Imperial College London

The Composites Centre

for research, modelling, testing and training in advanced composites

MSc in Composite Materials

Literature Review

"The effects of hygrothermal environment on composite laminate mechanical properties"

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Contents

Abstract

This report is the result of a literature survey and aims to review the literature available on the effects of hygrothermal environments on composite materials and their mechanical properties in particular. The paper focuses on the effect any given hygrothermal environment may have on polymer matrix composites and does not discuss the effects on metal or ceramic matrix composites. It is a supplement and an update to the very interesting and thorough work done by D. Demetriou and Professor J. Hodgkinson (1990). A number of experimental procedures, concerning mainly aeronautical applications have been reported from various sources and their results are discussed. The computational results published lately exceed the corresponding number of experimental results obtained lately and the reasons for this will also be discussed in the report. The response between theoretical models and experimental results published is also dealt with. Also, the development (or not) of accepted standardised methods for the particular phenomenon is reported. Future research and the paths which should be examined in this field are considered. Finally, certain conclusions concerning the literature work found will be outlined.

List of symbols and abbreviations

BMI	Bismaleimide
c	Moisture concentration inside the plate
c_∞	Saturation moisture concentration
D	Effective Diffusivity through thickness (mm^2/sec)
D_0	Constant of diffusivity
DFPO	Double Fibre Pull Out
DMTA	Dynamic Mechanical Thermal Analysis
E_d	Activation Energy (in kcal/mole)
E	Young's Modulus (in GPa, unless stated as MPa)
FT-IR	Fourier Transform Infra Red
G_{Ic}	Critical strain-energy release rate for mode I failure
G_{IIc}	Critical strain-energy release rate for mode II failure
ILSS	Interlaminar Shear Strength
PMC	Polymer Matrix Composite
R	Universal gas constant
RH	Relative Humidity
RTM	Resin Transfer Moulding
SAXS	Small Angle X-Ray Scattering
T	Temperature (Absolute T in K, Temperature in °C)
t	Time (in sec, unless stated otherwise)
TGA	Thermo-Gravimetric Analysis
VARTM	Vacuum Assisted Resin Transfer Moulding
Γ_I	Interface Fracture Energy
$\Delta G(t)$	Change in fibre strain
ΔL_d	Debond growth
$\Phi(t)$	Ambient humidity ratio

1. Introduction

The word hygrothermal comes from the Greek meaning wet (or moist) and hot (or warm) combined and is used to describe environmental conditions that are just that. It is a known fact that polymers and all polymer based materials such as polymer matrix composites (PMC) tend to absorb moisture from the atmosphere. As the procedure is controlled by temperature is becomes apparent that sorption issues will become serious and even forbid the structural application of polymer composites at elevated temperatures. The literature is very rich in studies dedicated to hygrothermal ageing of all kinds of polymer matrices and their composites. This fact alone signifies the importance of the phenomenon for the scientific and industrial communities.

Alteration of a PMC's physical properties because of the environment will definitely have an effect on its mechanical properties. Because the matrix is more susceptible to moisture absorption than the reinforcing fibres, it can be assumed that the properties of unidirectional laminate composites will be only slightly affected in the direction of the reinforcement and degraded mainly in the transverse and shear directions. Are such assumptions though, too simplified when it comes to multi-directional reinforcements and discontinuously reinforced composites? It should also be borne in mind that the fibres too, yet at a far lesser degree than the matrix, are affected by the environmental conditions. More importantly, fibre/matrix interfaces and interfacial bonds are also susceptible to environmental degradation.

Under ambient conditions, moisture absorption of the resin matrix is controlled by the relative humidity of the environment. The mechanism is complex and has been extensively described in many texts such as the work done by Shirrell & Halpin (1977) in the early days of composite materials. For most organic resins, moisture sorption is described well enough by Fick's law of diffusion:

$$\frac{\partial c(z,t)}{\partial t} = D\frac{\partial^2 c(z,t)}{\partial z^2}$$

Where, c is the moisture concentration, t is the time (in sec), z is the thickness co-ordinate and D is the Effective Diffusivity through the thickness (in mm^2/sec).

Although it is quite apparent in many polymer systems that the prediction from 1-D Fickian diffusion theory described above is not accurate, it is adequate enough for it to be used even today for computational projects, since it is quite easy compared to other sorption equations.

In civil aerospace applications, structural elements will endure life cycles of varying temperatures ranging from -60°C to 60°C and humidity between 1 and 100%RH. Military aircraft (Fig.1.1) that fly at supersonic speeds as well may encounter skin temperatures of up to 150°C. However, because of the enormous fuel consumption, military aircraft do not maintain supersonic flight for more than a few minutes each time. During deceleration, skin temperatures may drop at a rate of even 500°C/min. Such severe heating and cooling cycles are referred to as thermal spiking and can have a tremendous effect on the hygrothermal behaviour of laminate structures.

At these temperatures, its effect must be considered since moisture absorption is an energy driven process and, considering the material as homogeneous regarding the moisture diffusion process, the parameter D is strongly dependant on the temperature, following an Arrhenius-type relationship:

$$D = D_0 e^{\frac{-E_d}{RT}}$$

Where E_d is the activation energy (in kcal/mole), R is the universal gas constant, T is the absolute temperature (in K). D_0 is a constant of diffusivity.

After a rather long (but varying among polymers) period of constant exposure to steady temperature and relative humidity, a saturation moisture concentration (c_∞) will be asymptotically reached:

$$c_\infty = a[\Phi(t)]^b$$

Where Φ(t) is the ambient humidity ratio and α, b are material dependant constants.

Fig.1.1
Even aircraft with super-cruise capabilities, such as the Eurofighter Typhoon, must deal with thermal spiking.

Of course, composites are not used only in aeronautical applications but in civil engineering as well. Environmental effects on, and stability (and therefore, safety) issues of, composites in civil infrastructure are discussed by Helbling et al in an inspiring review article (Helbling et al, 2005).

2. Experimental testing

In the first years of 1990, most work on hygrothermal ageing of polymer matrix laminates was experimental. Scientists and researchers attempted to quantify the effects of relative humidity and increased temperature on a wide range of composites based on polymer matrices through rigorous experiments. The procedures of these experiments varied with each research team carrying out their experiments in a certain way and according to each of the composites tested.

1995 was the year that saw modelling and experimental collaborating about the specific problem. From 1999 and onwards, research has been intense and almost always interacting with computational projects. Signs of the times predict that this will be the case for any future work done on this particular field of research.

2.1. Unidirectional laminate composites

2.1.1. Unidirectional carbon fibre reinforced laminates

Zhou & Lucas (1995) experimented on the effects of temperature on moisture absorption characteristics of a unidirectional T300/934 graphite/epoxy system while immersed in water. As was expected, after measuring the specimen dimensions, essentially no expansion due to water absorption was detected along the fibre direction (Zhou & Lucas, 1995). On the other hand, significant swelling occurred in the other two directions although at elevated temperatures a thickness decrease was accounted for. This thickness decrease was due to 'surface resin dissolution and peeling' (Zhou & Lucas, 1995).

Asp (1997) studied the effects of moisture and temperature on the mode I, mode II and mixed interlaminar shear strengths of HTA 6376C composites, manufactured with the standard prepreg and autoclave curing procedure. It was found that the moisture uptake indeed increased with the increase of temperature, consequently affecting the interlaminar strength of the composite. In pure mode II tests, the critical energy release rate decreased with moisture content. In mixed mode I/II failures, the critical strain-energy release rate was also reported to decrease. In contrast, the strain energy release rate for mode I remained unaffected and even exhibited a slight increase at elevated temperatures (Asp, 1997). Despite the results showing that temperature does not have a significant effect on G_{IIc}, an increase in temperature should have a negative effect on moisture uptake, effectively reducing all properties affected by moisture content. No answer as to why whilst G_{IIc} drops, G_{Ic} remains unaffected is given in the paper.

In 2002, Bao and Yee published several reports (2002a; 2002b; 2002c) on their work on bismaleimide (BMI) resins and how their moisture absorption characteristics are affected by temperature. They used uni-weave fabric and woven fabric, both composed of Hexcel IM7 carbon fibres. That is to say they studied both unidirectional and multidirectional composites. They proposed a two stage moisture absorption mechanism, each dominated by a different physical property of the matrix (Bao & Yee, 2002b; Bao & Yee, 2002c). Typical results from their work can be seen in Figures 2.1.1a and 2.1.1b.

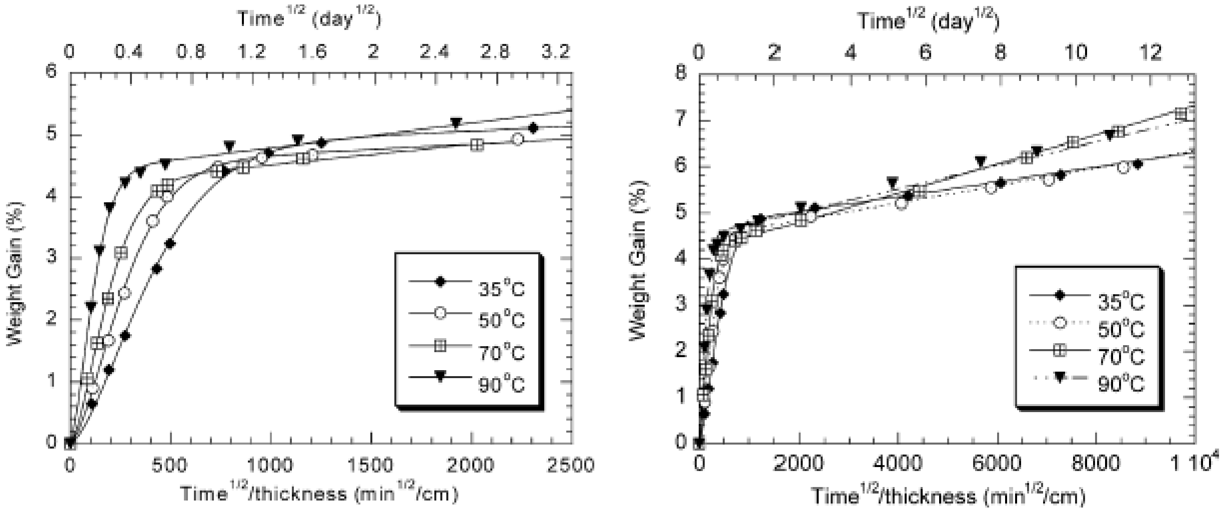


Fig.2.1.1a **Fig.2.1.1b**

Short (Fig.2.1.1a) and Long (Fig.2.1.1b) term weight gain curves for uni-weave 3-ply composites. Lines are fits by the current two-stage model. From (Bao & Yee, 2002)

Choi and co-workers (2001) published their thorough experimental work on various hygroscopic aspects of carbon fibre/epoxy systems in an exceptional report. Various lay-ups, curing and ageing cycles were considered. The laminates were subjected to several different environments that could be potentially encountered by aircraft and aspects such as the specimen thickness, the void volume ratio and internal stresses were investigated. What must be taken into account and given credit for is the theoretical analysis on possible diffusion mechanisms that has been taken to length. One of the conclusions Choi et al came to is that the T_g of the matrix, decreases linearly with increasing moisture absorption. Moisture absorption in turn, is very dependant on the hygrothermal temperature history. Another experimental result showed that increase in void volume ratio results in an increase of moisture absorption. This is probably due to void filling by the absorbed moisture. The absorbed moisture also helps relieve internal stresses of the material, which in turn, causes a decrease in specimen curvature (Choi et al, 2001). This may be beneficial for a single panel but, if a curved panel is used on an aircraft structure, bonded with other composite panels, a change in curvature will cause issues concerning structural stability and integrity. Of special importance is the conclusion that 'for the water absorption in the through thickness direction (…) lay-up sequence does not affect diffusion rate or equilibrium water uptake' (Choi et al, 2001). This conclusion allows us to generalize results for any particular matrix/fibre system, regardless of the stacking sequence.

In 2005, Hough et al published a comprehensive report on the effect of thermal spiking on a number of properties of three different carbon fibre unidirectional reinforced epoxy laminates: Narmco Rigidite 5245C (a BMI modified epoxy resin), Fibredux 924 (a thermoplastic/epoxy blend) and Fibredux 927 (a high temperature, modified epoxy blend). 140°C was the spiking temperature for which a maximum moisture concentration within 5245C and 924 was observed. The corresponding spiking temperature for Fibredux 927 was 160°C. Xiang & Jones had reached to the same conclusions about the effect thermal spiking would have on the moisture absorption of 5245C (Xiang & Jones, 1997). 'The addition of thermosetting components such as BMI to the epoxy matrix reduced the total moisture absorbed relative to the epoxy/thermoplastic blend' (Hough et al, 2005). Amazingly, no micro-cracks or voids were observed in the wet laminates after they had been thermally spiked. This leads to the only logical conclusion that the absorbed moisture was present in the polymer network of the matrix. The transverse flexural modulus was only slightly affected by thermal spiking (and most evidently of 924) or enhanced moisture absorption (Fig.2.1.2a). The reduction in flexural strength observed in 927 and 5245C composites (while that for 924 seems to form a plateau) after thermal spiking (Fig.2.1.2b) is apparently due to the structural changes in the thermosetting components observed mainly through DMTA (Hough et al, 2005).

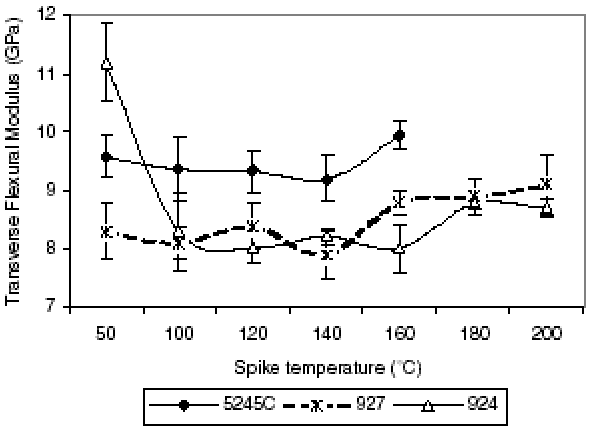


Fig.2.1.2a

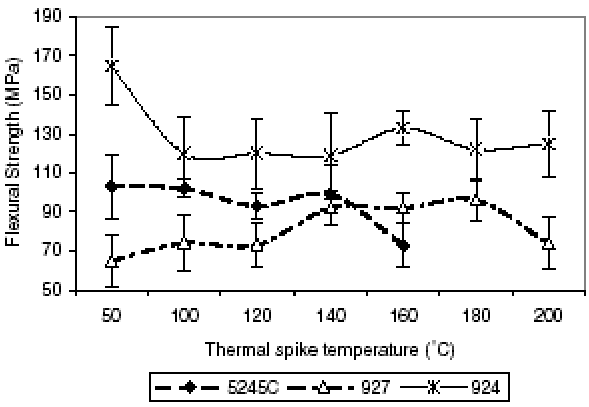


Fig.2.1.2b

Transverse flexural modulus (Fig.2.1.2a) and strengths (Fig.2.1.2b) of wet 5245C laminates after spiking and conditioning at 96% R.H./50 °C h (5245C/927) and 5100 h (924). From (Hough et al, 2005)

2.1.2. Unidirectional glass fibre reinforced laminates

Vauthier and co-workers (1998) did extensive lab work over a two year period on the interactions between hygrothermal ageing of unidirectional glass fibre reinforced epoxy matrix materials and their fatigue damage. Raising the temperature to no more than 90°C, fatigue (three point bending) and monotonic (tensile testing) tests (Fig.2.1.3) were executed. Optical microscopy was used in conjunction with the three point bend tests. The tests concluded that during fatigue tests, an interaction between the crack tip and the absorbed moisture in the matrix develops which can lead to significant increases in crack propagation rates (Vauthier et al, 1998). Temperature contributes to this effect and the crack propagation rates are even higher at elevated temperatures (Vauthier et al, 1998).

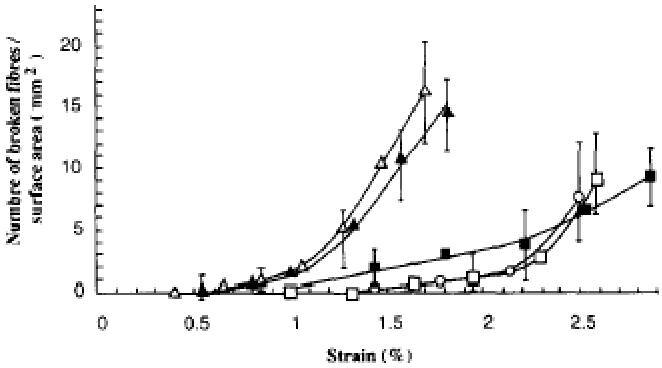


Fig.2.1.3
Changes in the density of broken fibres as a function of the applied monotonic strain- The last point on each curve corresponds to the appearance of macroscopic damage.
(■): Unaged composite, (□): 160days at 50°C/60% RH, (○): 180days at 70°C/60% RH, (Δ): 77days at 60°C/immersion, (▲): 11days at 90°C/immersion.
From (Vauthier et al, 1998)

2.2. Multidirectional laminate composites

2.2.1. Multidirectional and quasi-isotropic carbon reinforced laminates

Qi, Herszberg and co-workers did thorough experimental testing on various laminate composites (Qi et al, 1997). Qi and Herszberg also studied laminates made out of T300 tows impregnated with epoxy resin by the resin transfer mould (RTM) process with a lay-up of $[0/90, 0/90, \pm45°]_s$ (Qi & Herszberg, 1999). Their goal was to assess ‘the effects of hygrothermal cycling and low velocity impact on damage resistance and residual compressive strength’ (Qi & Herszberg, 1999). After achieving their initial experimental data, Qi and Herszberg found that the residual compressive strength of the composites tested is decreased due to degradation of the resin matrix caused by the hygrothermal cycling with which they treated the test specimens. Using their data to go a step further, Qi and Herszberg developed a semi-empirical model to predict the residual compressive strength of the laminates. The model includes the damage effects from both the impact and the exposure to the hygrothermal environment. Based on this model, the residual strength (in compression) of the examined laminates can be related to damage width and intensity, the strength of the undamaged material and a degradation factor due to hygrothermal cycling. All the quantities mentioned previously are measurable and have resulted from the tests carried out by Qi and Herszberg. The writers conclude that 'the results from the analysis coincide reasonably with the data from the PW laminates' (Qi & Herszberg, 1999). The statement, while seemingly significant does not provide more than one would expect, since the analysis was done using a semi-empirical model, developed on the same experimental results. This however, should not lower the significance of the work carried out.

Patel and Case studied the effects of hygrothermal environments on woven composites containing epoxy matrix and graphite reinforcement mainly destined for use in aircraft engines (Patel & Case, 2000). The material was found to be only marginally affected by the imposed environments as far as initial and residual, fatigue (Fig.2.2.2) and tensile properties were concerned. During quasi-static loading, the majority of micro-cracks appeared close to failure but did not reduce the axial modulus of elasticity (Patel & Case, 2000). However, the same report showed that damage progression was highly dependant on the test environment, therefore life prediction models must take into account various possible conditions such as off-axis loading (Patel & Case, 2000). Fig.2.2.1 that follows shows a typical mission profile for (mainly military) aircraft engines.

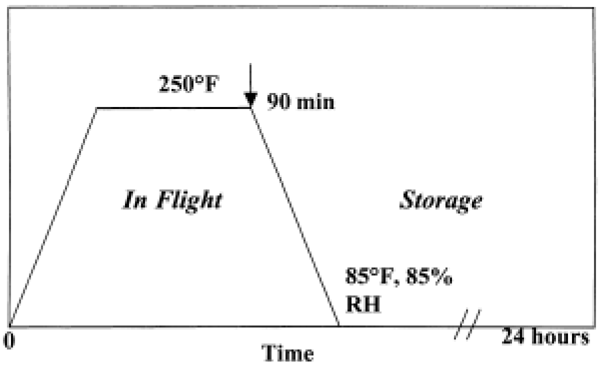


Fig.2.2.1
Mission profile for aircraft engine. From (Patel & Case, 2000)

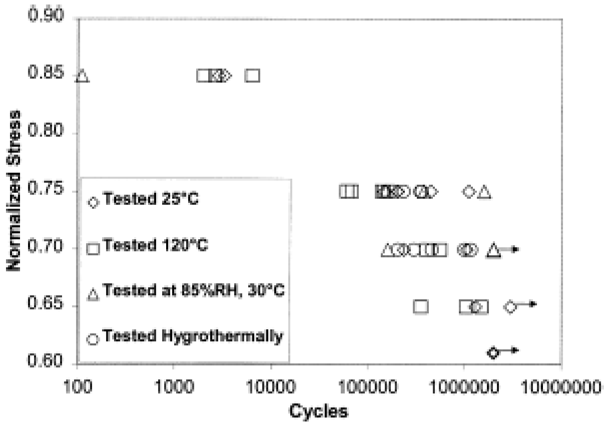


Fig.2.2.2
Normalised maximum fatigue stress as a function of test cycles to failure for the four environmental conditions examined. From (Patel & Case, 2000)

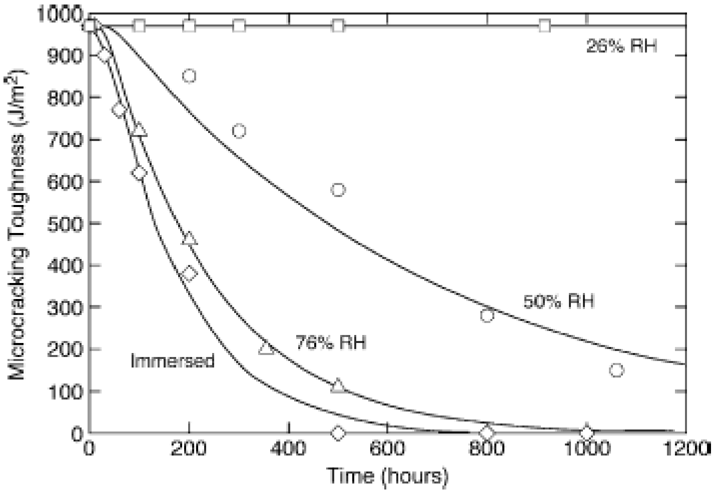
Probably the most important conclusion made by Patel and Case was that 'hygrothermal cycling during fatigue was found to result in greater crack density during fatigue than did any of the other three conditions (…) The fatigue life of this material may be more adversely affected by environment for off-axis loading situations than was captured by the fibre direction loading case considered in this work' (Patel & Case, 2000).

Kellas, Morton and Curtis studied the effects of hygrothermal environments on both tensile and compressive properties of notched laminated composites in static (Kellas et al, 1990a) and fatigue loading (Kellas et al, 1990b). The laminates were prepared from XAS/914C prepreg but the lay-up sequence was $[\pm45°/0_3/\pm45°/0]_s$ for one material and $[0/\pm45°/0_2/\pm45°/0]_s$ for the other. Sharp notches or circular holes were cut in the centre of the specimens and un-notched specimens were tested at room temperature to obtain baseline results. Notched tensile strengths tend to increase with temperature or moisture content. However, when both temperature and humidity were increased significantly, the drilled specimens exhibited a decrease in tensile strength contrary to the notched specimens. Significant differences were observed between the results from the notched and the drilled specimens. Unlike tensile properties, compressive strength exhibited a 'consistent reduction with moisture content and/or temperature increase' (Kellas et al, 1990a). The fatigue tests did not show a different behaviour as far as the tensile strength is concerned. However, the opposite was observed for compression tests. 'Furthermore, compressive residual strength was found to be very sensitive to the fatigue damage even after as little as 10^3 cycles' (Kellas et al, 1990b).

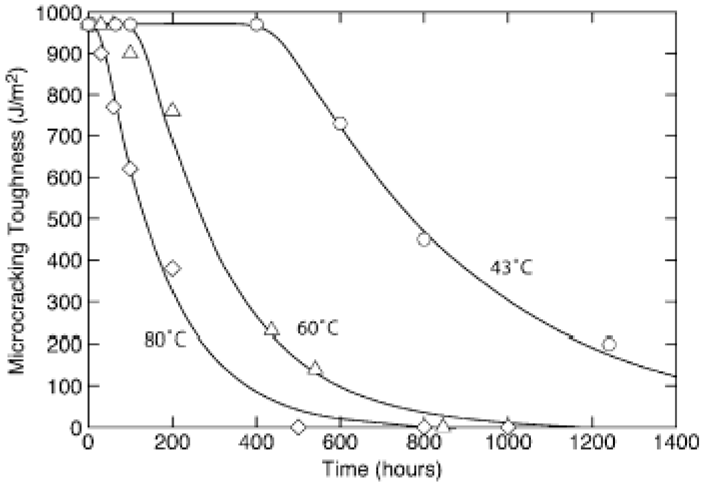
Nairn and Han (2003) describe testing two different quasi-isotropic composites (DuPont Avimid® K3B/IM7 carbon fibre and PETI-5/IM7 carbon fibre composites, laminated into $[0, 90°]_s$) and subjecting them to various temperatures and levels of humidity (Han & Nairn, 2003). The panels were provided by Boeing. After selected ageing times, specimens were subjected to microcracking experiments in order to measure the microcracking toughness as a function of aging time. For Avimid® K3B/IM7 laminates, experiments at 80°C, 60°C and 43°C were done for immersed samples and for samples at 26, 50 and 76%RH. It should be noted that the reasons for selecting a test temperature of specifically 43°C (instead of, e.g. 40°C) are not stated in the text. The graphs that follow (Fig.2.2.3a and Fig.2.2.3b) plot the results for G_{mc} as a function of aging time for Avimid® K3B/IM7 under various humidity conditions and full water immersion, all at 80°C (Fig.2.2.3a) and G_{mc} as a function of aging time for Avimid® K3B/IM7 at certain temperatures whilst immersed in water (Fig.2.2.3b). These results clearly show that test specimens immersed in water at 80°C degraded at a very higher rate than test pieces exposed to 26% RH which preserved their original toughness over a 1000 hour ageing period. They also show that increase in temperature caused an acceleration of the degradation rate and an apparent threshold time limit for each temperature below which, degradation does not occur. For PETI-5/IM7, the only experiments done were for samples immersed in water at 80°C at various temperatures. The reason for this was that during 3500 hours of water immersion at 80°C, only a 30% drop in toughness was witnessed (Fig.2.2.4).

To determine the toughness as a function of aging time, the density of microcracks as a function of the applied load was measured. For each aging condition, three separate specimens were dried, tabbed with aluminium end tabs and loaded at room temperature. Loading was periodically interrupted and the specimens were removed and observed on edge by means of optical microscope to record the density of micro-cracks in the 90° plies. It is clearly stated in the text that ‘all micro-cracking toughness tests were done at room temperature on dry specimens. Although elevated temperatures and moisture-induced stresses affect the micro-crack formation during ageing, those conditions are not relevant to the analysis of the room-temperature, dry toughness tests. The toughness tests assess the effects of all prior aging on laminate properties’ (Han & Nairn, 2003).

The lines drawn in the graphs that follow are fits of the experimental results to simple first-order kinetics by assuming there is some threshold water concentration below which no degradation occurs (such as the concentration for 26%RH). The rate constants calculated from these fits can be used to shift all results to a master plot for hygrothermal aging which was exactly what Han & Nairn’s main objective was (Fig.2.2.5).



(a)



(b)

Fig. 2.2.3a. The microcracking toughness, Gmc, as a function of aging time for Avimid® K3B/IM7 laminates at 80°C for water immersion or for various levels of relative humidity. The smooth lines are fits to first-order hydrolysis analysis with threshold water concentration for the onset of degradation. From (Han & Nairn, 2003)
Fig. 2.2.3b. The microcracking toughness, Gmc, as a function of aging time for Avimid® K3B/IM7 laminates while immersed in water, but aged at various temperatures. The smooth lines are fits to first order hydrolysis analysis with threshold water concentration for the onset of degradation. From (Han & Nairn, 2003)

By extrapolating rate constants to other temperatures and humidity values, it is possible to use this master plot for predictions at any constant temperature and humidity. By calculating the integrated exposure to water under any hygrothermal conditions, such as hygrothermal cycling, it might also be possible to use the master plot to predict the extent of toughness degradation caused by even more compelling conditions. However, an underlying assumption of the model is the single degradation mechanism which would be reason enough for uncertainties to exist if extrapolations for the master plot were extended significantly outside the temperature range of the basic characterization experiments. The writers believe that constructing hygrothermal ageing master plots for other material systems could potentially be an accelerated test method for characterising the hygrothermal stability of composite laminates, regardless of their composition and lay-up. The minimal experiments would be measuring the toughness degradation at the reference temperature whilst immersed in water and at several other temperatures, again while immersed in water (Han & Nairn, 2003). The fact though that the two materials in the paper developed so different hygrothermal behaviour, with respect to fracture toughness, must be taken into serious consideration and therefore no extrapolations made from master plots for one material to another.

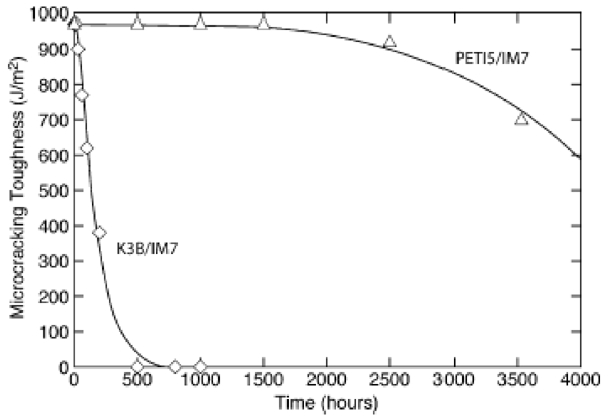


Fig.2.2.4
Comparative plot of the toughness G_{mc} of the two materials tested as a function of ageing time while immersed in water at 80°C. From (Han, Nairn, 2003)

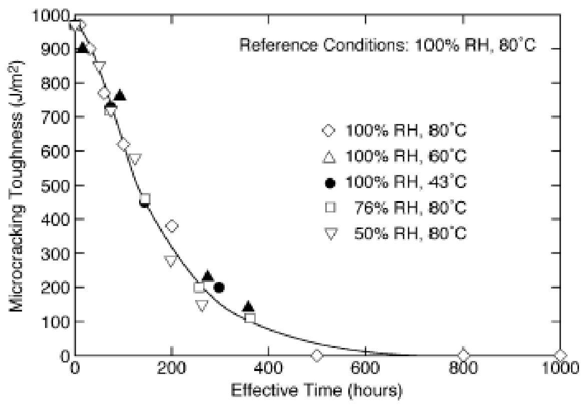


Fig.2.2.5
Hygrothermal master ageing plot for Avimid® K3B/IM7 laminates. From (Han, Nairn, 2003)

After studying the mechanical degradation of VARTM produced, 3D braided composites due to moisture sorption (Wan et al, 2005a), Wan et al studied the effect that external stresses may have on the same materials (Wan et al, 2005b). However, more emphasis was given on the effect relative humidity would have, than temperature. As can be seen in the following graph (Fig.2.2.6) external stresses, accompanied by hygrothermal ageing and consequent moisture uptake cause a degradation of mechanical properties but, according to the writers, do not alter the sorption mechanism which remains the same as suggested in previous works such as (Nairn & Hahn, 2003; Wan et al, 2002). The writers claim that in general, the 3D composites followed Fick's second law of diffusion, as has been suggested for unidirectional laminates. However, and exactly because of the 3D reinforcement, 3D composites exhibited a lower diffusion rate than unidirectional laminates.

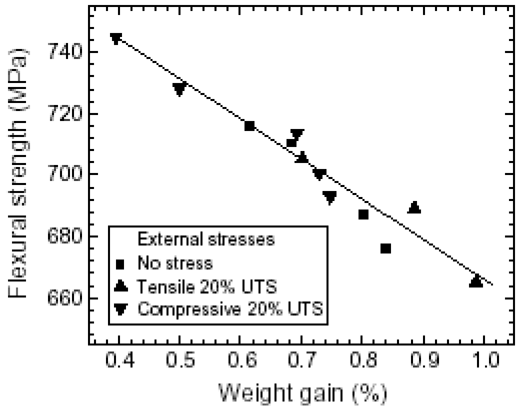


Fig.2.2.6
Flexural strength as a function of moisture content, under no external stresses (■), 20% tensile stresses (▲) and 20% compressive stresses (▼). From (Wan et al, 2005b)

2.2.2. Multidirectional and woven glass fibre reinforced laminates

Ray (2004) studied the effect of sub zero temperatures on woven glass fibre composites that had previously been exposed to hygrothermal conditioning. Also studied was the effect of the cross-head velocity. Because no relative standards had been developed, the hygrothermal chamber used is presented in the work (Fig.2.2.7). The effects of sub zero temperatures are very important since the absorbed moisture freezes and consequently, degrading the mechanical properties of the material. Three point bend tests provided experimental proof of this showing a decrease of the interlaminar shear strength (ILSS) of the woven composites as a function of ageing time. Moreover, at a particular ageing period, the frozen samples exhibited lower values of ILSS (Fig.2.2.8). The differences are not all that significant (also taking into account the standard deviation) but 'the more detrimental effect because of frozen moisture is permanent' (Ray, 2004).

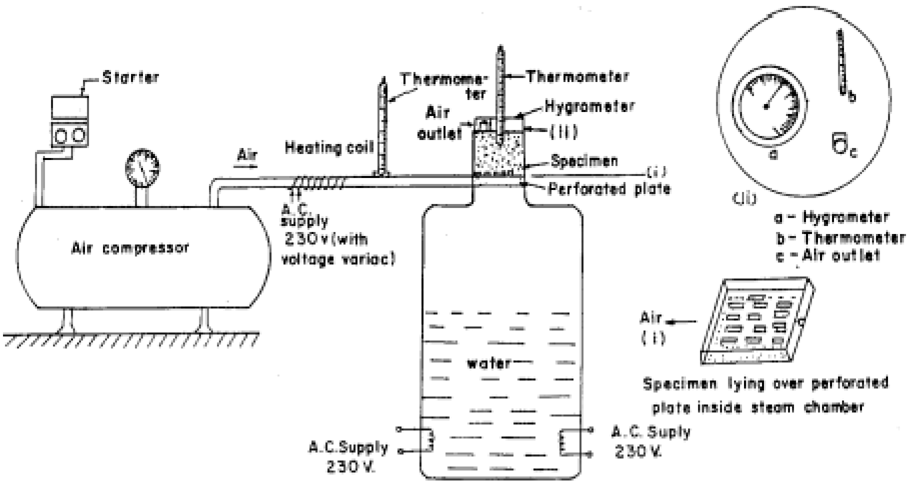


Fig.2.2.7
The hygrothermal chamber. From (Ray, 2004).

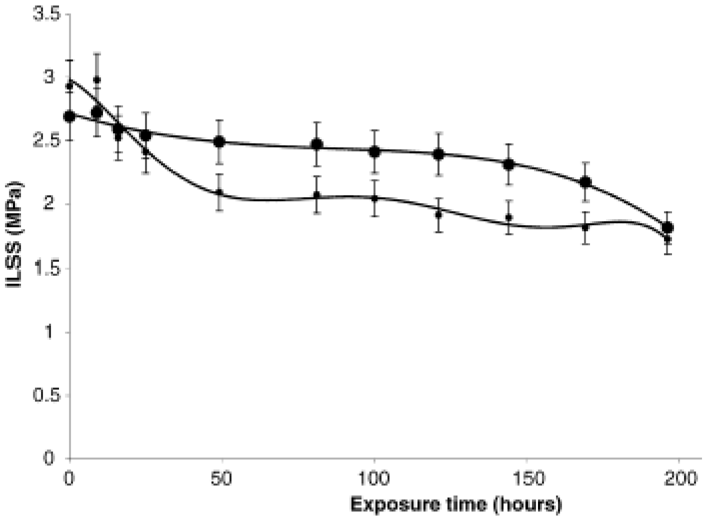


Fig.2.2.8
Comparison of ILSS values as a function of exposure time of plain moisture (●) and frozen moisture (•) conditioned glass fibre woven composites at 1mm/min crosshead speed. From (Ray, 2004)

Nine years earlier though, in 1995, Hong, Yalizis and Frantziskonis had evaluated the hygrothermal degradation in glass fibre/epoxy bi-axially woven laminates through stress wave factors (Hong et al, 1995). It is a significant report in that it exhibited the importance of real time hygrothermal degrading via nod-destructive testing. Through this method it is possible to continuously record the decrease in strength, not only of lab specimens, but more importantly, of actual structural elements. SEM and 3-point bend tests were also used to correlate with the signals plotted from the transducers (Hong et al, 1995). The writers measured a decrease in flexural strength, due to hygrothermal degradation by 1/3 of the original strength (Hong et al, 1995).

2.2.3. PET and PBT glass fibre reinforced composites

Short glass fibre reinforced PET (at 30%wt) composites, produced by DuPont were tested by Foulc and co-workers (Foulc et al, 2005), immersed in water in an autoclave at 1.6bar and a temperature of 120°C. Material characterization was done with a number of methods including TGA, SAXS and FT-IR. It is notable that while tests to assess the degradation of mechanical properties were carried out, they were involved in a larger project aimed to identify degradation mechanisms in PET composites. The effects on mechanical properties of the composites are in good agreement with results obtained for PBT composites by Mohd Ishak et al (2001). Water immersion, as in the previous paper discussed, proved to cause a drastic decrease of the mechanical strength of the composites (Fig.2.2.9a and 2.2.9b). This is caused by absorbed water from the very beginning of the ageing process, in a non-Fickian mechanism. It induces a slight plasticization of the matrix and hydrolysis of the polymer chains in the amorphous region. The writers suggest that for very long ageing times, hydrolysis may even affect the crystalline regions of the PET matrix because the lamellar thickness is reduced. Photo-mechanics can be used to assess the extent of the damage at a mesoscopic scale. The writers conclude that final osmotic cracking is responsible for the failure of the material (Foulc et al, 2005).

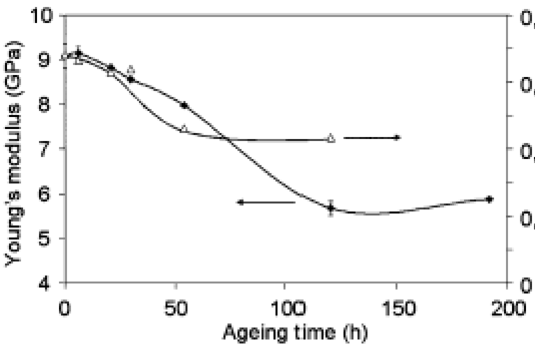


Fig.2.2.9a
Evolution of Young's modulus (●) and Poisson's ratio (Δ) with time. From (Foulc et al, 2005).

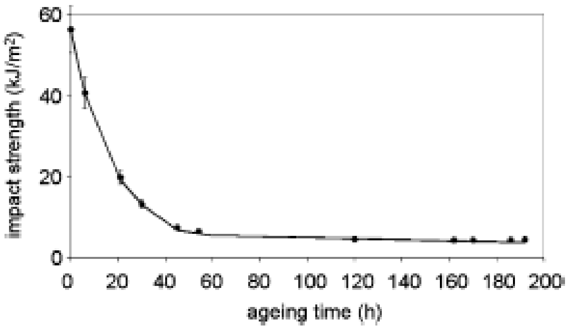


Fig.2.2.9b
Degradation of impact strength as a function of ageing time. From (Foulc et al, 2005).

It should be mentioned that the ageing time is not very long but the effects of the hygrothermal environment on the impact strength of the PET composite, significant. The decrease in Poisson's Ratio is about 50%. Young's modulus appears to form a plateau after about 50 hours of immersion in water.

The effects of hygrothermal environments on the thermal (Pagoretti & Penati, 2004a) and mechanical (Pagoretti & Penati, 2004b) properties of short glass fibre reinforced composites incorporating recycled PET as the matrix have also been studied. This aspect is important as 187.4ktons of PET were recycled in Europe, in the year 2000. All DSC tests carried out showed that the glass transition temperature (T_g) decreased by 3-6°C (depending on the percentage of the fibres and the RH) after 32 weeks of ageing (Pagoretti & Penati, 2004a). The stress-strain curves in Fig.2.2.10 from (Pagoretti & Penati, 2004b), show clearly mechanical degradation of the material after immersion in water.

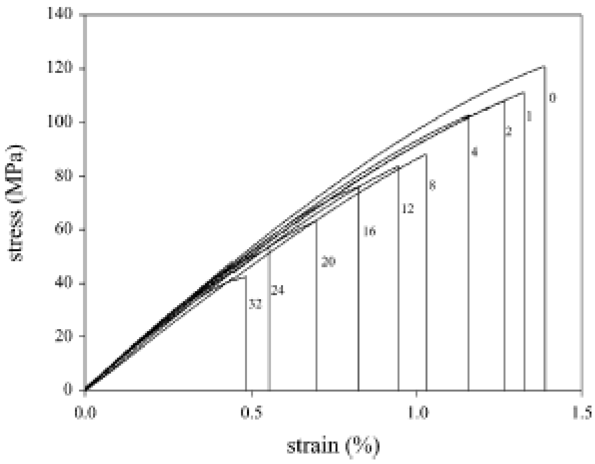


Fig.2.2.10
Stress-Strain curves for recycled PET/glass fibres (30%wt) composites. Numbers refer to weeks of immersion in water. From (Pagoretti & Penati, 2004b)

PBT glass fibre composites under hygrothermal conditioning were also studied by Mohd Ishak et al (2000). It was found that depending on the ageing temperature relevant to the T_g of the matrix, either plasticization ($T<T_g$) or hydrolysis ($T>T_g$) of the matrix occurred (Mohd Ishak et al, 2000). It is apparent that the mechanisms for hygrothermal degradation are the same among the various polymer matrices, regardless of their chemical formulae.

Bergeret and co-workers (2001) studied the hygrothermal behaviour of Nylon 66 (30%wt fibre reinfocement), PBT (15%wt fibre reinfocement) and PET (30%wt fibre reinfocement) composites. They focused however on the life-prediction of the thermoplastic composites and also raised the matter of accelerated hygrothermal test methods (Bergeret et al, 2001).

2.2.4. Other materials tested in hygrothermal environment

Experimental studies of the effect of hygrothermal environments have also been carried out on hybrid composite laminates such as Fibre Metal Laminates (Botehlo et al, 2005). Because of the A.A.2024-T3 aluminium alloy laminae of the laminate, hygrothermal degradation of the hybrid composite is almost half, in terms of moisture absorption and drop in mechanical properties, of that observed in glass fibre/epoxy systems. Because this is a relatively new category of composite materials, extensive research is carried out globally.

Because of their common use as core materials in sandwich composite panels (Gupta et al, 1999), syntactic foams have also been tested in hygrothermal environments (Gupta & Woldesenbet, 2003). Their strength in compression in such environments could be crucial for the integrity of the sandwich panel. A decrease of about 55% in compressive strength was calculated for Syntac 350 foam by Ishai and co-workers (1995) for a moisture content of 15%. A 60% decrease in compressive strength has been determined for K46 syntactic foams in high temperature salt water (Gupta & Woldesenbet, 2003).

2.3. Experimental Test methods

Even until 2005, there had not been a globally accepted accelerated test method for hygrothermal testing of composites. Jedidi, Jacquemin and Vautrin (although the latter two are more known for their computational work in the field) attempted to cover this gap and presented a paper (Jedidi et al, 2005) on accelerated cyclic tests that simulate the flight cycles of an aircraft operating at both subsonic and supersonic speeds (Fig.2.3.1). The materials tested were quasi-isotropic IM7/977-2 laminates, consisting of 30 plies, typical composite material for wing applications. The writers consider the moisture diffusion process as being in general agreement with the classical 1-D Fick's law and although the idea is quite original, flaws can be found. Possibly the most important one, being the fact that each temperature cycle during flights is too long and not really typical of the cycles one may meet in a military aircraft's service lifetime. Usually a typical military (intercept or close air support) aircraft mission would not last more than one hour (and certainly not eight). In this one hour time period supersonic flight (and temperatures) will be encountered for only a few minutes, corresponding to not more than 12% of the flight time. This forces us to assume that no thermal spiking issues have been dealt with by the writers, despite the use of supersonic speeds. Finally, it is very likely that temperature values below zero be achieved before landing. All these factors mark the insufficient planning of the flight cycle. This may be the one of the reasons the accelerated cycles produce different results for moisture uptake than the true, in service cycles. However, the general idea, as said before, is very good. The mission profile suggested by Patel & Case (2000) appears closer to reality than this one. However, the storage and maintenance part of the cycle is better profiled in the work by Jedidi et al (2005). The maintenance cycle is quite representative of the environment found in maintenance facilities around the globe and only a redesign of the test cycle may give far better results. A future modification of the cycle to incorporate unscheduled maintenance work (minor incidents, ground tests etc) would improve the model even more and should be taken into account.

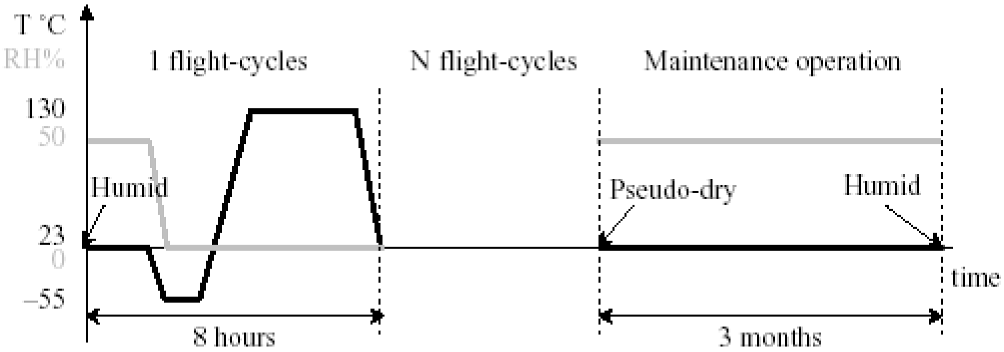
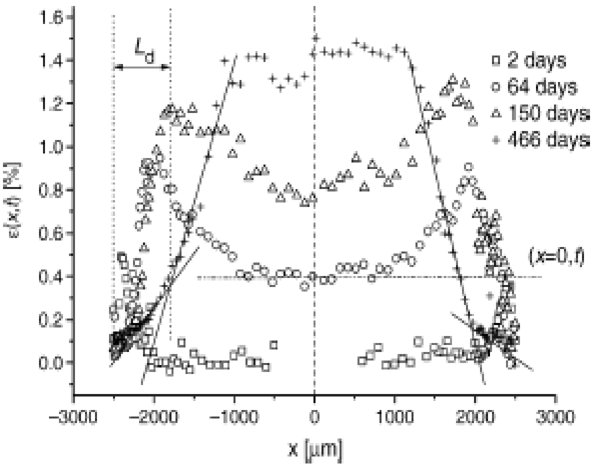


Fig.2.3.1
Conditions of service life: Flight cycles and maintenance. Details of the humid and pseudo-dry state.
From (Jedidi et al, 2005).

Another test method devised by Gigliottia, Molimard, Jacquemin and Vautrin was presented in 2005 (Gigliottia et al, 2005). This time, the goal was to develop an experimental set-up to characterize internal stresses in thin, unsymmetric 0/90° composite plates, induced by hygrothermal loads. The reason for this is that as is the case with thick laminates, very thin composite 0/90° plates may deform with a rather complex behaviour (Gigliottia et al, 2005). The writers conclude that the method has several great advantages over the already existent methods. Its greatest advantage is probably the fact that it is a contact free methodology.

A very interesting series of papers by Cervenka and co-workers, (2005a; 2005b), correlates Raman spectroscopy and fibre strains with hygrothermal ageing (Cervenka et al, 2005a; Cervenka et al, 2005b). In their work, which continues the work published in 1998 (Cervenka et al, 1998) they used two different model composites to study the micromechanical phenomena taking place during the ageing of surface treated Twaron fibres (Cervenka et al, 2005a) and compare those results with the results from PBO and M5 fibres (Cervenka et al, 2005b). One of the conclusions drawn is that ‘the decay in the Raman shear lag parameter for a specimen subjected to short-time mechanical loading under dry conditions is lower than those caused by hygrothermal ageing’ (Cervenka et al, 2005a). However, an ‘attempt to correlate changes in the fibre strain $\Delta G(t)$ with debond growth ΔL_d and to derive the interface fracture energy Γ_I has not been successful due to a large scatter in experimental data’ (Cervenka et al, 2005a).



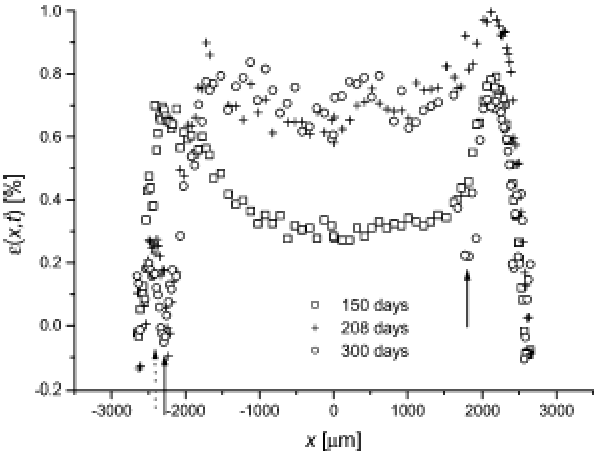


Fig.2.3.2a **Fig.2.3.2b**

Raman strain profiles at selected exposure times for DFPO specimens containing a Twaron fibre with a surface finish (Fig.2.2.6a) and an M5 fibre (Fig.2.2.6b). From (Cervenka et al, 2005a and Cervenka et al, 2005b)

Another interesting test just worth mentioning is the innovative test design by Chen (2001) for exposure to hygrothermal cycling of bolted joints in composites and measurement of their strength (both static and fatigue). The main characteristic that makes this particular work interesting (regardless of the results) is the fact that Chen found an apparatus that enabled testing composites as they would be used in an actual application and not just laboratory specimens.

3. Theoretical and Computational

During the past decade, experimental work and the relative number of published papers on the effects of hygrothermal environments on the properties of laminates decreased. In a continuing attempt to discover the mechanisms of the related phenomena (hygrothermal, thermal spiking degradation) and link them with the decrease observed in the mechanical properties of composite structures, researchers turned their interest in computation. The main reason for this is the rapid increase in computational power during this period of time. One might recall that computers with Pentium processors were not commercially available until 1997-1998.

3.1. Analytical and semi-empirical techniques developed

This does not of course, mean that computational work was not done before 1995 and an exceptional (for its time) paper by Kollar on work done in 1992 was published in 1994. The paper deals with stresses developed in composite cylinders in varying hygrothermal environments and as most papers in the field, with analytical methods and not with finite element analysis (Kollar, 1992). A good agreement was found between the results in the paper and previously published results was established. The previous results cited in Kollar’s paper all date back to the late 1970’s.

In a paper by Shen (2001), a micro-macro mechanical model was reported to yield results showing ‘that the buckling load and postbuckling strength will degrade with increasing moisture concentrations and temperature’ (Shen, 2001). It is also reported that the characteristics of postbuckling are greatly influenced by many parameters such as fibre orientation, fibre volume fraction, initial geometric imperfections, the total number of plies and so on.

A series of papers by Jacquemin and Vautrin published recently (2002a; 2002b), attempt to look at the environmental aspects of the behaviour of composite pipes, from a slightly different angle. Developing (Jacquemin & Vautrin, 2002a) and adopting a semi-analytical model for their calculations, the researchers assessed the internal stresses related to both the moisture concentration and the temperature change. The most important probably characteristic of the model is perhaps the fact that it can be applied to both homogeneous and heterogeneous ply arrangements (Jacquemin & Vautrin, 2002a).

Whilst Seferis and his co-workers were modelling the heat and water mass transfer processes (Seferis et al, 2000), Adda-Bedia and co-workers developed the previous year a new analytical method for modelling mechanical properties after exposure to hygrothermal environment (Sereir et al, 2005). The methodology was the same used by Tounsi & Adda-Bedia (2003). The paper deals with computation of transient hygroscopic stresses in UD laminates taking into account the change of mechanical properties due to moisture and temperature. The method’s great asset and the forward driving force is that it allows direct determination of such stress values without having to calculate the actual moisture concentration. The results seem to be in good agreement with previously published computational results.

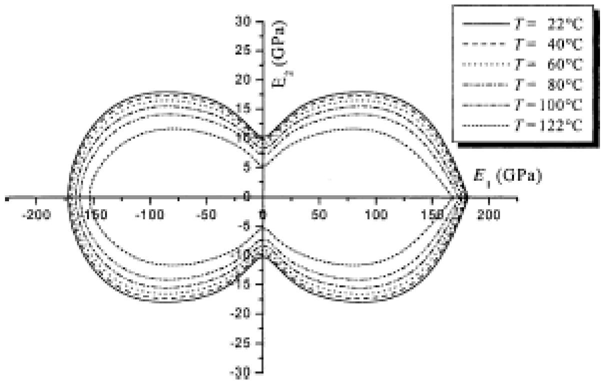


Fig.3.1.1a
Young's moduli (E_1, E_2) of the UD laminate with variation of the temperature. From (Sereir et al, 2005)

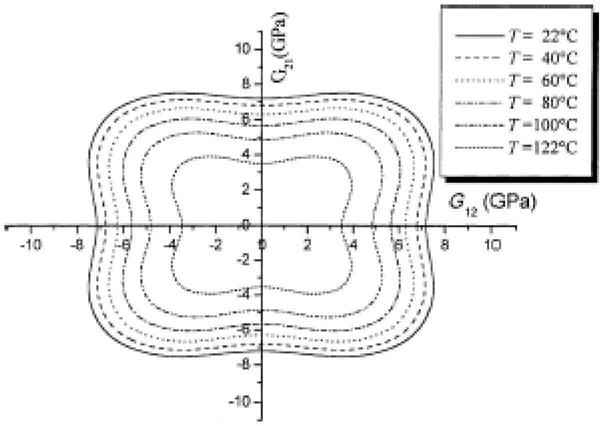


Fig.3.1.1b
Shear moduli (G_{12}, G_{21}) of the UD laminate with variation of the temperature. From (Sereir et al, 2005)

The same model was used by Boukhoulda, Adda-Bedia and Madani to determine the effect of fibre orientation angles of T300/5208 and E-glass fibre/epoxy composites on humidity diffusion (Boukhoulda et al, 2005) and predict the saturation time for both materials.

3.2. Finite element models

Adda-Bedia and co-workers have also worked with finite element analysis, in an attempt to shed light into the solution of a major composites' problem- bonded composite repairs in aircraft. In particular, the work by Megueni et al (2005) is targeted at providing a predictive model for the mechanical properties of laminates used as repair patches but happen to be subjected to hygrothermal environments over their operational life. An analytical formula for the derivation of Young's modulus as a function of temperature and moisture is used. Despite having only a short communication so far, important conclusions are made and a series of graphs point them out. The final conclusion Megueni et al make is that 'designers must be taking into account the negative effect of an aged composite patch' (Megueni et al, 2005). It may seem as elementary but, considering the (elementary) mistakes that have lead to disaster and have been discovered after the disaster has occurred, in the investigation procedures, pointing it out can be only useful.

Ogi, Kim, Maruyama and Takao did work on quasi-isotropic carbon/epoxy laminates to establish the relationship between the hygrothermal ageing of the materials and the damage processes (Ogi et al, 1999). Taking their experimental research a step further, they proposed a finite element model to describe the changes in Young's modulus and Poisson's ratio caused by the hygrothermal environment (Ogi et al, 1999).

Finite element analysis was also used by Patel and co-workers (2002) to evaluate the structural behaviour of thick composite laminates, subjected to hygrothermal environments. Using a higher order theory, they showed that shear deformation theory is inadequate for the analysis of thick laminates, unless slope discontinuity in the in-plane displacements is taken into account (Patel et al, 2002).

Also worth mentioning is that Swamy Naidu & Sinha (2005a; 2005b) used non-linear finite element analysis in order to model the complex bending behaviour of composite cylindrical shell panels.

Recent work of Tang and co-workers (2005) has lead to finite element models for moisture diffusion in woven composites. Since woven composites (Fig.3.2.1) have seen application in many new fields of industry, the mechanisms (and especially the micromechanical mechanisms of absorption and desorption) must be fully understood. According to the writers 'woven composites exhibit quicker diffusion than that of a unidirectional laminate with the same overall fiber volume fraction. The plain weave with a lenticular tow and large waviness is seen to exhibit the quickest diffusion process. (…) When the detailed microstructure of a weave is determined using microscopic examination, and the diffusivity properties considering the effect of irregular fiber distribution are used, computational micromechanics simulations of moisture diffusion tests for the 3-ply woven hybrid composites can produce results that are in good agreement with the experimental results' (Tang et al, 2005).

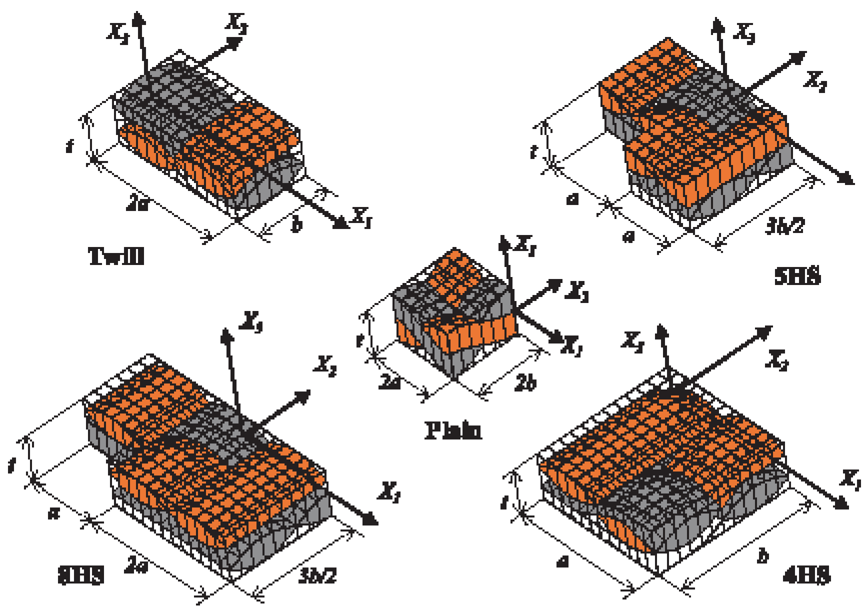


Fig.3.2.1
Finite element models of weaves with lenticular tows for through-thickness diffusion analysis.
From (Tang et al, 2005)

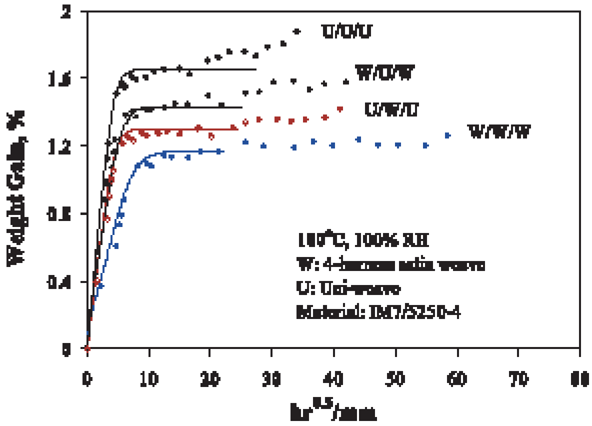


Fig.3.2.2
A prediction of moisture diffusion behaviour of 3-ply satin/uni-weave hybrid laminates at 100°C and 100%RH. The symbols and solid lines are for the experimental and analytical results, respectively. From (Tang et al, 2005)

3.3. Other numerical and computational studies

An interdisciplinary report which is proof of the importance of composites' long-term stability in industry is the work by Guedes and co-workers (2002). The paper focuses on computer programming and the development of a programming code which will enable the calculation of the life expectancy of any given PMC in any given environment.

Hybrid composites have also been studied numerically (Wang et al, 2005). Laminates with piezoelectric actuators tend to fail due to delamination and numerical calculations concerning the hygrothermal degradation and corresponding delamination of such structures have been published (Cho & Yoon, 1999).

A report also worth mentioning is the work done by Seng et al, (1997) in which, analytical models, initially used to predict elastic properties of woven fabric composites at room temperature, have been expanded to predict tensile properties of both wet and dry glass fibre/epoxy fabric composites at increased temperatures (Seng et al, 1997). While the idea, in general, is the ultimate goal of all research groups, from 1997 to the present day, no one has accepted the proposed analytical model. This alone, unfortunately reduces the credibility of the work.

4. Conclusions

Disasters don't just happen. They are a series of events, either ill-treated or neglected all together. Polymer matrices do indeed absorb moisture. This phenomenon, known throughout the scientific community, can have disastrous effects on the structure it involves, either that is an aerospace application, a civil engineering structure and so forth. That is why scientists are studying the degradation of all composites (regardless of the matrix and the reinforcement).

Moisture absorption is enhanced by temperature and depending on the matrix material the increase in moisture equilibrium uptake can be rather substantial. If thermal spiking occurs, water absorption is even more significant. Even though Fick's law is relatively easy to use and solve, it has now become apparent that many polymer matrices (commercially in use) follow a moisture diffusion process which deviates significantly from Fick's law. The deviation factor is enhanced even more in rather thick and very thin, un-symmetric laminates.

While the diffusion process is dominated by the matrix, the reinforcing phase contributes in a retarding way, by effectively reducing the reactive matrix area. This results in a slower diffusion process in the composite material after a very similar (between the pure resin and the composite), initial behaviour.

All laminate parameters (such as lay-up, fibre orientation etc) affect the composite's resistance to moisture uptake and swelling but because of matrix domination, the mechanical properties where the reinforcement is the key element are not affected significantly. There are some reports that even suggest a slight increase in Young's modulus in the fibre direction due to stress relaxation. However, the transverse tensile strength and the through-thickness mechanical properties, all exhibit a significant decrease. Another mechanical property affected is the interlaminar shear strength. The degradation of the ILSS becomes more significant with the increase of laminate thickness as resin rich (affected by the hygrothermal environment) areas are created.

Inserting second elements to the matrix may increase its ability to withstand water mass absorption. It has also been seen that increase in fibre volume ratio promotes a decrease in moisture absorption, but this is only up to a certain volume ratio and not infinite. A very promising solution to the problem seems to be the further development of hybrid composites such as Glare and Arall. Moisture uptake is significantly lowered in these materials but galvanic corrosion at the interfaces is still a potential threat. It should also be noted that hygrothermal master plots of composite laminates would make an excellent database for future reference and more researchers should turn in that direction.

As was seen, experiments in hygrothermal environments are a time consuming procedure. Because computational power has increased substantially the past fifteen years, the ratio of computational and simulation results to experimental results has grown passed unity the past few years. That said, there are many papers (or series of papers) that have undergone both computation and experimental reproduction of the simulated hygrothermal environments and studied their effects on composite laminates. These papers are an excellent way of investigating the mechanisms of sorption and diffusion in laminates and composites in general. They also show a good response between theoretical models recently developed and experiments in the environments simulated, but only when Fick’s law is taken into account as a baseline and not the calculation model.

Experimental results are obtained mainly by testing (cyclic or not) in varying temperatures and percentages of humidity (or immersion in water) for various time periods. The fact that no globally accepted standard has been developed, despite knowing the problem exists for the past fifteen or twenty years is, at least, discouraging. Despite attempts by various researchers to transform their test methods into standardised procedures, no globally accepted standard has been developed for experiments investigating this phenomenon. This situation can only be dealt with scepticism but reasons and excuses can be found. In any case, the temperature and RH levels are so loose that experiments may be conducted at a variety of conditions, such that it would be a shame to restrict them to just a few standardised temperature and humidity “couples”. Also, the fact that the different tests that are conducted after the hygrothermal ageing (tensile, compressive, flexural testing), incorporate different standard specimen dimensions is a parameter that cannot be overlooked. So, there is still relative freedom as to the way each research group conducts their experiments.

In summary, hygrothermal environments can have serious detrimental effects on laminate composites and pose as a potential hazard for all existing structures. This however is something we must learn to live with, as hygrothermal environments are constantly present and nature’s way of signifying her presence. What can and should be done is the continuation of all research, experimental and computational so that we may have an absolutely complete understanding of the problem. Only then will we be able to produce materials able to withstand some aspects of the might of nature.

5. References

- Amara K.H., Tounsi A., Benzair A., *"Transverse cracking and elastic properties reduction in hygrothermal aged cross-ply laminates"*, Materials Science & Engineering A 396 (2005) 369-375.
- Asp, L.E., *"The effects of moisture and temperature on the interlaminar delamination toughness of a carbon/epoxy composite"*, Composites Science and Technology 58 (1998) 967-977.
- Bao, L-R., Yee, A.F., *"Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fiber composites"*, Polymer 43 (2002a) 3987-3997.
- Bao, L-R., Yee, A.F., *"Moisture diffusion and hygrothermal aging in bismaleimide matrix carbon fiber composites-part I: uni-weave composites"*, Composites Science and Technology 62 (2002b) 2099-2110.
- Bao, L-R., Yee, A.F., *"Moisture diffusion and hygrothermal aging in bismaleimide matrix carbon fiber composites-part II: woven and hybrid composites"*, Composites Science and Technology 62 (2002c) 2111-2119.
- Bergeret, A., Pires, I., Foulc, M.P., Abadie, B., Ferry, L., Crespy, A., *"The hygrothermal behaviour of glass-fibre-reinforced thermoplastic composites: a prediction of the composite lifetime"*, Polymer Testing 20 (2001) 753-763.
- Botelho, E.C., Pardini, L.C., Rezende, M.C., *"Hygrothermal effects on damping behaviour of metal/glass fibre/epoxy hybrid composites"*, Materials Science and Engineering A 399 (2005) 190-198.
- Boukhoulda, B.F., Adda-Bedia, E., Madani, K., *"The effect of fiber orientation angle in composite materials on moisture absorption and material degradation after hygrothermal ageing"*, Composite Structures (2005) Article in press.
- Cervenka, A.J., Bannister, D.J., Young, R.J., *"Moisture absorption and interfacial failure in aramid/epoxy composites"*, Composites: Part A 29A (1998) 1137-1144.
- Cervenka, A.J., Young, R.J., Kueseng, K., *"Micromechanical phenomena during hygrothermal ageing of model composites investigated by Raman spectroscopy. Part I: Twaron fibres with different surface treatments"*, Composites: Part A 36 (2005a) 1011-1019.
- Cervenka, A.J., Young, R.J., Kueseng, K., *"Micromechanical phenomena during hygrothermal ageing of model composites investigated by Raman spectroscopy. Part II:*

Comparison of the behaviour of PBO and M5 fibres compare with Twaron", Composites: Part A 36 (2005b) 1020-1026.

- Chen, H-S., *"The static and fatigue strength of bolted joints in composites with hygrothermal cycling"*, Composite Structures 52 (2001) 295-306.
- Choi, H.S., Ahn, K.J., Nam, J.-D., Chun, H.J., *"Hygroscopic aspects of epoxy/ carbon fiber composite laminates in aircraft environments"*, Composites: Part A 32 (2001) 709-720.
- Foulc, M.P., Bergeret, A., Ferry, L., Ienny, P., Crespy, A., *"Study of hygrothermal ageing of glass fibre reinforced PET composites"*, Polymer Degradation and Stability 89 (2005) 461-470.
- Gigliottia, M., Molimard, J., Jacquemin, F., Vautrin, A., *"On the nonlinear deformations of thin unsymmetric 0/90 composite plates under hygrothermal loads"*, Composites: Part A (2005) 1-6.
- Guedes, R.M., Morais, J.J.L., Marques, A.T., Cardon, A.H., *"Prediction of long-term behaviour of composite materials"*, Computers and structures 76 (2000) 183-194.
- Gupta, N., Woldesenbet, E., *"Hygrothermal studies on syntactic foams and compressive strength determination"*, Composite Structures 61 (2003) 311-320.
- Han M. H., Nairn J. A., *"Hygrothermal ageing of polyimide matrix composite laminates"*, Composites: Part A 34 (2003) 979–986.
- Han, M.-H., Nairn, J.A., *"Hygrothermal ageing of polymide matrix composite laminates"*, Composites: Part A 34 (2003) 979-986.
- Helbling, C., Abanilla, M., Lee, L., Karbhari, V.M., *"Issues of variability and durability under synergistic exposure conditions related to advanced polymer composites in the civil infrastructure"*, Composites: Part A (2005) 1-9.
- Hong, G., *"Hygrothermal degradation in glass/epoxy- evaluation via stress wave factors"*, Composite structures 30 (1995) 407-417.
- Hough, J.A., Karad, S.K., Jones, F.R., *"The effect of thermal spiking on moisture absorption, mechanical and viscoelastic properties of carbon fibre reinforced epoxy laminates"*, Composite Science and Technology 65 (2005) 1299-1305.
- Ishai, O., Hiel, C. Luft, M., *"Long-term hygrothermal effects on damage tolerance of hybrid composite sandwich panels"*, Composites Vol.26, No. 1 (1995) 47-55.
- Jacquemin, F., Vautrin, A., *"A closed-form solution for the internal stresses in thick composite cylinders induced by cyclical environmental conditions"*, Composite Structures 58 (2002a) 1-9.

- Jacquemin, F., Vautrin, A., *"The effect of cyclic hygrothermal conditions on the stresses near the surface of a thick composite pipe"*, Composites Science and Technology 62 (2002b) 567-570.
- Jedidi, J., Jacquemin, F., Vautrin, A., *"Design of accelerated hygrothermal cycles on polymer matrix composites in the case of a supersonic aircraft"*, Composite Structures 68 (2005) 429-437.
- Kellas, S., Morton, J., Curtis, P.T., *"The effect of hygrothermal environments upon the tensile and compressive strengths of notched CFRP laminates. Part 1: Static loading"*, Composites, Vol.21, No. 1 (1990a) 41-51.
- Kellas, S., Morton, J., Curtis, P.T., *"The effect of hygrothermal environments upon the tensile and compressive strengths of notched CFRP laminates. Part 2: Fatigue loading"*, Composites, Vol.21, No. 1 (1990b) 52-62.
- Kollar, L.P., *"Three dimensional analysis of composite cylinders under axially varying hygrothermal and mechanical loads"*, Computers & Structures, Vol.50 No.4 (1994) 525-540.
- Megueni, A., Tounsi, A., Adda-Bedia, E., *"Evolution of the stress intensity factor for patched crack with bonded hygrothermal aged composite repair"*, Materials and Design (2005) Article in Press (Short Communication).
- Mohd Ishak, Z.A., Ariffin, A., Senawi, R., *"Effects of hygrothermal aging and a silane coupling agent on the tensile properties of injection molded short glass fiber reinforced poly (butylenes terephthalate) composites"*, European Polymer Journal 37 (2001) 1635-1647.
- Mohd Ishak, Z.A., Ishiaku, U.S., Karger-Kocsis, J., *"Hygrothermal ageing and fracture toughness of short-glass-fiber-reinforced rubber-toughened poly (butylene terephthalate) composites"*, Composites science and Technology 60 (2000) 803-815.
- Nairn J.A., "*Applications of finite fracture mechanics for predicting fracture events in composites*." Fifth International Conf. on Deformation and Fracture of Composites, London, UK; March 1999, p. 18–19.
- Ogi, K., Kim, H.S., Maruyama, T., Takao, Y., *"The influence of hygrothermal conditions on the damage processes in quasi-isotopic carbon/epoxy laminates"*, Composites Science and Technology 59 (1999) 2375-2382.
- Patel, B.P., Ganapathi, M., Makhecha, D.P., *"Hygrothermal effects on the structural behaviour of thick composite laminates using higher-order theory"*, Composite Structures 56 (2002) 25-34.

- Patel, S.R., Case, S.W., *"Durability of a graphite/ epoxy woven composite under combined hygrothermal conditions"*, International Journal of Fatigue 22 (2000) 809-820.
- Pegoretti, A., Penati, A., *"Effects of hygrothermal ageing on the molar mass and thermal properties of recycled poly (ethylene terephthalate) and its short glass fibre composites"*, Polymer Degradation and Stablity 86 (2004a) 233-243.
- Pegoretti, A., Penati, A., *"Recycled poly (ethylene terephthalate) and its short glass fibre composites: effects of hygrothermal ageing on the thermomechanical behaviour"*, Polymer 45 (2004b) 7995-8004.
- Qi, B., Herszberg, I., *"An engineering approach for predicting residual strength of carbon/ epoxy laminates after impact and hygrothermal cycling"*, Composite Structures 47 (1999) 483-490.
- Qi, B., Herszberg, I., Baker, A.A., Bannister, M., *"The residual compression strength of stitched and unstitched plain-weave carbon/epoxy laminates after impact and hygrothermal cycling"*, ICCM-11, Gold Coast, July 1997.
- Qi, B., Herszberg, I., Bannister, M., *"Impact performance of carbon/ epoxy laminates after environmental conditioning"*, International Aerospace Conference, Sydney, February 25-27, 1997.
- Ray, B.C., *"Effects of crosshead velocity and sub-zero temperature on mechanical behaviour of hygrothermally conditioned glass fibre reinforced epoxy composites"*, Materials Science & Engineering A 379 (2004) 39-41.
- Seferis, J.C., Chung, K., Buehler, F.U., Takatoya, T., *"Heat and water mass transfer modelling in polyimide based advanced composites"*, Polymer Degradation and Stability 68 (2000) 43-51.
- Seng, L.K., Earn, T.T., Shim, V.P.W., *"Hygrothermal analysis of woven-fabric composite plates"*, Composites: Part B 28B (1997) 573-581.
- Sereir, Z., Adda-Bedia, E.A., Tounsi, A., *"Effect of temperature on the hygrothermal behaviour of unidirectional laminate plates with asymmetrical environmental conditions"*, Composite Structures (2005) Article in Press.
- Shen, H-S., *"Hygrothermal effects on the postbuckling of shear deformable laminated plates"*, International Journal of Mechanical Sciences 43 (2001) 1259-1281.
- Shirrell, C.D., Halpin, J., *"Moisture absorption and desorption in epoxy composite laminates"*, ASTM Special Techn, Publ. 617, 1977.

- Swamy Naidu, N.V., Sinha, P.K., *"Non-linear finite element analysis of laminated composite shells in hygrothermal environments"*, Composite Structures 69 (2005a) 387-395.
- Swamy Naidu, N.V., Sinha, P.K., *"Non-linear transient analysis of laminated composite shells in hygrothermal environments"*, Composite Structures (2005b) Article in Press.
- Tang, X., Whitcomb, J.D., Li, Y., Sue, H-J, *"Micromechanics modeling of moisture diffusion in woven composites"*, Composites Science and Technology 65 (2005) 817-826.
- Vauthier, E., Abry, J.C., Bailliez, T., Chateauminois, A., *"Interactions between hygrothermal ageing and fatigue damage in unidirectional glass/epoxy composites"*, Composites Science and Technology 58 (1998) 687-692.
- Wan, Y.Z., Wang, Y.L., Huang, Y., He, B.M., Han, K.Y., *"Hygrothermal aging behaviour of VARTMed three-dimensional braided carbon-epoxy composites under external loads"*, Composites: Part A 36 (2005b) 1102-1109.
- Wan, Y.Z., Wang, Y.L., Huang, Y., Zhou, F.G., He, B.M., Chen, G.C., Han, K.Y., *"Moisture sorption and mechanical degradation of VARTMed three-dimensional braided carbon-epoxy composites"*, Composites Science and Technology 65 (2005a) 1237-1243.
- Wang, X., Dong, K., Wang, X.Y., *"Hygrothermal effect on dynamic interlaminar stresses in laminated plates with piezoelectric actuators"*, Composite Structures 71 (2005) 220-228.
- Xiang, Z.D., Jones, F.R., *"Thermal-spike-enhanced moisture absorption by polymer-matrix carbon fibre composites"*, Composites Science and Technology 57 (1997) 451-461.
- Zhou, J., Lucas, J.P., *"The effects of a water environment on anomalous absorption behavior in graphite/epoxy composites"*, Composites Science and Technology 53 (1995) 57-64.