbon/graphite are termed as advanced composites. This impressive class of materials has given a turning point in the design of airframe and space craft structures and continues being the most promising materials for future innovations in the field.

Aircrafts and spacecrafts are weight sensitive structures. For example, in commercial transports, the value of weight savings in airframe structures is about \$800/lb. In spacecrafts, it is \$30,000/lb [1]. The use of composites in this industry, where the benefits of high strength to weight and high stiffness to weight ratios are exploited, it can prove to be cost-effective. The challenge of making structures as light as possible without decreasing strength and stiffness in aircraft design is often a belittled challenge.

The requirements dictate the need to stabilize thin sheets, often called skins, to withstand tension and compressive forces and a combination of both in the forms of shear, bending and torsion. Traditional metal designs of airframe structures have overcome this challenge by adding longitudinal stiffeners, stringers, ribs, and frames. This turns out to be a cumbersome process as

it adds hardware weight, assembly hours and possibilities for inaccurate assemblies leading to catastrophic results. The stabilization of surfaces - creating resistance to deforming forces - can be efficiently effected by the use of two skins with a stabilizing medium between them - which is now termed a sandwich structure [1]. It is noteworthy to observe that this has been derived from nature - In the human skull, the bone structure comprises of two compact (Cortical) layers of bone separated by a cancellous bone forming a sandwich structure. The presence of core helps increase the moment of inertia helping the structure become more efficient in resisting bending and buckling loads.

Thin, strong skins bonded to low-density honeycomb core structure is attractive for applications where low-deflection structures of minimum weight are needed. Some examples of such applications would be aircraft nose radomes, bullet fairings, leading and trailing edges, fuselage floor panels etc. Honeycomb structures can be made out of any thin sheet material. They could be made out of metals, fiberglass, paper and even with advanced composite materials in the form of hexagonally shaped cells. Because of the core's light weight and high strength, the end product, being the panel with the twin skins and the middle core, need not have a high thickness.



Figure 1 - Sandwich structure construction [8]

Water Ingress

Even though the positive characteristics of each component, separately, are used for the advantage of the end result product, there are disadvantages to composite structures. Whereas composite sandwich structures in addition to the complexity of issues faced by composites, adds on considerable amount of structural complexity. The sandwich construction panels in the aircraft industry are susceptible to degradation due to moisture ingress due to environmental agents. For example, Rotor blades of the McDonnell Douglas Apache and Boeing Chinook helicopters are known to have problems with accumulation of water in the cells of their honeycomb core. Thermographic inspection of Boeing 767 operated by United Airlines showed the nose landing gear doors, which were composite honeycomb structures, held liquid water as much as 7500 cm², which can equivalent an extra 20 kg of weight if the cells were completely filled [2]. The elevator sandwich panels of an Airbus had disbonded areas due to water ingress, triggering an FAA airworthiness directive mandatory inspection and re-protection of affected susceptible surfaces against moisture ingress on all Airbus A330-200, A340-300 and A340-300 stabilizers and elevator panels [2]. In addition to adding extra weight water ingress can also

induce structural failure of composite sandwich structures. In 1999, a Canadian CF-18 Hornet had an in flight disintegration which is attributed due to degradation of mechanical properties due to water ingress.

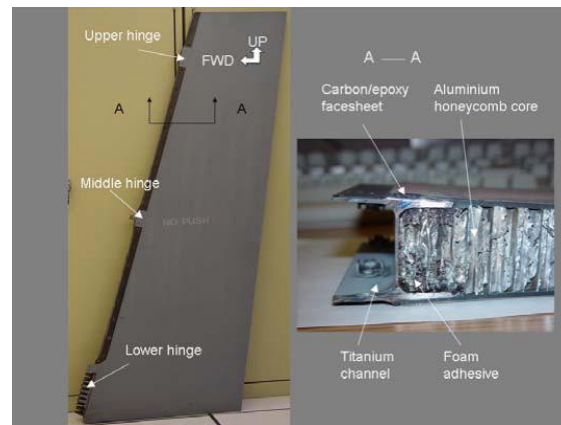


Figure 2 - Configuration of CF-18 rudder [2]

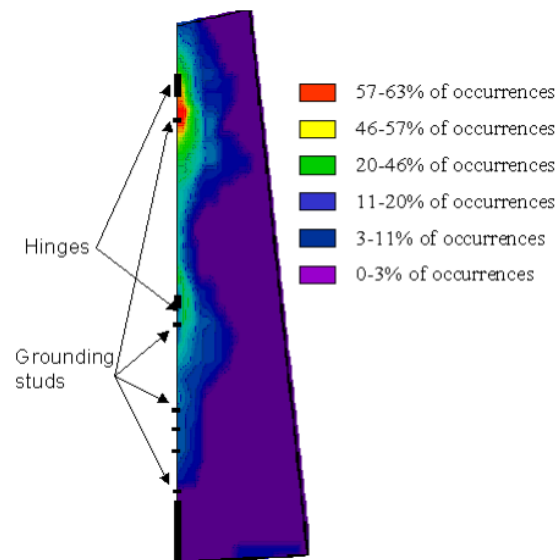


Figure 3- Water ingress cumulative occurrence map developed based on 202 CF-18 rudders inspected between 1999-2004 using thermography [2]

It is obvious that the water ingress phenomenon is not a random occurrence. For example, the majority of occurrences in CF-18 rudders concentrate in the upper and middle hinges, presumed to be due to the breakdown of the sealants used in those areas. Even though water ingress is a

common problem stemming from simple human judgment error such as one ill-fitted skin panel, hole drilled at the wrong place or at wrong angle, or poor sealing around the skin fittings, in all composite systems, it presents a unique more intensified problem with composite sandwich structures due to various reasons as discussed below.

Among the affected areas of various aircrafts, A320 elevators had panel edge inserts, bonding straps and panel surfaces water ingress. A300/310 rudders had disbond between cores and facesheets due to water and skydrol contamination [2]. Water accumulation is believed to induce rapid degradation of face to core bondline in addition to degradation of the composite facesheet thermo-mechanical properties itself. The water in the honeycomb cells expands after freezing breaking the cells [3]. Further repairs of bonded structures, or sometimes the part replacements itself are required for structural integrity of sandwich structures. Inadequate moisture removal could lead to bondline holding higher number of voids, degradation of adhesive bonds and sometimes even blow off skins owing to sudden build up of pressure due to fluid accumulation in the cells of the honeycomb structure [2].

Some of the other disadvantages of sandwich structures (in turn with composites) are lack of visual sign of damage, delaminations, variations of properties with temperature, etc.

Delamination, a failure mechanism when the different layers of the composite are no longer bonded together, is the ultimate result which could be triggered by impacts, fluid ingress, and manufacture defect or even by stresses and fatigue. Unlike metals, compressive loads can be the most destructive for composites as load tends to travel through the fiber which could cause buckling and microbuckling leading to reduction in stiffness of the component. Environmental agents such as electromagnetic effects, fire and high temperatures [4], lightning and electrical discharges, ozone causing chemical degradation, erosion by sand and wind, contact with organic

fluids such as fuels, lubricants etc, low energy impact causing Barely Visible Impact Damage (BVID) and uptake of unwarranted moisture cause loss of thermo-mechanical properties of composites.

Objective

The object of this project is to do a survey of existing literature to understand the phenomenon of moisture ingress in Fiber Reinforced Polymer Composites (FRPC) and to see if there is a way to quantify the susceptibility of a composite laminate to moisture ingress. Given the relative freshness of this field in mechanics, researches are still heavy on detecting existing moisture ingress and preventing moisture ingress, in response to the immediate requirements of the Aerospace industry. But long term benefits will emerge by characterizing the process of moisture ingress in FRPC panels and quantifying the susceptibility of the composite laminate to moisture ingress. This project implores this possibility by reviewing published literature.

CHAPTER 2

FAILURE MODES OF COMPOSITE CONSTRUCTION

2.1 Failure mechanisms of Composite panels

This chapter summarizes the various mechanisms of failure of composite material systems.

2.1.1 Matrix cracking

The ability of composites to remain functionally adequate is a safety and economic concern. In most cases, the first form of failure is the matrix cracking, happening long before the exhaustion of its load carrying capability. Matrix cracking is a highly local phenomenon occurring when the local stresses exceed the strength of the laminate. This kind of failure mode occurs in the weakest part of the laminate such as off-axis plies, interphases, and interfaces [5].

2.1.2 Fiber-matrix debonding

The interface between fiber and matrix plays a key role in the mechanical behavior of continuous fiber reinforced composite systems. A strong fiber-matrix interface assists in dissipating applied loads from the fiber to the matrix effectively. Thus the interface govern the critical parameter, the extent of load transfer between the two components [6]. In cases of weak bonding, isolated fiber fractures would be a common mode of failure leading to applied loads pulling fractured fibers and matrix apart causing fiber-matrix debonding. This limits the composite system functionally.

2.1.3 Delamination

Weak bonding causes delamination, a failure mode characterized by the inter-laminar fracture of various layers of the laminate.

2.1.4 Fiber fracture

Fiber fracture can occur in continuous fiber reinforced polymer systems due to tension or compressive loading conditions. The energy consumed by this fracture mechanism is much higher than those involving matrix cracking or fiber-matrix interface debonds. In compression, this process follows kinking of the fibers.

2.1.5 Fiber pullout

Fibers get pulled out of their sockets in the matrix during the crack propagation. This essentially begins after the interfacial debonding and fiber fracture have taken place earlier to enhance the pulling out of the fiber from the sockets.

2.1.6 Microbuckling

Under axial compression of continuous aligned fiber reinforced polymer systems, microbuckling occurs, where fibers undergo kinking locally.

2.1.7 BVID

Barely visible impact damage occurs when small damages not usually detected during maintenance using visual techniques in normal lighting conditions from a distance of five feet [7].

2.2 Failure modes of sandwich construction:

To understand the process of moisture ingress within sandwich structures, it is essential to understand the failure modes. Sandwich panels reach failure due to three main reasons - Insufficient strength, local instability, and general instability [8].

2.2.1 Insufficient strength:

When the construction fails due to the applied forces exceeding the designed strength, the following failure modes occur leading to various direct water ingress pathways.

Facing failure - Facesheets crack due to insufficient strength.

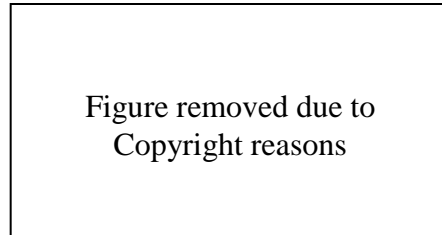


Figure 4 - Facing failure [8]

Transverse shear failure - Insufficient shear strength of the core or face to core bonding resulting in shear failure in the core or debonding of face to core adhesive.

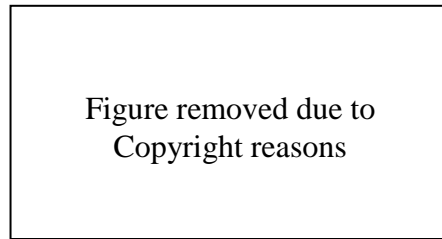


Figure 5 - Transverse shear failure [8]

Flexural core crushing - Insufficient compressive strength of the core during bending conditions result in local buckling in sections of the core.



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Figure 6 - Flexural crushing of core [8]

Flatwise tension or compression - Occurs in the ramp area where bag side facesheet changes direction. “The flatwise, or inter-laminar, stresses are induced at the ramp radii. A flatwise tension stress can cause face to core debonding, while a flatwise compression stress can cause core crushing” [8]. To mitigate this effect, in practice, options such as (i) denser core at ramp, (ii) extra adhesive at ramp base and top, (iii) increased corner radii at those locations, (iv) reduced ramp angle, and (v) increased face thickness in the ramp region are available to designers[9].



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Figure 7 - Flatwise tension or compression [8]

2.2.2 Local Instability

Local deformations occur that don't ripple through the whole component at the particular instant of loading.

Intracell buckling - The cells in a honeycomb construction have an unsupported length of the facesheet. This face sheet could wrinkle or dimple (buckle) in and out at the unsupported phase. The major trigger for this kind of failure is insufficient thickness of the facesheets.

Face wrinkling - Local buckling in and out of the facesheets accompanied by core crushing or core to face debonding occurring due to low density of the core or improper bonding of face to core.



Figure 8 - Kinds of local instability [8]

2.2.3 General Instability

General buckling - With the facesheets and core remaining intact buckling occurs as in metals

Shear crimping - Local core shear failure and lateral dislocation of facesheets characterize this general instability occurring when the wavelength of each buckle is the same order as the cell size. Due to the small magnitude of shear crimping, it is misunderstood as local instability, but due to its occurrence throughout the panel, it is a form of general instability.



Figure 9 - Types of General buckling [8]

CHAPTER 3

MECHANISMS OF MOISTURE INGRESS

The mechanisms through which fluids make way into a composite system can be divided into the direct and indirect mechanisms.

3.1 Direct Mechanism of Moisture ingress in Composites:

The direct mechanisms of fluid ingress happen when there are pre-existing cracks, frayed edges exposing disbonded matrix-fiber interface, unsealed fastener holes, holes within the cells of the core structure etc. Where there is an unobstructed pathway for liquid or gaseous moisture to penetrate inside the sandwich structure without having to resort to complex mechanisms, direct ingress takes place.

3.2 Indirect Mechanism of Moisture ingress in Composites:

The various methods of indirect fluid ingress are described below.

3.2.1 Diffusion:

The failure of dry laminates is in most cases, dominated by fiber related failure mechanisms. Whereas decrease in flexural strength after wet conditioning suggests that water ingress triggers different mechanisms by plasticizing of matrix[10]. Diffusion is defined as “a process by which matter is transported from one part of the system to another as a result of random molecular motions” [11]. Diffusion in most cases obeys the Fick’s law which postulates that diffusive flux goes from a region of high concentration to a region of low concentration with a measure that is proportional to the concentration gradient.

$$\mathbf{J} = -D(\delta\phi/\delta x)$$

where J is the diffusive flux, D is the diffusion coefficient, φ is the concentration and x being the position of measurement. It is important to note that Fick's law states that the absorption process is independent of moisture concentration. It is important to note that the diffusion coefficient displays a dependence on temperature characterized by the formula, $D(T) = Ae^{-B/T}$, where A and B are empirical constants dependent slightly on fluid content. In composite systems, in addition to Fickian behavior, there is non-Fickian behavior as well. In some cases, penetrant molecules get trapped in random sites in the polymeric chains. Attachments such as these are temporary and over time, exchanges occur between free, mobile penetrant molecules and the vaulted molecules.

Diffusion is dependent on two time dependent variables namely - Diffusion across the thickness of the polymer system and the relaxation of the polymer chains which is time dependent. The relaxation time is enhanced by fluid content, this coupling of processes, depends heavily on the thickness of the polymer system. A very thin polymeric system will attain equilibrium in terms of uniform diffusion much more quickly than the time taken for the progression of the relaxation process. Hence the mechanism of fluid ingress is driven by the diffusivity of an unrelaxed polymer. But for a thicker slab, the diffusion tends to be slower than the relaxation process pushing the phenomenon of fluid ingress to be dominated by the relaxation process [14]. For an intermediate thickness of a polymer system, we can see parallel coupling of both the phenomenon as shown in the figure below.

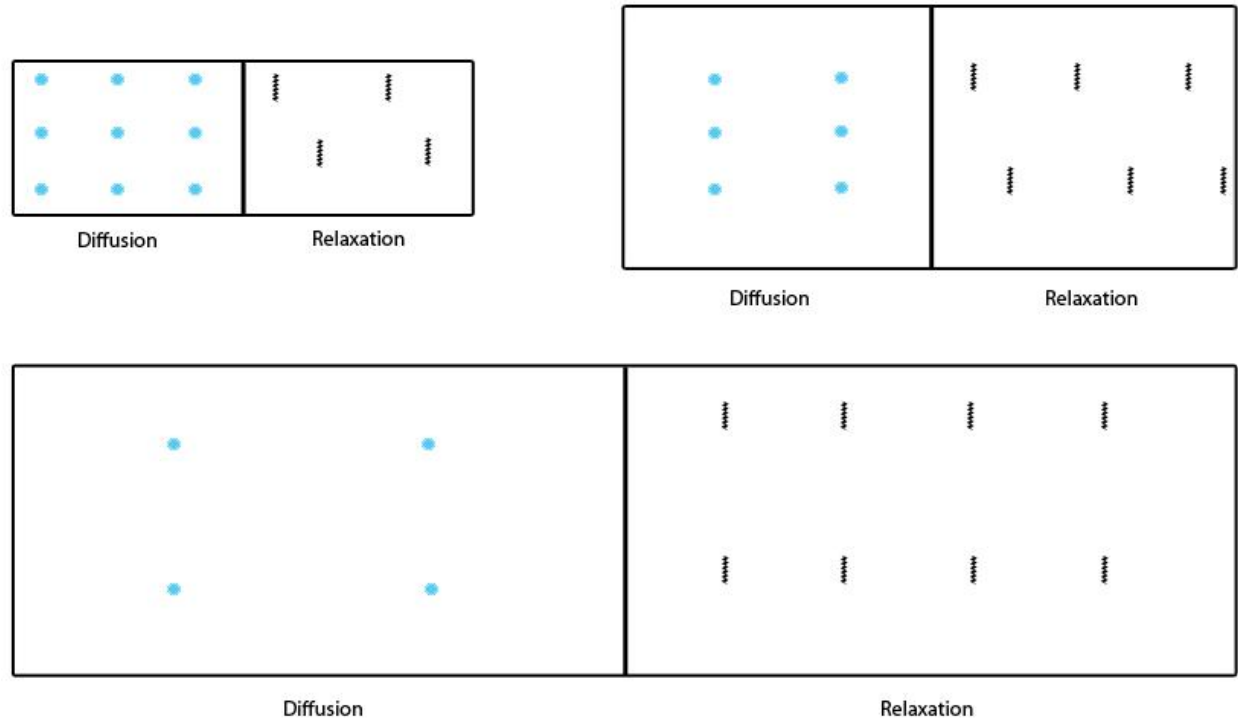


Figure 10 - Two stage diffusion process in composite panels with varying thickness

This phenomenon is described as two stage diffusion, a combination of Fickian and Non-Fickian behavior. Diffusion and polymeric creep happen at similar timelines except in the extreme cases of very thin and very thick plates. T_s , the saturation time is proportional to h^2 (h is the thickness of the panel). The mechanics and formulations are not discussed in this work as it is beyond the scope of this work. In [12], two samples of epoxy molding compounds with varying thicknesses (1mm with a diameter of 50mm and 2mm with a diameter of 100mm) were subjected to diffusion tests. Both the samples showed Fickian behavior in the beginning but as time progresses, there is deviation from Fickian behavior suggestion dual stage diffusion as shown in the figure below.

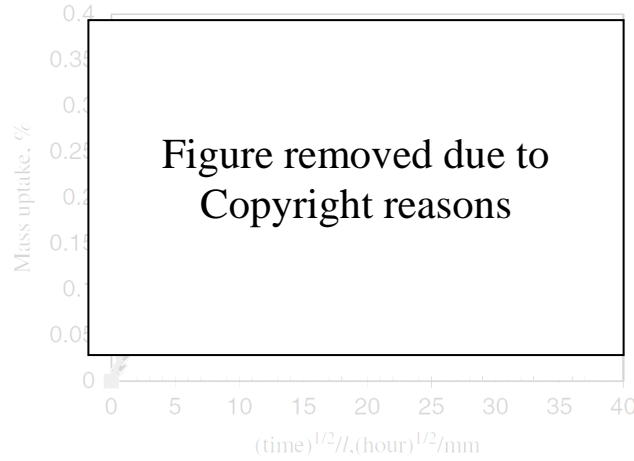


Figure 11 - Effect of sample geometry on non-Fickian behavior [12]

Diffusion of water molecules occurs with humid air as well. A honeycomb panel embedded with thermocouple and humidity sensors in the core area was subjected to environmental conditions of 55% RH at 40 deg C for a period of 9 months. The humidity levels were constantly monitored. The core humidity level increased from 24% RH to 46% RH. The increase in humidity is due to the diffusion of water molecules through the carbon-epoxy facesheets. Such high humidity causes increase in weight and danger of freezing in low temperatures. Such detrimental freeze thaw cycle is consistent in the flight profiles of all transport vehicles [13]. The equilibrium moisture content is dependent on relative humidity by the formula,

$$M(\text{infinity}) = a_m (RH/100)^{b_m} \quad [14]$$

where a_m and b_m are constants and $M(\text{infinity})$ is the equilibrium moisture content [14].

Fluid chemistry and molecular structure exert a significant effect on the sorption process. This is observed in the PEEK polymer, where there is an increasing saturation level, in the order of sea water, tap water, distilled water, methylene chloride and n-hepatine with the increasing activity levels. Similarly increasing the acidity of the penetrant molecules leads to increasing the sorption process strongly. The choice of the polymer also affects the water ingress in the composite

system. The higher fracture toughness of epoxy translates to higher fracture toughness of composite systems with epoxy. Even though the epoxy polymer system showed better performance in the dry testing when compared to alternate polymer systems like isophthalic polyester, vinyl ester and urethane acrylate etc, they experienced the highest loss in strength when compared to the alternate systems which indicates a higher sensitivity to absorption of water [15]. Using a coupling agent on the surface area of the fiber to enhance the resin-fiber interface and promote better adhesion, did not promote retention of strength after fluid absorption. This proves that the bulk of the matrix is affected by the absorption of fluid [15] and not just the interface areas between the fibers and matrix. The ingress of fluids with higher molecular weights like oils, is substantially inhibited.

Topology, interactions of polarity and molecular motions also combine together to state the direction of the ingress process [16]. In the figures below, nanopores in the polymer are shown containing water molecules. With active sites in the epoxy resin, such as the N...HO bonds, water molecules are drawn into the molecular structure. In the model presented by the work (in figures 12 and 13), the polar sites act as bottle-necks for the transport of water molecules which impedes the transport of water molecules by diffusion. The amount of internal hydrogen bonds dictates the rate of transport. In figure 14, where a non-amine resin is shown, the absence of polar trapping sites, leads to an improved diffusion coefficient.

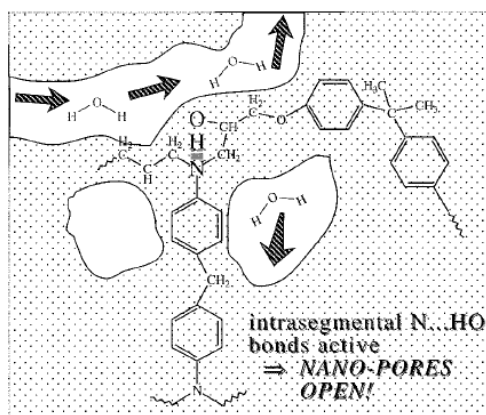


Figure 12 - Moisture diffusion through nanopores of amine-containing epoxy resin – I [16]

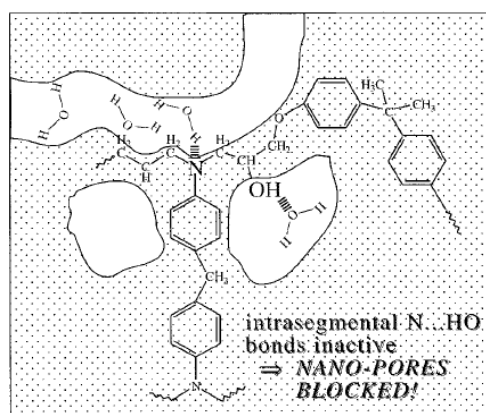


Figure 13 - Moisture diffusion through nanopores of amine-containing epoxy resin – II [16]

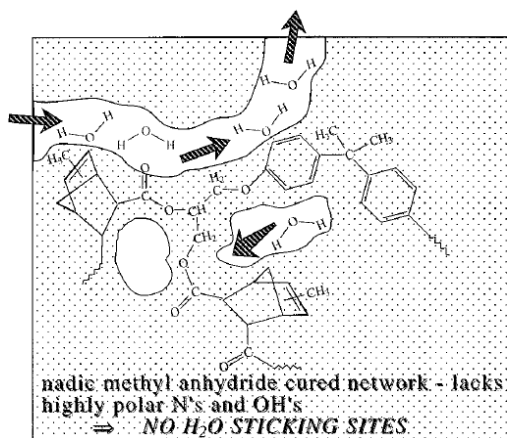


Figure 14 - Moisture diffusion through non-amine resin [16]

3.2.2 Directional Diffusion of water

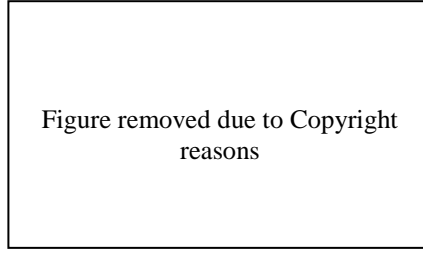


Figure 15 - Directional Diffusion of water [17]

Diffusion of water molecules seems faster along the direction of the fibers. This is because of the presence of straight moisture pathways along the direction of the fibers rather than the convoluted pathways across the fibers. Places with exposed fiber ends such as bolt holes and edges, water ingress would be substantially higher. The formula below shows the model for the directional water absorption phenomenon [17].

$$\frac{M_t}{M_e \sqrt{t}} = \sqrt{\frac{16}{\pi} \left(\frac{\sqrt{D_1}}{a} + \frac{\sqrt{D_2}}{b} + \frac{\sqrt{D_3}}{c} \right)^2}$$

The first term is the gradient of the initial weight uptake, with M_t the weight increase at time t and M_e is the equilibrium weight uptake (estimated from long time data). D_1 is the diffusion coefficient along the fibers, along section 1 of figure 15 and ' a ' is the dimension of the sample along the fibers. D_2 and b are similar for across the fibers but parallel to layers and D_3 and c are across fibers and layers like section 2 in figure 15. It can reasonably be assumed that the values of D_2 and D_3 are the same. In [17], we can see the variation of diffusion coefficients with respect to the orientation of the fibers as shown in table 1 below.

Condition	D resin (x 10 ⁻¹⁴ m ² /s)	D ₁ (x 10 ⁻¹⁴ m ² /s)	D ₂ (x 10 ⁻¹⁴ m ² /s)	D ₁ /D ₂
23°C Water	11.5	14.0	6.3	2.22
40°C Water	25.5	31.2	12.4	2.52
60°C Water	53.3	57.6	25.9	2.22
70°C Water	78.4	85.8	39.8	2.16
Activation Energy	4.1 kJ/mol	3.8 kJ/mol	3.9 kJ/mol	

Table 1 - Variation of diffusion coefficients with orientation [17]

3.2.3 Capillary Actions:

The stress concentrators pre-existing in the composite system will induce microcracks within the composites which enhances the system's fluid absorption capacity. Capillary paths are established by mechanically or thermally induced microcracks in the composite system which are channeled parallel to the reinforcement direction. The exposure to the ambient environmental and loading conditions will instigate the flow of fluid into these capillary channels. Experimental testing on capillary action was done by inducing microcracks in the transverse plies of cross plies graphite/epoxy samples. They were then turned side-ways to position all microcracks aligned vertically, bringing the end of the specimens towards the bottom, in touch with slightly acidic waters and then measuring the capillary action using the litmus paper placed on the dry top end [18]. The results are shown in the figure below. The speed of the capillary motion in this study was established to be 0.5 cm/min. This determines the rate of capillary climb [19]. Capillary action occurs at 6 orders of magnitude faster than diffusion [14]. An example of the rate of capillary climb in a precracked [0°/90°₃]s AS4/3501-6 Gr/ep coupon recorded along the transverse cracks in the 90° ply group is shown in figure 16 below.



Figure 16 - Rate of capillary climb of sea water in precracked $[0^\circ/90^\circ 3]_s$ AS4/3501-6 Gr/ep coupon, recorded along the transverse cracks within the 90° ply group [14]

3.2.4 Wicking Actions:

This fluid ingress process occurs in FRPs along the fiber and matrix interphase region also, which are in most composites typically only a few microns in thickness. This region consists of configurationally altered resin boundary layer that tends to absorb disproportionate amounts of fluids and provides pathways for wicking action. This phenomenon is observable by cutting samples perpendicular to the fiber direction and subjecting them to environmental conditions. Samples with higher ratios of edge surfaces tend to show a higher weight gain amount due to the increased fluid absorption by this process. This process is on an average 10 times faster than diffusion [14].

3.2.5 Osmosis:

All laminates, especially in marine environments will allow small quantities of fluid to pass through them, especially in vapor form. Any hydrolysable component inside the laminate draws water to it forming a concentrated solution. Under the presence of osmotic cycles more fluid is drawn to this concentrated solution to dilute the solution. The fluid pressure is increased by the increasing amount of fluid in the cell sometimes as much as 700 psi, eventually distorting the

laminate leaving a “chicken pox” like surface. To prevent osmosis from the very beginning, the use of resin with low moisture transmission rate and increased resistance to moisture penetration is essential.



Figure 17 - Interface failure of glass-polymer composite due to swelling caused by moisture ingress [20]

In many circumstances, the polymeric phase in a composite system acts as a semi-permeable membrane in the presence of external environmental vapor and fluid molecules causing an osmotic pressure inducing internal damage such as microcracks and enhancing the fluid absorption process. In some cases, composite panels did not have any fluid ingress in the absence of pressure difference between the inner and the outer layers which induces internal damages such as microcracks.

An alternative approach to understand the ingress of moisture into the polymeric phase can be to look at the average pore diameters. The average pore diameters for epoxy vary between 2.7 to 5 angstrom [14]. The water molecules are estimated to have diameters between 1.5 and 3 angstrom. The total free volume contained by the epoxy polymeric phase cannot be occupied by the water molecules because of the smaller size of the pores and some connected micro pores creating micro tubes being narrow for allowing free water molecule movement. Under stress or

temperature change, as the energy applied on the polymeric phase induces many inhomogeneous spots of pressure of “disparate amplitudes acting on highly anisotropic neighborhoods in the micro level. The localized centers of pressure would then squeeze water molecules along preferred directions into unoccupied and inaccessible portions of the free volume” [14].

CHAPTER 4

DAMAGE MECHANICS OF COMPOSITE STRUCTURES

“Damage mechanics, as applied to composites, studies the onset and growth of damage and aims to determine damage tolerance criteria and establish monitoring protocols for the lifetimes of composite structures” [21]. The major types of failure occurring in composites are inter and intra-laminar cracking, fiber-matrix interface failure, fiber pullout and fiber breakage. The fiber fabrics in the composites develop damage due to the friction caused by warp and weft, off axis loading causing in-plane rotation of fibers, and compressive forces forcing fibers to kink out of plane. Pre-existing manufacturing defects, loading conditions, operation environmental conditions, design features such as holes or other stress concentrators aid in buckling and micro buckling of fibers causing propagation of damage.

The facesheets in a sandwich construction resist the entire out of plane bending moments and the in plane loads. Due to their higher modulus and their farther location from the neutral axis of the component, they provide the bending stiffness. The core material transmits the shear forces between the face sheets making the sandwich construction more effective in bending about a common shared neutral axis along with providing a through shear thickness rigidity. They also help in stabilizing the facesheets while being loaded to stress levels higher than the limits prescribed for general buckling of thin plates [8]. Sandwich construction also proves efficient in fatigue conditions due to the continuous attachments of the face sheets to the core giving rise to minimal stress risers. Selection of materials for the core is immensely important and is based on the adhesive methods with the facesheets such as bond, braze or weld, environmental requirements of the operations and loading conditions.

4.1 Microcracks

The first form of damage in fiber reinforced composite material is matrix microcracking [22].

These are cracks that are intra-laminar and run through the thickness of the lamina parallel to the direction of the fibers contained in the lamina. These cracks normally develop perpendicular or transverse to the loading direction and hence also named transverse cracks. Microcracks form in any ply with a significant component of the applied load transverse to the fibers in the ply. For example in plies with 90° fibers loaded under axial 0° loads, microcracks develop along the direction of the fibers, 90° . Microcracks can be observed with various forms of loading such as tensile, fatigue, and thermal cycles (leading to temperature changes). Most importantly microcracks are observed in the lamina placed unaligned to loading directions. Microcracks cause immediate depletion in the thermo-mechanical properties of the laminate such as effective moduli, poisson ratios and thermal expansion coefficients. To eliminate microcracks constituting the failure, the design must account for the degradation of properties that are microcracks induced.

Microcracks can also cause cascade of secondary failure mechanisms such as delaminations, fiber breaks or provide pathways for fluid ingress. Such damage spots constitute stress concentrations or accelerated degradation of properties as in the case of fluid ingress, and subsequently lead to failure. Interest in the microcracks has perked since 1970s with the observation of the initiation of microcracks. Since then there have been various experimentations studying the loading and environmental states leading to the initiation of microcracks. Early attempts at understanding the formation of microcracks assumed they occurred when the stress in the unaligned plies reached critical strength values. But with the pool of experiments expanding,

this has been disproved. Fracture mechanics or energy balancing methods do a better justice in explaining the phenomenon of microcracks.

Some noteworthy facts regarding the formation of microcracks are,

- Transverse plies at the surface of the composite system need lower strain to initiate microcracks rather than the ones in the middle. This is attributed to the fact that the middle plies are constrained by the supporting plies whereas the ones on the surfaces are not as constrained and are free to develop cracks
- Initial microcracks develop easier in the thicker plies than in the thinner plies. This is assumed due to the lower imperfections in a thinner ply.
- [90m/0n]s laminates develop microcracks sooner, but [0m/90n]s laminates develop/contain more microcracks at saturation when load is applied in the 0° direction [22]. This is assumed because the surface plies in the first configuration develop microcracks at a lower strain rate and the presence of supporting plies in the 0° direction at the surfaces limit the microcracks formed in the 90° direction plies. In laminated plate theory calculations for [90m/0n]s and [0m/90n]s laminate, the strains in the 90° plies are unaffected by the stacking sequence. Thus first ply failure models cannot predict the initiation of microcracks.
- The onset stress where microcracks initiate preliminarily decreases as the thickness of the transverse plies increases. On continued loading, thinner 90° plies accumulate more microcracks.

- After an onset of microcracks there is a rapid rise in microcracks density followed by a slowing towards microcracking saturation at higher applied loads, when existing microcracks begin connecting to form bigger cracks

4.2 Microcracking Fracture toughness – Energy method

Looking at fracture mechanics or energy balancing methods for explaining the initiation of microcracks, when total energy released in the process of formation of a microcrack reaches a critical value called as microcracking fracture toughness, G_{mc} , the existence of microcracks begins [23]. Meaning, when the loads applied cause a localized critical value of concentrated stress at a point causing energy to rise and equal the microcrack fracture toughness, the tear or the crack initiates.

There are various advantages of analyzing microcracks using the energy methods. The fracture mechanics method can be used to analyze the experimental data to determine G_{mc} for a given type of composite material system. This material property, G_{mc} , can be used to order different composite materials with respect to their resistance to microcracking [23]. Since microcracking is the first form of failure encountered in composite laminates, this value of G_{mc} is a sensitivity measuring factor for laminate failure properties. By measuring the fluctuations caused in G_{mc} value under various ageing environments, the degradation of laminates and their durability can be predicted. It is extremely important for designers to know the effect of microcracks on the thermo-mechanical properties in order to establish the rate and amount of microcracking that can be withstood by the material before failure. The energy analysis facilitates in understanding most information about the degradation of thermo-mechanical properties observed in various

experiments. By extending this principle to fatigue induced microcracking, calculating the resistance of a composite material system to microcracks induced by fatigue can be carried out.

Microcracks are caused by static loading, cyclic loading (Fatigue) and thermal cyclic loadings. Since microcracks result in reduction in stiffness, thermal coefficients and are favorable sites for delaminations, it is essential to gain a qualitative understanding of initiation and propagation of microcracks doing monotonic and fatigue loadings. A recent energy release rate study [23] uses “improved stress analysis technique” developed by Hashin [24, 25], to accurately predict the reduction in stiffness due to the formation of microcracks using variational analysis principle. The new energy release rate analysis predicts the density of microcracks as a function of applied loads in a variety of composite systems. In the study, the improved stress analysis method was further modified to include the thermal effects as well.

As suggested in the references quoted above, it is assumed in the study [26] that microcracking is modeled in the most reasonable manner using energy release method. Taking the energy release approach to static load testing, it is postulated that the next microcrack will initiate formation when the energy released reaches a critical energy release rate, G_{mc} , which was earlier introduced as microcracking fracture toughness of the composite material system. To measure the fracture toughness G_{mc} and to use the energy release method, an expression for energy release rate - G_m is required. This is derived in the work by Liu and Nairn [26].

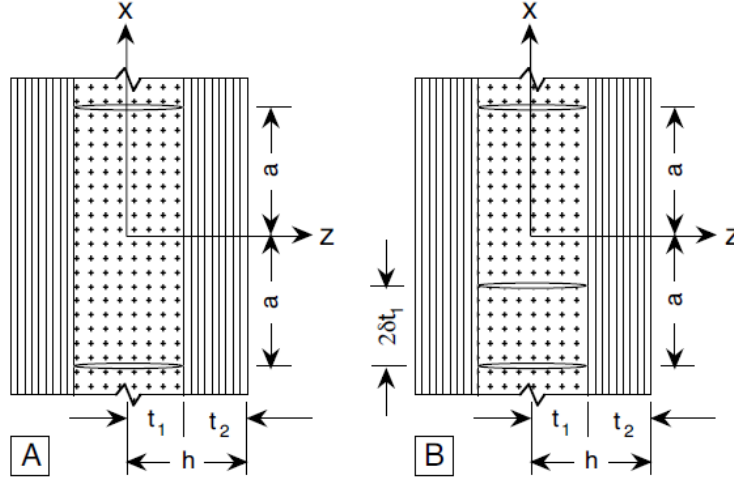


Figure 18 - Initiation of a microcrack [26]

In this work, the initiation of a microcrack in the k^{th} interval as shown in the figure above is considered. By differentiating the equation for total strain energy in the N crack intervals (from [23]),

$$U = \left(\frac{\sigma_0^2}{2E_c} + \frac{t_1 \Delta \alpha^2 T^2}{BC_1} \right) BWL + (C - C_0) \frac{B^2 W^2 E_c^2}{2E_T^2} \left(\frac{E_T^2}{E_c^2} \sigma_0^2 - \frac{\Delta \alpha^2 T^2}{C_1^2} \right)$$

we get,

$$G_m = \frac{\partial U}{\partial A} \Big|_{C_{\text{const.}u}} = \frac{B^2 W^2 E_c^2}{2E_T^2} \left(\frac{E_T}{E_c} \sigma_0 - \frac{\Delta \alpha T}{C_1} \right)^2 \frac{dC}{dA}$$

Using various estimations such as sample compliance functions, displacements of the sample due to the applied load and performing mathematical functions, we arrive at a final energy release rate expression of

$$G_m = \left(\frac{E_T}{E_c} \sigma_0 - \frac{\Delta \alpha T}{C_1} \right)^2 C_3 t_1 Y(D)$$

where $Y(D)$ is a calibration function that depends on the crack density $D=N/L$ where N is the crack spacing, E_t is the elastic modulus in the transverse direction of the ply material and E_c is modulus in the 'x' direction of the cross ply laminate [26].

Taking G_{mc} as a material property and doing the above calculations for various composite material systems, we derive the following values.

Composite Material	G_{mc} (J/m ²)
E-glass/Epoxy	200
AS4/Hercules 3501-6	220-260
IM7/Fiberite 954-2A	240
AS4/Dow Polycyanate	430-460
AS4/Polysulfone	450
IM7/Hercules 8551-7	525
AS4/Dow Tactix ® 556	550
Scotch Ply 1003 (E-Glass/Epoxy)	650
T300/Fiberite 934	690
G40-800/rubber modified Dow Polycyanate	720
AS4/Dow Tactix ® 696	825
IM6/DuPont Avimid ® K Polymer	960
IM7/PETI5	1080
T300/Fiberite 977-2	1800-2400
AS4/ICI PEEK	3000

Table 2 - Microcracking fracture toughness of several composite systems [26]

With this single microcrack fracture toughness it is possible to calculate the microcracks density as a function of applied loads. This work attempts to analyze fatigue experiment data using a modified Paris law which states

$$\frac{dD}{dN} = A \Delta G_m^m$$

where A and n are power law fitting parameters [26]. The traditional Paris-law approach relates “the rate of change in crack length to the range in the applied stress intensity factor”, ΔK [26]. In studying microcracks with the energy release method, ΔK is substituted for ΔG . Given a value of $\Delta \sigma_0$, calculating ΔG is a simple issue. This value is plotted against dD/dN yields a linear relationship as anticipated. An important characteristic of microcracking fatigue experiments is

that the variable ΔG stays constant till a high crack density (in lieu of the ΔK in fatigue crack propagations which changes) understandably due to the still intact thermo-mechanical properties requiring the same energy release rate for each microcrack formation. This constancy of ΔG was found to be held up to a density of 0.20 to 0.25 mm^{-1} . This constancy over a wide range facilitates carrying out simple fatigue experiments for microcrack propagation up to the crack density of 0.25 mm^{-1} while expecting it to increase linearly with the number of cycles. Experimental results are shown in the figure below showing the linear increase in the crack density up to 0.25 mm^{-1} after which the ΔG declines substantially as shown in the graph.

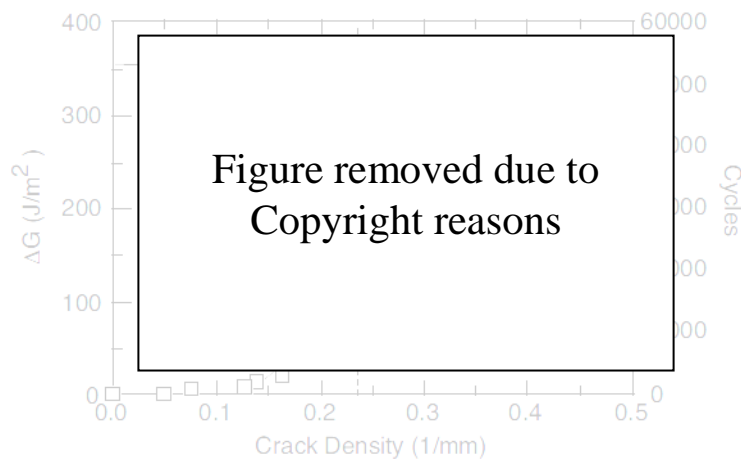


Figure 19 - crack density Vs energy release [26]

There is a discrepancy of values in the crack density up to 0.13 which is below the linear Paris Law growth region. It is suggested that this might be because of the already existing flaws in the laminate system due to manufacturing or material defects. The microcracks form, well below the prescribed fracture toughness of the material systems, located near the obvious flaws. The crack density Vs cycle number data is categorized into three obvious classes [26].

1. Flaw Dominated region - The formation of first microcracks at the obvious material defects.

Primarily controlled by the quality of laminate structure. This cannot be accommodated in prediction of behavior of the material system.

2. Constant growth rate - The crack density increases at a constant rate up to a critical crack density value following modified Paris Law. ΔG remains relatively constant.

3. Slow growth region - ΔG decreases. According to Paris law formation of cracks must reduce dramatically. Existing cracks take over the show leading to failure.

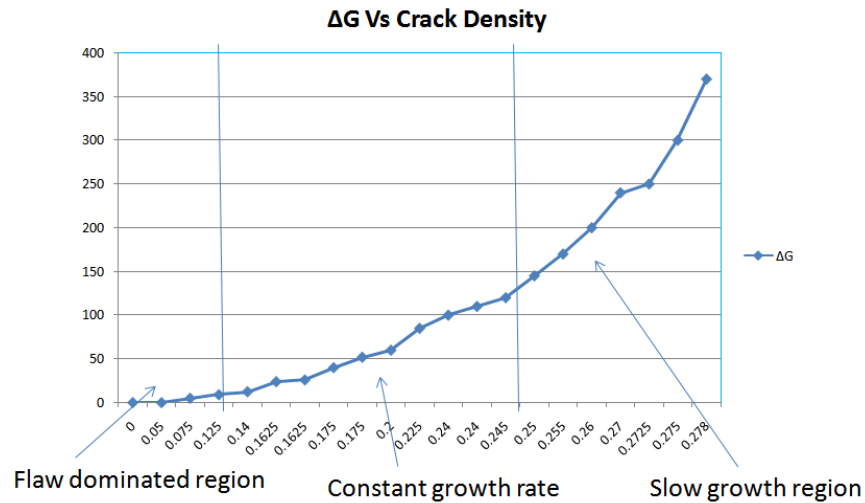


Figure 20 - Crack density Vs Cycle number [26]

As mentioned earlier, due to the use of these composite panels in hot and humid conditions, the hygrothermal stability of the composite laminates is of extreme importance. Polyimide laminates spontaneously develop microcracks when exposed to hot and wet environments due to the moisture induced degradation of fracture toughness in the composite material [27]. Experiments reveal that for quasi-isotropic Avimid K3B/IM7 laminates when immersed in water at temperatures ranging from 35 deg C to 95 deg C, microcracks develop spontaneously [27]. Also the water uptake to a certain level obeyed the Fickian behavior and after that certain limit, assumed to be saturation level, non-Fickian behavior is followed. Microscopy reveals that the

secondary absorption of water is caused by the spontaneous formation of microcracks in the transverse plies (90 deg plies) without the application of externally applied loads. Eventually, toughness drops sufficiently that microcracks develop with the presence of just residual stresses.

The results in this study [27], are interpreted with simple kinetic analysis showing that the rate of degradation depends on the amount and time of exposure to water. The microcrack fracture toughness was determined as a function of aging time. The microcracks density was determined as a function of applied load. The loading was interrupted in constant periods for microscopic observations and readings of the density of microcracks was recorded in the 90° plies. The resulting data was analyzed with methods referenced in [23, 25], to determine microcracking fracture toughness.



Figure 21 - Microcracking toughness G_{mc} as a function of aging time for Avimid K3B/IM7 laminates at 80° C for water immersion at various relative humidity levels [27]

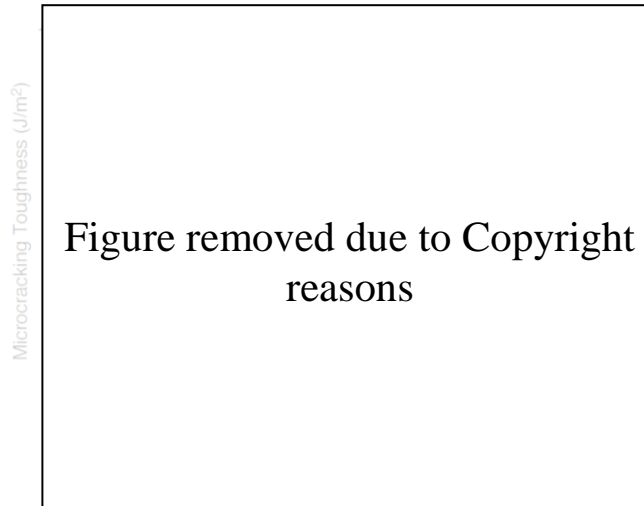


Figure 22 - Microcracking toughness G_{mc} as a function of aging time for Avimid K3B/IM7 laminates while immersed in water and aged at different temperatures [27]

4.3 Stress effects on fluid ingress

Weight gain data in the study [28] was collected on uni-directional AS4/3502 graphite-epoxy coupons which were loaded in the transverse direction with respect to the fiber direction and on “neat” 3502 samples. The specimens were bared to relative humidity 98% and $T = 40\text{ C}$ with various samples loaded in tension to 0, 15, 30, and 45% of the dry epoxy failure stress, 52 MPa.

The results show that $M(\infty)$ increases with the applied σ also suggesting that the diffusivity D increases with σ during absorption and subsequently decreases in the process of desorption.

The cyclic experimental data and stress dependent experimental data shown in the following figures can be confirmed by observations of damage induced by moisture in fiber reinforced composite material systems.



Figure 23 - Moisture content Vs square root of time [14]

The multitude of microcracks seem to develop at random sites. They develop around sites where the fibers are placed very closely and continue to meander along the fiber/matrix interfaces. Other locations for microcracks initiations and crack growth are between fibers and resin-rich regions. This could be due to the higher residual strength caused by swelling induced by fluid. Although difficult to qualify, these trends strongly suggest that damage stems in the form of microcracks produced due to fluctuating ambient humidity rather than constant humidity. An aircraft does go through constant changes in humidity during its flight profiles.

CHAPTER 5

FIGHTING WATER INGRESS

The table below from the paper [29] summarizes the possible factors leading due to which moisture ingress happens in sandwich composite structures.

Environmental	Physical	Chemical
<ul style="list-style-type: none">• Temperature• Relative humidity	<ul style="list-style-type: none">• Specimen geometry• Void content• Matrix mass loss• Composite swelling• The degree of disbanding between matrix and fibers	<ul style="list-style-type: none">• The polarity of the matrix molecular structure• The degree of matrix cross-linking• The degree of matrix <u>crystallinity</u>• The presence of residuals in the composite material• Absorbed solution composition• Chemical composition of matrix• Chemical composition of the fiber sizing

Table 3 - Factors inducing fluid ingress in composite materials [29]

Prime worry-causing spots for water ingress are problematic joints, closeouts, and inserts [9]. At any point if there are frayed surfaces along the panel edges, poor tolerances, improperly treated insert surfaces resulting in contamination, porous adhesive strip, subjected to thermal cycling and the faces of the sandwich structure, or the components of the composite system itself have different coefficients of thermal expansion, a high risk of creating ingress pathway is present. Since most of the above scenarios are more than plausible, moisture ingress poses a severe risk.

Carbon has different electrochemical potential when compared to most metals, especially ones used in the aerospace industry such as Aluminum and steel. When Carbon is placed in close contact with above mentioned metals, as in most applications in the industry, the carbon

fiber/metal pairing develops galvanic corrosion [30]. The ion motion between the carbon fiber composite material system and the metal in contact induces the electrical current which in turn induces the galvanic corrosion. This phenomenon is greatly increased in the presence of moisture and especially, sea water. Galvanic corrosion can induce fiber-matrix debonding at the interphase sites and also cause fiber cracking in addition to corroding the metal. Sometimes, rust formation or blistering within the matrix of the composite would cause a change in chemical composition leaving the composite system more vulnerable to moisture ingress [31]. In the case of glass fibers, exposure to fluids activates chemical reactions with specific chemical components of the glass fibers. Penetration of fluid inside the initial flaws can enhance and accelerate the chemical reactions, quickening fiber failure. This is observed also by the etched grooves in the microscopic level the fiber boundary. The corrosive fluids extracted from glass fiber composites system, confirms this [14]. Thus basic properties of glass fiber and their characteristic interactions with environmental fluids and applied stresses have strong implication on the behavior and mechanical properties of glass reinforced composites

Also, thermally or mechanically induced microcracking provides pathways for moisture ingress. Toughening additive in the matrix or modified sizing of the fiber provides a solution [32]. In [32] the mechanical properties of laminates were found to be substantially increased by the addition of nanoclay reinforcements in the proper concentration in the form of reduction of microcracking density. Porosity in the sandwich faces provides initial pathways for moisture ingress. This can be successfully mitigated by increasing resin content or the thickness of the part. Also adding a film of adhesive creates a seal preventing moisture ingress.

It is obvious that when facesheets are damaged by impacts, due to the lack of visible damage, it can go undetected for long periods of time, causing water ingress pathways. By increasing the toughness of the facesheets, the fracture toughness of the assembly can be increased. But for thin faces, the key question remains, how much of an impact energy can be absorbed by the core. In the patent [33], by using an advanced core composed of chopped non-oriented glass or carbon fibers with high strain resin, the tolerance to impact characteristic of a honeycomb sandwich structure was doubled in comparison to the same sandwich construction composed of nomex or korex honeycomb. The amount of energy that was required to create a BVID was 20 J for six ply carbon/epoxy faces on 2.5 cm korex core, 17 J for nomex core and 48 J for the chopped mat/BXA core. All the cores had an approximate density of 0.048 g/cm³.

But if water does make it to the cores, it requires a water removal method. Some of the common methods of moisture removal are heating, vacuum and vibrations. Heating is conducted by various methods such as convection, conduction, radiation and microwave. According to an earlier study, prolonged exposure to humid (Tropical) environment, which is typically above 85°C, may cause permanent degradation of the adhesive component [9]. Vacuum can travel through existing water pathways easily [2]. According to water phase diagrams, water evaporates at temperatures much below 100°C for pressures less than atmospheric pressures. Energy from vibration pushes water to be separated from base surfaces and flow/move better requiring minimal effort and energy. This method is immensely useful for heat-sensitive materials. This is effective for room temperature drying with just 1°C increase in temperature [34]. In the study [2], pressure of 11 KPa was used requiring only 70°C for water evaporation and ultrasonic vibration of the order 10 MHz was enhanced to 20dB and was transmitted to the bottom surface of the coupons. Below is the graph of effect of heat and vacuum on the moisture removal rates.

As we can see heat and vacuum produced the best results as opposed to heating or vacuum methods only.

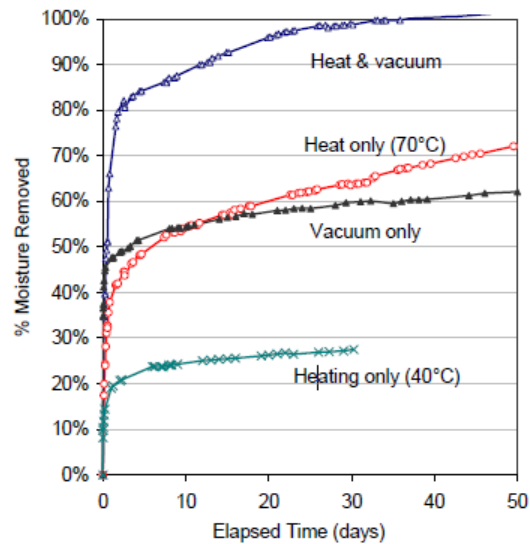


Figure 24 - Elapsed time Vs moisture removed using vacuum and heating methods [2]

Following is the graph of effects of vacuum and vibration. Vacuum and vibration yielded slightly lower results assumed due to increased complexity caused by the combination of both methods.

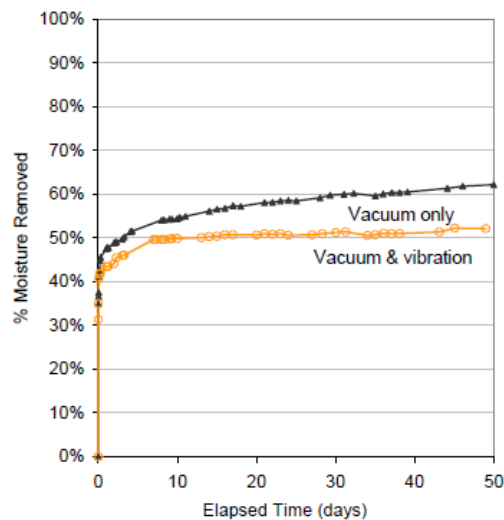


Figure 25 - Elapsed time Vs moisture removed using vacuum and vibration methods [2]

In an attempt for full understanding of moisture absorption, especially the effects of humidity and temperature, [17] work has studied the moisture absorption rates in various polymer samples and reinforced polymer samples, each 4mm thick, with the variables being temperature, humidity and fiber volume fraction.

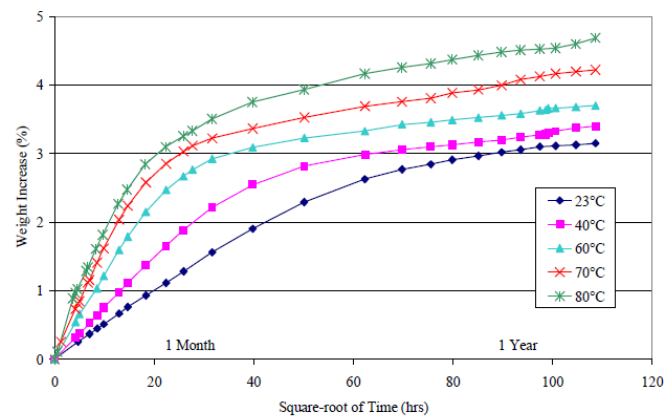


Figure 26 - Weight increase of unreinforced resin due to moisture ingress with respect to temperature [17]

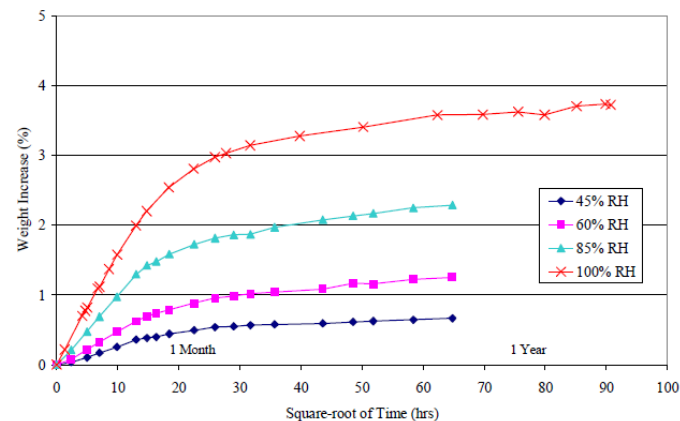


Figure 27 - Weight increase of unreinforced resin due to moisture ingress at 70deg C with various levels of Humidity [17]

Amount of water absorbed increases with temperature, but increases more dramatically with increasing relative humidity. It is note-worthy to observe that all the graphs showing the moisture intake behavior display a two stage diffusion process.

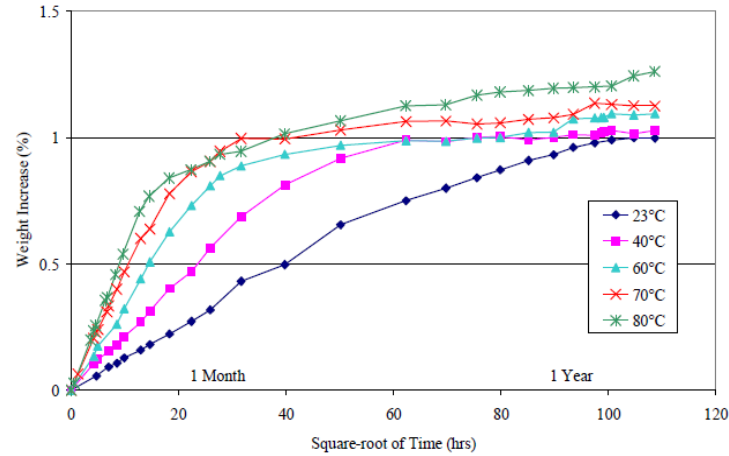


Figure 28 - Weight increase of unidirectional composite systems in various temperatures [17]

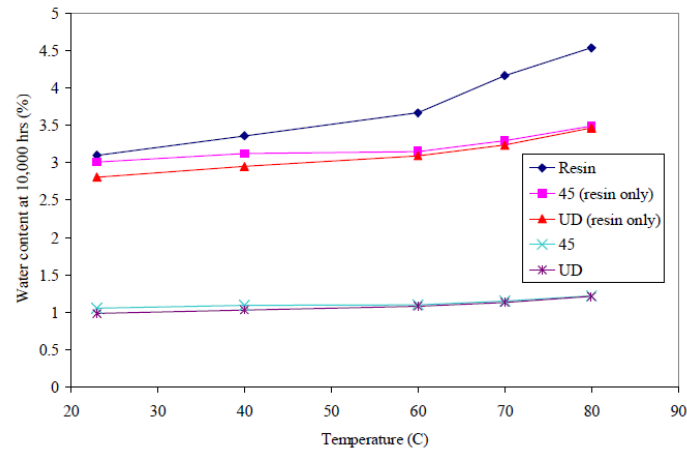


Figure 29 – Unidirectional and 45° samples at various humidity levels at 70 deg C [17]

The following figure shows the effects of drying and moisture removal from the samples. The samples conditioned at 70 or 80 deg C for 330 days were dried in desiccators at 23 deg C or 70 deg C. The data are plotted as a ratio of the original water content after conditioning.

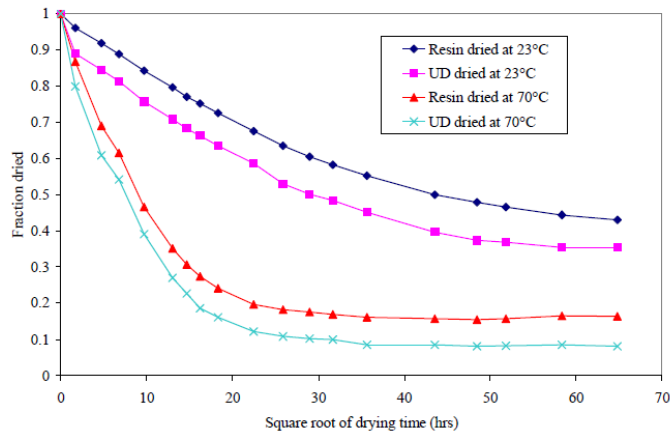


Figure 30 - Effects of drying and moisture removal from the samples [17]

Even with drying the samples, moisture is locked in the material. Moisture absorption is relatively higher for resin samples when compared to composite samples. This is assumed to be because of the extra constraints of fiber inhibiting relaxation. It could also be because of lesser number of active bonding sites. There are more reactive sites in the unreinforced resin than the composite.

CHAPTER 6

EFFECTS OF MOISTURE INGRESS ON COMPOSITE STRUCTURES

Moisture ingress in composite systems can lead to various detrimental effects. Some of those effects are discussed in this chapter.

6.1 Physical effects:

Absorption of fluids can be measured by the gain of weight of a composite material system over a period of exposure to various environmental agents. The uptake of moisture could lead to swelling of the composite leading to localized areas of stress and cracking of matrix. The stresses caused by the uptake of moisture works in the negative sign to the residual thermal stresses of the matrix produced as a result of curing. Swelling can be a reversible process through desorption [35]. But the cascade of damages caused by swelling, such as delamination between plies, microcracking of matrix is irreversible changes. Also cycling of composite through absorption and desorption exposes the composite material to swelling strains which can accelerate the degradation of the various properties of the composite material system.

6.2 Thermo-mechanical effects:

Reduction in the glass temperature T_g is caused by the absorption of fluids. This is termed as plasticization of the matrix. When a resin is chosen for the composite system, it should be chosen such that the T_g falls outside the operating range of the component. Environmental stress corrosion cracking can be quickened through the interfacial bonds between the matrix component and the fiber component being ruptured through chemical reactions [35].

6.3 Static and Fatigue strength:

The effect of moisture ingress in terms of static strength is determined by whether the property of fiber dominated or matrix dominated. If it is fiber dominated, moisture ingress has very little effect on the static properties such as tensile strength. But when it is matrix dominated such as compressive and flexural strength, in extreme cases, there can be a reduction in strength up to 30% [29]. The matrix tends to soften with moisture uptake and resists the propagation of crack leading to slightly better fatigue properties [35]. The following table shows the influence of water ingress on various properties for CFRP [36].

Property	Layup	Reduction due to water
0° Tensile strength [9]	UD	0
0° Tensile modulus [9]	UD	0
90° Tensile strength	UD	33%
90° Tensile failure strain	UD	37%
90° Tensile modulus	UD	3%
90° Compression strength	UD	21%
Inter-laminar shear strength	UD	9%
In-plane shear strength	±45	0
In-plane shear modulus	±45	8%
Open-hole compression strength	QI	5%
Filled-hole compression strength	QI	11%

Table 4 - Influence of water ingress on various properties for CFRP [36]

6.4 Adhesive properties:

The adhesive in CF-18 is a structural film adhesive that bonds the facesheets (or skin) to the core is Cytec FM-300. It is an epoxy film, supported by a tightly knitted scrim cloth, which cures at 177°C [37]. Moisture can have adverse effects on the cohesive properties of the adhesives [38]. The absorbed water gives rise to plasticization of matrix and leading to reduction of glass temperature of the polymer matrix that lowers the mechanical performance of composites. “The glass transition of a material is the reversible change into an amorphous polymer from (or to) a viscous rubbery condition to (or from) a hard and relatively brittle condition” [36]. This transition occurs at a narrow range of temperature called the glass transition temperature below

which most of the energy put into the material deformation is recovered on the removal of the applied load. In warm, moist, tropical environments, the adhesives tend to absorb moisture and swell until it is in a state of equilibrium with its environment. If load is applied in addition to the pre-existing humid environment, additional stress states are introduced leading to constant deformation requiring decreasing stresses. This decrease in stress for constant strain is described as stress relaxation. The reduction in strength this phenomenon causes is detrimental to the adhesives [39].

CHAPTER 7

CONCLUSION

Research conducted till date comprises of various experiments taking on the challenge of quantifying the effect of one degradation inducing phenomenon or a combination of a couple of phenomena. They could be the temperature effects, humidity and UV exposure etc on the thermo-mechanical properties of the composite systems. No one has till date established a practical method for measuring and using material property such as microcracking fracture toughness. Even though the term has been coined by Nairn et al, it is still in its infancy. Taking a look at the current ASTM standards for testing the structural soundness of composite sandwich panels, it has been observed that for moisture ingress effects, there are few standardized test or repair methods. Some of the tests are ASTM F1645 and ASTM D5229 / D5229M – 12. ASTM F1645 - Migration testing can be used to “characterize and compare the relative permeability of honeycomb core materials to determine the migration of moisture in honeycomb core materials” as defined by the ASTM website [40]. ASTM D5229 / D5229M - 12 – is a standard test method for “moisture absorption properties and equilibrium conditioning of polymer matrix composite materials. This method covers the procedure for determination of moisture absorption or desorption in the through-the-thickness direction in single-phase Fickian-diffusion solid panels” also defined by the ASTM website [41]. The calculation of the through-the-thickness, better described as the bulk moisture diffusivity constant assumes a single-phase Fickian material with absorption of moisture being a constant value, which by experimentation has been disproved. It has been observed that the key players in the Aerospace field like Boeing and Bombardier have their own methodologies to test and measure the moisture ingress mechanisms and effects. If the relationship between this microcracking fracture toughness property and the various constituents

of the matrix of the composite system can be established with standardized tests, it would revolutionize the field of damage tolerance of composites.

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