Damage accumulation in composite materials subjected to thermal cycles in space environments

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ABSTRACT

Carbon fiber reinforced cyanate ester composites are of interest for space structural applications where not only specific strength and stiffness are required but also dimensional stability and resistance to microcracking. However, because those materials are relatively new, there is a lack of knowledge with respect to their thermal cycling behavior and the related damage mechanisms. This thesis focused on studying the microcracking behavior of a carbon reinforced cyanate ester composite in order to understand the conditions under which microcracking initiates, and it also investigates the impact of microcracking on mechanical behavior. We have investigated the performance of such composite for space applications, focusing on the accumulation of damage from extreme thermal and externally applied stresses. For this purpose we subjected a five-harness satin weave fabric in [0/45]s to micromechanical testing in three point bending, TMA, DMA and thermal cycling using a "fast dipping" method. Micromechanical testing in three-point bending, combined with in-situ imaging, were used to understand the cracking behavior of the material subjected to external mechanical loading. TMA and DMA were used to assess the materials' thermal and mechanical properties under thermal cycling. The variation of CTE under thermal cycling was assessed by TMA and degradation of modulus due to damage accumulation monitored using a three point bending fixture under cold cycling in the DMA. Extreme thermal cycling was carried out and the effect of cold and hot cycling evaluated by imaging the material and measuring its modulus before and after cycling. Finally, three theoretical models based on the thermoelastic theory were developed: (i) one considering the case of a fiber in an infinite matrix allowing to assess thermal stresses induced by thermal cycling, (ii) one considering the case of a fiber coated in an infinite matrix allowing to assess thermal stresses induced by thermal cycling and (iii) one model allowing to determine mechanical and thermal properties of plies oriented in different directions.

KEYWORDS

Composite material, space application, cyanate ester, carbon fiber, thermal cycling, damage assessment, mechanical testing, TMA, DMA, modeling.

RÉSUMÉ

Les matériaux composites à base d'ester cyanate renforcés de fibres de carbone sont d'intérêt particulier pour les applications structurelles spatiales où non seulement les force et rigidité spécifiques sont requises mais aussi la stabilité dimensionnelle ainsi que la résistance à la microfissuration. Toutefois, puisque ces matériaux sont relativement nouveaux, il existe un manque significatif de connaissances quant à leur comportement face au cyclage thermique ainsi qu'au sujet des mécanismes d'endommagement reliés. Cette thèse rend compte des travaux de recherche effectués sur un matériau composite à base d'ester cyanate renforcés de fibres de carbone en ce qui attrait son comportement face à la microfissuration dans le but de comprendre les conditions sous lesquelles la microfissuration est initiée ainsi que les conséquences de cette dernière sur le comportement mécanique de ce matériau. Nous avons examiné la performance d'un tel matériau à des fins d'applications spatiales en mettant l'emphase sur l'accumulation du dommage engendré par l'application de stresses extrêmes thermique et externes. Dans ce cadre d'idées, nous avons soumis un laminé composite en tissu satiné tissé en 5-harnais superposé en [0/45]_s, à des tests micromécaniques de flexion en trois points, TMA, DMA ainsi qu'à du cyclage thermique en utilisant une méthode dites de « trempe ». Les tests micromécaniques de flexion en trois points combinés à de l'imagerie in-situ ont été utilisés afin de comprendre le comportement de microfissuration du matériau soumis à des contraintes mécaniques externes. Les tests de TMA et DMA quant à eux ont été utilisés afin d'évaluer les propriétés thermiques et mécaniques du matériau assujetti à du cyclage thermique. La variation du coefficient de dilatation thermique (CDT) fut évaluée par TMA et la dégradation du module d'élasticité par DMA à l'aide d'un système de flexion en trois points sous cyclage à froid. Des tests de cyclage thermique extrêmes ont été menés et l'effet des cyclages à froid ainsi qu'à chaud évalués par imagerie et par mesure du module d'élasticité avant et après cyclage. Finalement, trois modèles fondés sur les principes de thermoélasticité ont été développés : (i) un modèle considérant le cas d'une fibre dans une matrice infinie permettant d'évaluer les stress thermiques induits par cyclage thermique, (ii) un modèle considérant une fibre enrobée dans une matrice infinie permettant d'évaluer les stress thermiques induits par cyclage thermique et (iii) un modèle permettant de déterminer les propriétés mécaniques et thermiques des plis orientés dans différentes directions.

MOTS-CLEFS

Matériau composite, application spatiale, ester cyanate, fibre de carbone, cyclage thermique, évaluation du dommage, essais mécaniques, TMA, DMA, modelage.

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NOMENCLATURE

σ	Stress
Е	Strain
Р	Load
L	Span length or Sample length
b	Sample width
h	Sample thickness
δ	Displacement
D	Damage variable
D _c	Critical damage variable
T_g	Glass transition temperature
E	Instantaneous modulus
E ₀	Initial modulus
E _m	Young's modulus of the matrix
E_f	Young's modulus of the fiber
Es	Young's modulus of the coating
<i>E</i> ₁	Young's modulus along the fiber
$E_{ heta}$	Young's modulus in a θ° ply
E ₂	Young's modulus across the fiber
G_f	Fiber's shear modulus
G_m	Matrix's shear modulus
<i>G</i> ₁₂	In plane shear modulus
ν_m	Poisson's ratio of the matrix
ν_f	Poisson's ratio of the fiber
ν_s	Poisson's ratio of the coating
ν_{12}	In plane poisson's ratio
CTE	Coefficient of thermal expansion
α_m	CTE of the matrix

α_f	CTE of the fiber
α_s	CTE of the coating
$\alpha_{ heta}$	CTE in a θ° ply
α ₁	CTE along the fiber
α2	CTE across the fiber
а	Fiber radius
b	Coating radius
φ	Volume fraction of the fiber
ΔT	Temperature difference
$\varepsilon_1^{(f)}$	Axial strain in the fiber
$\varepsilon_1^{(m)}$	Axial strain in the matrix
ε_1	Strain along axis 1
<i>E</i> ₂	Strain along axis 2
$\sigma_1^{(f)}$	Axial stress in the fiber
$\sigma_1^{(m)}$	Matrix stress along the fiber
α_x	CTE along axis x
$\tau(x)$	Shear stress as function of x (position)
p(x)	Peeling stress as function of x (position)

PART I INTRODUCTION

PART I

I.1 Motivations

The space industry has contributed tremendously to the design, development and optimization of new materials. Among others, carbon fiber reinforced composites have been given special attention in the past decades thanks to their remarkable optical, thermal, electrical and mechanical properties [1-19]. For this reason, they are used in high performance applications including but not restricted to: satellites, space vehicles, cryogenic tanks, aircrafts and helicopters [1, 6, 7, 9, 11, 12, 14, 15, 17, 20-26].

Most of those applications relate to harsh and extreme environments where operating conditions are very demanding. In the particular case of space applications, objects orbiting around the earth are subjected to changes in temperature ranging from -160° C to $+130^{\circ}$ C. These object are therefore subjected to temperature difference of almost 300 °C which is the case for satellites.



Figure 1: Satellite tracking map showing the trajectory of satellites orbiting around the earth and subjected to temperature differences as they cross the earth's shadow or sunlight [27]

Figure 1 shows satellites' trajectory as they orbit around the earth. As they go in and out of the earth's shadow, their temperature increases and decreases as shown further on Figure 2.



Figure 2: Satellite on orbit showing the region associated with the earth's shadow [28]

The temperature reached by the satellite depends on the angle at which it is reached by the sunlight. As it goes through the earth's shadow the satellite cools and reaches a temperature of -160°C whereas as it goes out of the earth's shadow it reaches a temperature of 130°C once it is exposed to the earth's sun light. This phenomenon refers to what is known as thermal cycling. Thermal cycling has been found to induce damage in various composite material systems. However the damage mechanisms are yet to be properly understood, in order to establish proper design practices and guidelines for safety factors. Microcracking is one of those damage mechanisms that are induced by thermal cycling and that may alter the behaviour of the material. Figure 3 shows a microcrack developed in a cross-ply laminate.



Figure 3: Microcrack caused by thermal cycling in a cross-ply laminate [1]

Microcracking depends on various parameters among which; the composite constituents, the number of thermal cycles and the environment in which it is cycled. Additional factors in the low-earth orbit atmosphere affect the damaging process, and may act in synergy with thermal effects. These factors include [6, 23]:

- High vacuum
- Outgassing
- Ultraviolet radiation (UV)
- Atomic oxygen (AO)
- Charged particles
- Electromagnetic radiation
- Micrometeoroids
- Man-made debris

Therefore in order to understand the effect of thermal cycling on the behaviour of a material system, it should be isolated from the other variables mentioned above. Epoxy-based composite materials have dominated the aerospace and space market in this category of material for quite a long time. However, the hydrophilic nature of epoxy has prevented it from being used in moisture-sensitive applications because moisture absorption is responsible for dimensional changes which can be detrimental in some cases [29, 30]. Cyanate ester-based composites have emerged as an alternative to epoxies due to their higher inherent toughness, lower moisture absorption, lower dielectric loss and excellent processing characteristics [16, 30-33]. Another parameter to take into consideration during the material selection is the geometry of the laminate composites. It has been demonstrated that woven composites were a better choice for applications where dimensional stability is a requirement because it provides more balanced properties in the fabric planes compared to unidirectional composites [3] and it provides greater stability when subjected to a thermal cycling environment as compared to cross-ply laminates [34].

Epoxy-based composites have dominated the market of high performance applications for decades. This is due to their very good mechanical properties but also because over time, the knowledge and data available in the literature has been developed extensively and almost exclusively for those materials. In the past two decades, other emerging categories of polymer-based composites have been given attention. Cyanate ester-based composites are certainly one of those categories.

A few studies have been dedicated to the latter which have proved themselves successful in terms of excellent mechanical properties and processability. It was found that in terms of processability, they were comparable to epoxies and that they demonstrated lower moisture absorption than epoxies which is the main driving force for the recent development in that area. Because the space environment is one where standards and tolerances are very strict in terms of properties and performance and because moisture absorption has for consequence dimensional changes, cyanate esters appeared as interesting candidates to take over epoxies in this particular field.

However, because those materials are relatively new, there is a lack of knowledge with respect to their thermal cycling behaviour and the related damage mechanisms. Notably, their microcracking behaviour under thermal cycling is not well understood and this requires further research that would benefit the composite materials scientific community.

I.1.1 Objectives and thesis organization

This thesis focuses on studying the microcracking behaviour of a carbon reinforced cyanate ester composite. The objective is to understand: (i) the conditions under which microcracking initiates and; (ii) the consequences on the mechanical behaviour of this material.

In order to meet this objective, the work involved in this thesis was divided in different categories:

- Develop a theoretical model to determine thermal stresses induced by thermal cycling and determine if a coating applied at the interface between the fiber and the matrix could reduce those stresses
- Perform a constitutive response set of experiments to understand the effect of thermal cycling on the mechanical behavior of this material
- Perform a set of experiment to determine the effect of thermal cycling on the microcracking behaviour of this material
- Perform a set of experiment to determine the effect of thermal shocking on the microcracking behaviour of this material

The present thesis is divided in the following eight different chapters:

<u>Part I</u>: presents a literature review on cyanate esters, carbon reinforced cyanate esters and woven fabric processing, and reviews theoretical models used to determine the mechanical properties of satin weave composites, thermal cycling of composite materials and their microcracking behaviour, as well as the assessment of damage through Young's modulus monitoring.

Part II: presents the selected material and geometry.

Part III: presents the sample preparation procedure.

<u>Part IV</u>: demonstrates a micromechanical analysis to explain the mechanical behaviour of the material under 3 point bending.

<u>Part V</u>: provides a thermomechanical analysis and demonstrate the effect of thermal cycling on the variation of the coefficient of thermal expansion of the composite.

<u>Part VI</u>: provides a dynamic mechanical analysis and demonstrates the effect of cold thermal cycling on the mechanical behaviour of the composite.

<u>Part VII</u>: provides an analysis on the effect of thermal shocking on the microcracking behaviour of the composite using microscopy and demonstrates the effect of the latter on its mechanical behaviour.

<u>Part VIII</u>: presents a theoretical model developed to determine thermal stresses associated with thermal cycling.

<u>Part IX</u>: presents the conclusions drawn from this work, its contribution as well as the proposed future work.

I.2 Literature review

This section intends to provide an overview of the literature available on the following topics:

- The chemistry and synthesis of cyanate ester polymers
- The manufacturing of cyanate ester composites and their properties
- Thermal loading of polymer-based composites and its effect on material properties
- Assessment of damage accumulation based on mechanical properties

Although this study focuses on a carbon fiber reinforced cyanate ester composite, the third and fourth topic discussed in this literature review addresses mainly carbon fiber reinforced epoxy composites, the reason being the lack of available literature on thermal loading of carbon fiber reinforced cyanate ester composites. The objective here is not to make a direct comparison between epoxy-based and cyanate-based composite materials but rather to provide an idea on how high performance polymeric-based composites behave under thermal loading since both materials fall into that category.

I.2.1 Cyanate ester resins

High temperature organic polymers originated in the late 1950s to fulfill the needs and demands of the aerospace and electronics industries. Since then, epoxies have drawn a significant amount of the overall resources invested in research and development on advanced thermosetting polymers, the main reasons being their ease of handling and processability [32]. Over the two or three last decades, cyanate esters (CEs) have captured the attention of the aerospace and space industries among others. Because epoxies demonstrated difficulties in areas where higher temperature resistance and lower moisture absorption are required, cyanate ester (CE) resins have emerged as potential candidates [29, 32]. CEs are now recognized as a unique class of high-performance thermosetting polymers that can substitute both epoxies and bismaleimides thanks mainly to their superior dielectric properties and lower moisture absorption [29, 31-33, 35].

I.2.1.1 Synthesis, structure and processing of cyanate esters

Five routes for the synthesis of cyanate ester monomers have been depicted in the literature. These consist of the [32]:

- i. Reaction of a phenol with a cyanogen halide;
- ii. Thermolysis of thiatriazoles;

- iii. Heavy metal oxide dehydration of *O*-alkyl thiocarbamates;
- iv. Acylation and decomposition of O-alkyl-N-hydroxythiocarbamates;
- v. Alcohol exchange reaction with thiocyanates

Although only two of those routes are practical, only (i) is widely used and have proved itself to be successful [31, 32, 36]. The following scheme illustrates the basics of the synthesis of a CE achieved from the reaction of phenol with cyanogen chloride:



Figure 4: Reaction of phenol with cyanogen chloride

A few issues need to be addressed in order to successfully achieve the synthesis of the cyanate ester monomer. This reaction has to be carried out in solution under the presence of an acid scavenger such as triethylamine and a solvent such as acetone. Once the CE monomer synthesized, it has to be purified through either distillation using a non-solvent such as water or isopropanol, or through recrystallization. This purification step is very important in the processing of CEs because it avoids the formation of excess phenoxide: the latter would compete with phenol to react with cyanogen chloride and thus, would result in loss of wanted product, phenyl cyanate, at the expense of an imidocarbonate:



Figure 5: Reaction of excess phenoxide with cyanogen chloride leading to the formation of an imidocarbonate

Other important issues involved with this reaction are the low reaction temperature and selection of a cyanogen chloride rather than a cyanogen bromide. These two parameters are essential to suppress the von Braun reaction from occurring since it would lead to the formation of an undesirable by-product from the reaction of triethylamine, a tertiary amine, with cyanogen bromide, as shown in Figure 6 [32, 36].

 $(C_2H_5)_3N$ + BrCN \longrightarrow $(C_2H_5)_2N$ CN + BrHC₂H₅



A few comments related to monomer synthesis and properties are worth to mention here [30, 32]:

- Purity is an essential feature as impurities resulting from residual solvent can generate voids;
- Better processability is achieved with low melting temperature and viscosity monomers: monomers with lower degree of symmetry;
- Aryl cyanates are of interest as opposed to alkyl cyanates since these are instable monomers;
- Cyanate ester monomers exhibit relatively low toxicity and mutagenicity

Although various monomers have been synthesized, only a few are of commercial interest. Table 1 provides a sample of commonly used commercial monomers along with their backbone structure which is a key element in the determination of their properties. This table is linked to Figure 7 which illustrates the 3D structure of those monomers. The usual determining properties in the selection of a monomer are the glass transition temperature (T_g), the melting point (T_m), the percent moisture absorption and the dielectric constants.

Chemical name	Commercia	2D structure
	l name	
2,2' Bis(4- cyanatophenyl)isopropylide ne	AroCy® B- 10	
2,2' Bis(4-cyanatophenyl)- 1,1,1,3,3,3- hexafluoroisopropylidene	AroCy® F- 10	
<i>1,1' Bis(4-</i> cyanatophenyl)ethane	AroCy® L- 10	
Bis(4-cyanato-3,5-	AroCy® M-	H ₃ C CH ₃
dimethylphenyl)methane	10	OCN CH ₂ CH ₂ OCN



Table 1: Commercial monomers and their 2D structure (Table based on information from [32])



Figure 7: 3D structure of selected monomers: a) *AroCy*® *B-10* **b)** *AroCy*® *F-10* **c)** *AroCy*® *L-10* **d)** *AroCy*® *M-10* **e)** *AroCy*® *T-10* **f)** *RTX 366* (Molecules drawn from information based on **Table 1**)

I.2.1.2 Polymerization and development of cyanate ester networks

Cyanate ester networks are built through the polycyclotrimerization of monomers. This reaction is of the step-growth addition polymerization type, more specifically polyaddition. It involves the coupling of at least two monomers containing the – *OCN* functional group and do not lead to the formation of volatiles or by-products. Upon curing, cyanate functional groups cyclotrimerize to oxygen-linked triazine rings leading to the formation of a highly stable crosslinked 3D polytriazine network as shown on Figure 8 [30, 32, 35-38]. However, this cannot be achieved without the help of a catalyst: either a metal cation such as Cu^{2+} or an active hydrogen initiator such as ArOH. The reaction can behave as an autocatalytic one, that is one which doesn't require the addition of a

catalyst during the process, however, this cannot be achieved without the presence of a small amount of initial impurities forming an intermediate iminocarbonate compound that catalyses the reaction [30, 32, 36, 37]. Furthermore, this was found to be unpractical as 90% conversion was found to be achieved only after 300 hours at 200°C [30]. Curing of commercial cyanate resins have been reported to occur at temperatures ranging between 120 and 175°C. However, post-curing might be required to achieve full conversion which necessitates temperatures reaching 225 to 250°C [30].



Figure 8: Cyclometrization: addition polymerization of cyanate ester monomers

I.2.1.3 Properties and applications of cyanate ester resins

As mentioned earlier, cyanate ester resins became very attractive for a range of applications where high fracture toughness, low moisture absorption, good dielectric properties and epoxy-like processing characteristics were required [16, 29]. Because these resins remain expensive at this time, their usage is currently direct towards applications where long-term durability under severe environmental conditions is required [16].

Properties of cyanate esters are directly dependent on the structure of their backbone. The following section will address briefly the advantageous properties of those resins and relate each of them to the element in their structure which is responsible for or contributes to those good properties.

-O – Linkages

- ✓ Provide low viscosity and good flowability of monomer and polymers of CEs [30];
- ✓ Help dissipating localized residual stresses [30, 31];
- ✓ Contribute to the intrinsic toughness of the cured resin [30]

Carbon-Nitrogen aromatic ring



✓ This unique aromatic ring is highly stable and stiff causing good stiffness [33]

Lack of strong dipoles and absence of strong hydrogen bonding

- ✓ Provide low viscosity and good flowability of monomer and polymers of CEs [30];
- ✓ Results in low dielectric constants and dissipation factors [30-32];
- ✓ Results in low moisture absorption [30-32];
- ✓ Weak dipoles lead to little tendency for electrons to be transmitted through the structure resulting in low dielectric losses [31-33]

Triazine rings

- ✓ The strength of chemical bonds in the triazine ring and its nature contribute to the high thermal stability of CEs [31, 32, 38];
- ✓ High glass transition temperatures obtained as a result of the high aromatic content and density of triazine rings in CE networks [30-32];
- ✓ The symmetry of the triazine rings contributes to the resistance of CEs to moisture absorption [31]

Crosslink densities

- ✓ The low density of the CE networks contributes to the good toughness of those resins [31, 32];
- ✓ May increase formation of char resulting in increased resistance to fire [32]

Cyclotrimerization

This addition polymerization route consists of the condensation of molecules and do not result in the formation of by-products which results in little tendency from CEs to out-gas in high vacuum [31, 33].

Char formation

✓ Char formation at the surface of the CE polymers act as a barrier to gaseous products and shield the polymer from surface flux which reduces flammability [31-33, 38].

As a result of enhanced properties, CEs form a unique class of high temperature and performance materials. As such, they are commonly used by two main industries: aerospace/space and electronics. The following section gives an idea of some applications where CEs have been successfully used.

Space/Aerospace applications

- ✓ Radomes [30-33, 36, 38]
- ✓ Reflectors [36];
- ✓ Space optical instrument pipes [36];
- ✓ Satellite applications [36];
- ✓ Weather radars [32];
- ✓ High-gain antennas [30-32];
- ✓ Skins covering phase-array antennae [33];
- ✓ Solar array substrates [36];
- ✓ Primary and secondary aircraft/spacecraft structures [30, 32, 33, 36]

Electronic applications

- ✓ Printed circuit boards for high-speed computers [30, 32];
- ✓ Microelectronics packaging [32];
- ✓ Conductive adhesives [32];
- ✓ Encapsulants for semiconductor devices [32]

Other applications

- ✓ Curing agent for epoxies [30];
- ✓ Structural film adhesives for microwave applications [36]

I.2.1.4 Additives for cyanate ester resin systems and resin toughening

Cyanate ester laminates can be modified by the use of additives or modifiers in order to fulfill requirements which are dependent on applications. Those compounds are numerous and include but are not restricted to [32, 36]:

- Epoxy prepolymers
- ✤ Thermoplastics
- ✤ Rubbers
- Fibers

Main applications for those additives are reduction of curing times and temperatures, adhesion improvement, but also resin toughening to improve fracture resistance as successfully achieved with rubber and thermoplastics [10, 30, 31, 33].

Further toughening of CEs is required for some applications. This can be achieved by the introduction of rubber or by a thermoplastic dispersed phase resulting in a cyanate ester blend [32, 35, 36]. Rubber toughening has been successfully achieved using the following rubbers [35]:

- ✤ Amine-terminated butadiene-acrylonitrile copolymers
- Amine-terminated polybutylene ethers
- Hydroxyl-terminated polydimethylsiloxane-polyester block copolymer

Thermoplastics have also successfully been used for toughening. Those include amorphous thermoplastics such as [32, 36]:

- Polyetherimides
- Polysulphones
- Polyethersulphones
- Polyarylates
- Polyimides

Great care should be taken during selection of an additive as toughening should not occur at the expense of other necessary properties achieved by resin curing such as thermal stability and high glass transition temperature [32, 36]. In order to obtain a homogeneous blend, the additive should be dissolved using a solvent such as dichloromethane which will be removed under vacuum before curing [32].

I.2.1.5 Processing of cyanate ester composites

Cyanate esters can be processed through any common routes used for composite manufacturing. These include prepregging, resin transfer molding (RTM), filament winding (FW) and sheet molding. This processing ability has been a major factor in selecting CEs for high performance applications. In the following section, prepregging of cyanate ester resins will be discussed in more depth as it is the most widely used fabrication technique and the one of interest for the scope of this study [32, 36].

I.2.1.5.1 Holt-melt prepregging of cyanate ester resins

Hot-melt prepregging of thermosetting resin is one of the most commonly used prepregging fabrication routes. As depicted on Figure 9, a thin film of molten resin is continuously applied on a release paper using a doctor blade. Both the resin film and the fiber tows enter the impregnation zone consisting of a high pressure and temperature environment. As the resin is impregnated by the fibers, the formed prepreg goes through a chill plate where it is quenched in order to maintain its shape. Finally, the upper part of the release paper is removed from the surface of the prepreg and the prepreg itself is wound around a roller with the lower part of the release paper [32, 36, 39].



Figure 9: Hot-melt prepregging process. (Based on[32])

Parameters of primary and secondary importance describe the prepregging process. Primary parameters consists of: temperature, pressure, production rate, whereas secondary parameters consists of: geometry of fiber tows, resin film thickness, impregnation roller type, fiber tension and release action of coating paper [39]. Not to discuss all parameters, the performance of the prepregging process have been quantified using a dimensionless number, *the Prepreg Flow Number (PFN)*, which is assumed to be greater than one if impregnation is complete and equal to zero if no impregnation occurs. This dimensionless number is defined as follows:

$$PFN = \frac{KP_e}{\mu VY_f} \tag{1}$$

where K is defined as the bed permeability, P_e the effective pressure, μ the resin impregnation viscosity, V the production speed and Y_f the fiber bed thickness [32, 39].

I.2.2 Carbon fiber reinforced cyanate ester composites

Carbon fibers cyanate ester based composites have gained increased interest in the aerospace and space industries thanks to the unique combination of properties they provide [10, 32].

I.2.2.1 Carbon fibers

Carbon fibers are recognized as number one choice for high temperature and performance applications since they demonstrate outstanding thermal and mechanical properties, mainly high modulus and low coefficient of thermal expansion (CTE). This section will provide a brief overview on carbon fibers properties and reinforcement forms.

Carbon fibers are manufactured through three possible routes: polyacrylonitrile (PAN), pitch or rayon where the former two are of greater interest. PAN-based carbon fibers are mainly used for standard modulus products and provide good properties at low cost. On the other side, pitch fibers are high modulus fibers with good thermal stability that are mainly used for higher performance applications. Those fibers are available in various grades from different manufacturers [33].

I.2.2.2 Woven fabric composites

Woven fabric composites gained increased interest in various structural applications due to the ease of fabric manufacturing combined with the great properties of composite materials. Fabric

composites demonstrate good resistance to buckling along with higher impact resistance where the latter is attributed to the bidirectional nature of the reinforcement. Furthermore they have demonstrated enhanced balanced properties in fabric planes in comparison with unidirectional composites as well as resistance to damage such as delamination [3, 16]. The ease of manufacturing fabrics provides them with the ability of producing near-net-shape products [40]. Furthermore, since the number of various patterns achievable is theoretically unlimited, fabric composites provide a great potential for the manufacturing of tailored designs for an increased number of applications. Major advantages of such composites over unidirectional laminates have been reported in the literature and are responsible for the selection of fabric composites in structural applications such as the horizontal stabilizer in the Boeing 737 airplane as well as in other components in the F22 aircraft [5]:

- Easiness of handling and lower manufacturing costs attributed to available state-of-the-art weaving equipment thanks to the textile industry;
- Possibility of solving the delamination problem by the use of 3D preform manufacturing processes;
- ✤ Higher through-thickness strength;
- ✤ Improved impact resistance
- Possibility of producing 3D components without the use of joints

I.2.2.3 Open molding

Major problems have been associated with wet lay-up and spray-up methods. The main ones can be summarized as follows [33]:

- ✤ Fiber alignment in precise directions;
- ✤ Amount of fibers to achieve highest possible properties;
- Control of fiber/resin ratio;
- ✤ Obtaining full fiber wet-out;
- Reducing void content;

Open molding systems for manufacturing of advanced composites have overcome those issues by achieving the following [33]:

- ✓ Control of fiber orientation and location;
- ✓ Control ply thickness;

- ✓ Control fiber-resin ratio;
- ✓ Minimizing void content;
- ✓ Reduce internal stresses

Vacuum bagging is widely used to produce high performance components. This manufacturing process has the advantage of removing volatiles that might be entrapped in the resin which could lead to the presence of void in the composite part. Moreover, the nature of the bagging system itself allows the movement of resin during curing which leads to the flow of molten resin between layers of prepreg and thus, decreases the probabilities of delamination to occur [33]. Figure 10 illustrates the vacuum bagging system. Before building up the part, the mold is coated with a mold release agent in order to remove the part effectively at the end of the process. The prepreg layers are placed on top of each other by carefully respecting the required orientations and number of layers resulting in a laminate stack. The porous release film, usually Teflon[®], is placed over the laminate stack.



Figure 10: Vacuum bagging [33]

The porosity allows for the excess resin to flow through which is absorbed by a bleeder material applied on top the laminate stack. Afterwards, the vacuum bag is applied on the assembly which is generally made of nylon but can be made out of any polymeric film that is strong enough to hold the vacuum. Finally, an air-tight seal is created around the vacuum bag and the latter is activated.

I.2.3 Thermal cycling of polymer-based composites

"Thermal cycling involves repeatedly cycling a specimen or material between two temperatures with a sufficient dwell time at either extreme to allow thermal equilibrium to be attained." [41]

Thermal cycling of composite materials has been studied mainly to understand their behaviour in harsh environments. Applications subjected to such environments include but are not restricted to: satellites [7, 20, 42]), space vehicles [6, 7], launch vehicle cryogenic tanks [1, 7], aircrafts [22], helicopters and boats [22].

Studies in the literature have focused essentially on epoxies and have been conducted under different temperature ranges and environments. This section intends to provide an overview of the conditions under which thermal cycling tests have been carried out and their consequences on the behaviour of the tested materials.

Ahlborn [21] subjected two carbon reinforced thermoplastic composites, AS4/PEEK and HTA 7/PC, to a thermal schedule consisting of a cold cycle carried out from 20°C to -196 °C at a cooling rate of 1.8°C/s. The following conclusions were drawn: the crack density in cross-ply laminates is not influenced by thermal cycling under that operating thermal schedule as shown on Figure 11.



Figure 11: Crack density vs. number of cold cycles for a cross-ply laminate where black triangles refer to HTA7/PC with [0/90]₂s lay-up, white triangles to HTA7/PC with [0/90]₂Os lay-up and white circles to AS4/PEEK with [0/90]₄5 lay-up [21]

Furthermore, it was reported that the crack density is dependent on the orientation of the fibers as seen in Figure 11 where transversal cracks were found to have a greater density than longitudinal cracks. Finally, the interfacial strength between fibers and matrix was discussed in the study. Composites with high interfacial strength as AS4/PEEK were exempt from cracks until 120 cycles.

Bechel et al. [42] studied the effect of thermal cycling on three carbon reinforced thermoset composites (IM7/977-2, IM7/977-3 and IM7/5250-4) to the study their microcracking behaviour in order to prevent gas leakage paths in reusable launch components such as fuel tanks and cryogenic fuel delivery lines. The different materials were cycled from 196°C to 120°C for the epoxy-based composites and -196°C to 177°C for the bismaleimide composite. A comparison between cold cycling ($T_{room} \rightarrow -196^{\circ}C \rightarrow T_{room}$) and combined cycling ($T_{room} \rightarrow 177^{\circ}C \rightarrow T_{room} \rightarrow -196^{\circ}C \rightarrow T_{room}$) was made with respect to microcracking densities.

Figure 12 a) shows the microcracking density of a bismaleimide-based composite as a function of the number of thermal cycles for the case where a combined cycle is applied whereas Figure 12 b) shows the microcracking density as a function of the number of thermal cycles for the case where only cold cycling is applied. The various curves demonstrate the microcracking behaviour curve for different lay-up configurations and measured in different plies. It can be observed that the effect of combined cycling is much more detrimental in terms of damage to the composite than cold cycling alone. From Figure 13, it can be seen that the same trend is observed for the epoxy-based composite.



Figure 12: Microcracking density vs. number of thermal cycles for a bismaleimide-based composite (IM7/5250-4): a) Combined cycling; $T_{room} \rightarrow 177^{\circ}C \rightarrow T_{room} \rightarrow -196^{\circ}C \rightarrow T_{room}$ b) Cold cycling; $T_{room} \rightarrow -196^{\circ}C \rightarrow T_{room}$



Figure 13: Microcracking density vs. number of thermal cycles for a epoxy-based composite (IM7/977-2): a) Combined cycling; $T_{room} \rightarrow 177^{\circ}C \rightarrow T_{room} \rightarrow -196^{\circ}C \rightarrow T_{room}$ b) Cold cycling; $T_{room} \rightarrow -196^{\circ}C \rightarrow T_{room}$ [42]

Brown [43] studied the effect of thermal cycling on a carbon reinforced thermoset-based composite with RS-3 as the thermosetting matrix. He performed thermal cycling going up to 3000 cycles using different thermal schedules. It is reported that the onset of microcracking and the microcracking density is greatly affected by the layer thickness of the plies in the laminates. Thin layer samples were found to have a delayed onset of microcracking in comparison with thick layer samples. However after thousands of thermal cycles, thin layer samples demonstrated higher microcracking densities in comparison to thick layer samples. It was demonstrated that samples

with higher fiber modulus had a lower initial microcracking rate and that the matrix type had an effect on the onset of microcracking. Finally, it was demonstrated that varying the upper and lower temperatures of thermal cycles had an effect on the microcracking density. Basically, it was shown that a greater difference between the upper and lower temperatures resulted in a saturation in microcracks after fewer cycles in comparison with a lower difference between upper and lower temperatures and a greater microcracking density.

Bechel et al. [1] thermally cycled a bismaleimide-based composite (IM7/997-2) from -243°C to 127°C and back to room temperature with cross-ply and quasi-isotropic laminate configurations. It was reported that no microcracks in quasi-isotropic laminates were observed after ten cycles and that their mechanical properties and permeability was unaffected. It was also reported that microcracks due to thermal cycling typically formed parallel to the fibers and that microcracks appeared in surface plies in comparison with inner plies. In fact, microcracks appeared in surface plies up to 145 cycles before they started appearing in inner plies.

Biernacki et al. [2] studied the effect of thermal cycling on a polyester-matrix composite through fiber protrusion from -25°C to 50°C. They observed fiber protrusion on samples as well as crack formation which was explained to arise from the combination of radial and axial stresses generated at the free surface during thermal cycling. They also reported crack initiation and growth at the interface in the cold cycling part ($T_{room} \rightarrow -25^{\circ}C$).

Han et al. [6] reported on the effect of low earth orbit (LEO) on polymer matrix composites. It was reported, among others, that thermal cycling caused fatigue cracking while atomic oxygen (AO) caused surface erosion. To simulate the effect of earth's shadow and sun-facing effects on space-crafts in orbit, thermal cycling was conducted on a graphite reinforced epoxy composite from - 150°C to 150°C. Degradation of tensile stiffness was observed and the synergic effect of LEO space environmental effects reported.

Issoupov [7] thermal cycled a carbon/epoxy composite from -160°C to 160°C. He reported that no change in mechanical properties were observed upon cycling up to 120 cycles. However, combined

with mechanical loading, an important decrease in bending modulus was observed. Microcracking would not lead directly to failure but rather facilitate other failure modes such as delamination.

Kim et al. [23] studied the effect of thermal cycling on a carbon reinforced epoxy-based composite (AS4/3501-6) and carbon reinforced epoxy-based cyanate ester composite (XN-70/RS3) of unidirectional and cross-ply laminate configurations. Thermal cycling was performed from -101°C to 121°C. Regarding the unidirectional cyanate ester-based composite, no cracks were observed and the longitudinal and transversal CTEs remained almost identical.



Figure 14: Variation in longitudinal and transversal CTEs for a carbon reinforced cyanate ester composite (XN-70/RS3) cycled between -101°C and 121°C [23]

Lafarie-Frenot et al. [24] studied carbon reinforced epoxy cross-ply laminates subjecting them to thermal cycling between -50°C to 150°C and -50°C to 180°C. They demonstrated that thermal cycling induced different types of damage mechanisms dependent on the orientation of the plies, their thickness and more importantly, the environment where thermal cycling is carried out. Samples cycled in oxygen and air were subjected to accelerated damage explained by the higher oxygen content leading to oxidation processes reported to cause a coupling effect with microcracking as shown on Figure 15.


Figure 15: Effect of thermal cycling environment on transverse microcracking density [24]

Three types of damage mechanisms were observed during experiments:

- Permanent deformation of the matrix caused by shrinkage
- Debonding between fibers and matrix
- ✤ Matrix cracking

Lee et al. [29] thermal cycled a graphite reinforced cyanate ester composite (IM7/ICI 954-2) from room temperature to 150°C and 204°C using dry heat. No presence of microcracks was observed in this case, however, for the case where samples have been cycled in a moisture-containing environment, extensive cracking occurred in the form of delamination between plies.

Lafarie-Frenot et al. [44] studied the effect of thermal cycling from -50°C to 180°C on cross-ply and quasi-isotropic laminates on a carbon reinforced epoxy composite. The same damage mechanisms as reported in [24] were reported in the scope of this study. Significant matrix shrinkage was observed in samples thermal cycled in oxidative environments, that is, air and oxygen. Crack opening was measured and found to be larger for samples cycled in oxygen. Furthermore, samples cycled in air or oxygen demonstrated a higher number of transversal microcracks, a wider crack opening and higher microcracking kinetics with respect to an increasing number of thermal cycles. The onset of microcracking was found to arise earlier in air than in nitrogen and the higher the oxygen concentration, the faster damage processes occur. Finally, as reported in [24], the microcracking density is much more significant in oxidative environments than in nitrogen.



Figure 16: Variation of the microcracking density with respect to the number of thermal cycles as function of the cycling environment (oxygen, air or nitrogen) where dash lines refer to the microcracking density measured inner plies whereas the plain lines refer to the microcracking density measured in outer plies [24]

Tompkins [34] studied the effect thermal cycling on different composites and lay-up configurations. It was reported that fabric laminates significantly eliminated crack formation and demonstrated higher stability in a thermal cycling environment in comparison with cross-ply laminates. As a result, no significant change in CTE was observed in fabric laminates with respect to an increasing number of cycles as shown on Figure 17:



Figure 17: Effect of thermal cycling on the variation of the CTE of a plain weave and cross-ply epoxy-based laminate composite [34]

Rouquie et al. [14] thermal cycled a carbon/epoxy composite from -50°C to 180°C. Only a few cracks were observed in cross-ply laminates cycled in nitrogen and no crack at all were found in symmetric angle-ply laminates. In cross-ply laminates the onset of microcracking occurs between 100 and 200 thermal cycles whereas in symmetric angle ply laminates the onset is shifted between 200 and 300 cycles.

Shimokawa et al. [26] thermal cycled a bismaleimide-based thermoset composite (G40-800/5260) and two polyimide-based thermoplastic (IM7/PIXA and IM7/K3B) composites from -54°C to 177°C. In the case of IM7/PIXA, the onset of microcracking occurred at 10 cycles whereas it was not until 1500 for IM7/K3B. Regarding G40-800/5260, the onset of microcracking occurred at 1000 cycles.

Tai et al. [45] thermal cycled a quasi-isotropic carbon/PEEK composite from -60°C to 60°C. It was reported that thermal cycling affected the fatigue life of the laminate but that its stiffness at failure remained within 5% of its initial stiffness.

From the various studies in the literature, a few conclusions can be drawn. The onset of microcracking is delayed for the cases where the interfacial strength is high, the laminates are thinner and the fiber modulus high. Furthermore, the greater the difference between the upper and lower cycling temperature, the earlier the microcracking saturation occurs. The environment in which thermal cycling is conducted accelerates the microcracking process: environments containing moisture and oxidative environments (air or oxygen) accelerate the onset at which microcracking occurs. Combined cycles (cold + hot cycling) are much more detrimental to the material than either hot or cold cycling only. Under thermal cycling, the coefficient of thermal expansion remains constant for fabric materials but varies for unidirectional composites. Finally, it is not clear whether mechanical properties are affected by thermal cycling: some studies claim they do some claim they don't. The answer to this question seems to be dependent on multiple factors acting in synergy such as the laminate configuration (unidirectional, cross-ply, fabric) and the thermal schedule to which the material is subjected. More research at the microscopic level is

required to understand how the material behaves and explain the different mechanisms involved during microcracking.

I.2.4 Assessment of damage accumulation based on Young's modulus

A method to easily and accurately assess the amount of damage within a component without the need for complex preparation and imaging is needed. Various models (theoretical or FEM-based models) based on the monitoring of Young's modulus to assess damage accumulation have been discussed in the literature. This section intends to provide a short review of theoretical models which have been previously proposed.

Ahlborn [21] assessed damage accumulation in a unidirectional thermoplastic composite by monitoring the variation of modulus with respect to the initial modulus of the laminate as a function of the percent number of cycles achieved as shown on Figure 18. The drop in modulus is determined by the following relation: E_s/E_1 where E_s refers to the secant modulus and E_1 the initial one. The degradation of the Young's modulus is also determined as a function of crack density where the following relation applies:

$$\Delta E = E_1 - E_s = c \times \overline{\rho} \tag{2}$$

Where *c* refers to constant dependent on elastic parameters and ply thickness and $\bar{\rho}$ the crack density.



Figure 18: Damage accumulation assessed through monitoring of Young's modulus compared to its initial value as a function of the percent number of thermal cycles achieved. [21]

Boccaccini et al. [46] assessed the development of microcracking damage through the measurement of the Young's modulus and the internal friction (or damping). An expression reported from another study was provided for the effective modulus of a microcracked composite and consists of the following relation:

$$\frac{E}{E_0} = \left[1 + \frac{2L_d}{L} \left(\frac{E_0}{E_f V_f} - 1\right) + \frac{2}{\beta L} \tanh\beta \left(\frac{L}{2} - L_d\right) \frac{E_m \left(1 - V_f\right)}{E_f V_f}\right]^{-1}$$
(3)

Where

$$E_0 = E_m \left(1 - V_f \right) + E_f V_f \tag{4}$$

And where

$$\beta = \frac{1}{r_0} \left(\frac{2E_0}{E_m \left(1 + \nu_m\right) \left(ln \frac{1}{V_f} + V_f - 1 \right)} \right)^{\frac{1}{2}}$$
(5)

From Figure 19 it can be seen that a slight decrease in the modulus is observed with increasing number of thermal cycles. A significant increase in the internal friction as a function of increasing number of thermal cycles is also observed.



Figure 19: Relative Young's modulus as a function of thermal cycles and internal friction as a function of thermal cycles [46]

Bonara et al. [47] developed a model to assess damage accumulation which may be caused by the following damage mechanisms:

- Transverse matrix cracking
- Fibres failures
- Fibre-matrix debonding
- ✤ Longitudinal matrix cracking
- ✤ Delamination

Their effect on the mechanical properties of a composite is determined as follows:

$$\frac{\Delta E}{E_0} = \frac{E_0 - E_D}{E_0} \tag{6}$$

Where E_0 refers to the strain energy of a composite free of defects and E_D the strain energy of a composite with defects. The previous relation is elaborated as follows:

$$\frac{\Delta E}{E_0} = \frac{2}{E_1^0(w_s l_s)} \frac{A \log_{10} N}{1 + \rho(\sigma_{max}) \log_{10} N} \hat{l}_c \hat{w}_c f_c \times \left[k_3 + k_7 \left(v_{12}^0 \right)^2 - k_{13} v_{12}^0 \right]$$
(7)

Which relates the drop in modulus to the microcracking density as a function of the number of cycles. For the case of a glass/epoxy composite subjected to mechanical loading, the following results were obtained using the model:



Figure 20: Young's modulus reduction as a function of increasing number of cycles [47]

Colombo et al. [48] evaluated the variation in elastic modulus using the following relation:

$$D = 1 - \frac{E}{E_0} \tag{8}$$

Where *E* refers to the elastic modulus as a function of the cycling number and E_0 the undamaged value. As seen on Figure 21, the Young modulus decreases as the number of cycles increase. Depending on the material tested and mechanical load, this decrease in modulus can be more significant.



Figure 21: Variation in elastic modulus as a function of percent increase in number of mechanical cycles. [48]

Duan et al. [49] developed a model to assess the damage accumulation in a single ply and a laminate. This model is based on microcracking and the fracture mechanics theory. A damage variable is defined as a function of the matrix cracking density as D = f(2L) where L refers to the average spacing between the cracks.

Fujii et al. [50] assessed the damage accumulation by monitoring the modulus decay as a function of percent number of cycles achieved as shown on Figure 22.



Figure 22: Modulus decay as a function of percent number of mechanical loading cycles achieved. [50]

Kharoubi et al. [51] studied the effect of cyclic loading on the Young's modulus reduction of a glass fiber reinforced epoxy composite. The modulus degradation is assessed and the damage is determine from the same relation as equation (8). Results demonstrate a drop in modulus with increase in number of cycle as shown on Figure 23.



Figure 23: Drop in modulus as a function of increasing number of loading cycles as reported in [51] Kim et al. [9] also assessed the damage using equation (8) as reported in [48, 51]. Damage was quantified using a normalized fatigue modulus where an undamaged coupon refers to a damage value of $D = D_0 = 0$ at $= E_0$. Stiffness reductions are attributed to microcracking in the matrix which developed mainly perpendicularly to the longitudinal loading direction prior to any debonding between fibers and matrix.

Liu et al. [52] reported a critical global damage variable D_f defined as:

$$D_f = 1 - \frac{E_f}{E_0} = 1 - q \tag{9}$$

Where q refers to the failure factor. This model is the same one as discussed by Columbo et al., the only difference here is the focus on the critical case represented by the failure factor q. For cases other than the critical damage value, equation (8) is used where the stiffness loss is assessed by replacing with E/E_0 .

Schubbe et al. [15] studied damage accumulation in a 5-harness woven graphite reinforced epoxy laminate to assess the effect of microcracking on the variation of mechanical properties, mainly the Young's modulus. As the case for [9, 48, 51], the damage is assessed using equation (8).

Plumtree et al. [53] assessed the cyclic damage evolution in the same fashion as done by [9, 15, 48, 51], based on the number and length of the cracks developed in the material. The damage is first represented as the effective damaged area over the total area and from that, a damage model based on the modulus is derived using the concept of effective stress and principal of strain equivalence (equation (8))

$$D = \frac{A_D}{A_0} \tag{10}$$

In this study the damage is reported as a two stage process where initially there is a quick increase in the damage parameter due to a large increase in cracking density which is followed by a slower increase in the damage parameter to a slower increase in cracking density. This two stage damage process is modeled as follows:

$$D_{T} = D_{1}^{\prime} \left\{ 1 - exp \left[\frac{N}{\alpha} \right]^{\beta} \right\} + D_{2}^{\prime} \left\{ 1 - exp \left[\frac{N}{N_{f}} \right]^{\gamma} \right\}$$
(11)

Where α and β are constants dependent on the material and loading conditions, N the number of cycles, D_T the total damage accumulated and D_1' and D_2' the amount of damage at the end of stages 1 and 2 respectively.

Boccaccini et al. [54] assessed the damage resulting from thermal cycling of Nicalon-fiber reinforced glass-matrix composites from room temperature to 700°C up to 1000°C. Thermal cycling was found to result in the generation of microstructural damage detected from the

simultaneous drop in Young's modulus and increase in internal friction of the composite as a function of increasing number of thermal cycles as shown in Figure 24.



Figure 24: Relative Young's modulus drop as a function of increasing number of cycles and increase in relative internal friction as a function of decreasing Young's modulus and increasing number of thermal cycles. [54]

PART II MATERIAL AND SAMPLE PREPARATION

PART II

II.1 Material selection

Several cyanate ester prepregs are found on the market mainly for aerospace and space applications. A few companies manufacture those prepregs but TENCATE (California, United States) is the leader in this area. The following table provides a few of commercial toughened prepregs for aerospace and space applications.

Name	Tg (°C)	Tg (°C) with post cure	Moisture absorption @ saturation (%)	CTE (ppm/°C)
BTCy-1A	185	207	1	77
EX-1515	121	163	0.04	61
RS-3	191	254	0.69	43

Table 2: TENCATE commercial prepregs for aerospace and space applications ([55])

As shown on Table 2, EX-1515 has the lowest level of moisture absorption at saturation. Furthermore its total mass loss represents 0.179% which is also of interest. Because thermal and dimensional stability are very important for space applications this prepreg is a choice of interest for space applications such as satellite antennas. This prepreg was also chosen since the manufacturer claimed EX-1515 demonstrated its ability in resisting microcracking under severe thermal cyclic and high levels of radiation exposure conditions. As per TENCATE, typical applications for this prepreg are:

- High dimensional stability space structures;
- ✤ Optical benches;
- ✤ Reflectors;
- ✤ Radomes and antennae;
- ✤ Low observables;
- Radar transparent structures

For the scope of this study, pitch fibers have been selected in YSH grade commonly used for aerospace and sports goods. The selected fibers are found under the commercial name YSH-50A-10S and manufactured by Nippon Graphite Fiber Corporation. These 7µm diameter fiber bundles consist of 1000 filaments and their properties are reported on the following table:

Commercial Name	YSH-50A-10S
Fiber density (g/cm3)	2.08-2.12
Mass per unit length (g/km)	73.0-77.0
Sizing content (Mass %)	1.1-2.2
Tensile modulus (GPa)	496-544

Tensile strength (GPa)	3.65
Ultimate elongation (%)	0.6

Table 3: Carbon fiber properties

Those carbon fibers are manufactured as fabric reinforcements and consist of 5-harness satin weaves. Weaves can be manufactured under the following forms: plain, basket, twill, satin/harness, crowfoot or leno. 5-harness satin weaves have one warp strand weaving on top of four strands then under one fill strand as shown on Figure 25.

Figure 25: 5 harness satin weave [56]

These fabrics are extensively used for aircraft and space applications such as radomes where complex shapes are required [33].

Once the material components selected, a lay-up configuration for laminates was chosen. The laminate composite studied here is a symmetric laminate which means that from the plane of symmetry, the upper laminate should be a reflection of the lower part of it as shown on the following figure.



Figure 26: Symmetric laminate

The chosen laminate for the scope of this work consists of a four plies symmetric laminate oriented at 0° and 45° , $[0/45]_{s}$, with each ply having a thickness of 0.46 ± 0.05 mm. Some useful properties for the selected composite, YSH-50A-10S/EX-1515 are presented in the following table:

vm	0.3	
Vf	0.2	
Em	3.25	GPa
Ef	520	GPa
α _f	-1.40E-06	°C ⁻¹
αm	6.12E-05	°C-1
Φ	0.6	
1-Ф	0.4	
h	0.5	mm

Table 4: Selected material properties for the YSH-50A-10S/EX-1515 material system

II.2 Sample preparation

Samples of carbon fiber reinforced cyanate ester were cut, grinded and polished for testing and imaging purposes. The following sub-sections describe the procedure followed for each step of the material preparation.

II.2.1 Cutting

A precision diamond saw manufactured by Struers was used to cut samples of different dimensions (Figure 27). The samples width was cut larger to compensate for material loss involved during grinding and polishing steps.



Figure 27: Struers precision diamond saw

II.2.2 Grinding and polishing

Samples cut were grinded and polishing using a Buehler Metaserv 2000 grinder/polisher (Figure 28). Grinding involved four steps:

- ✤ 320 grit
- ✤ 600 grit
- ✤ 800 grit
- ✤ 1200 grit

Polishing was performed using suspension particles and involved two steps:

- ✤ 6 µm
- ✤ 1 μm



Figure 28: Buehler Metaserv 2000 grinder polisher

PART IIIDAMAGE IN A THREE POINT BENDINGTEST

In-situ three-point bending tests were performed to assess damage in the material by recording load vs. displacement curves. The objective was to determine if such a test, which is relatively simple, could allow us to characterize damage in specimens. If so, it would allow bypassing the imaging process which is tedious and time consuming. For this reason, monotonic and cyclic tests were carried out. Monotonic tests allowed to track strain and stress levels inducing damage events in a sample, from the onset of microcracking up to failure of the material. Cyclic tests allowed to determine the decrease in stiffness with increasing number of cycles and consequently, to quantify damage in the material using a damage variable (D) related to the variation in stiffness. Each cycle was associated to a damage variable leading to the determination of a critical damage variable D_c, representing the level of damage required to cause failure of the material.

III.1 Experimental procedure

Tests were performed using a miniature loading stage in 3-point compression bending. The 3-point bending fixture was used to measure the modulus of the composite laminate under mechanical loading. It was placed under the microscope allowing for in-situ testing and consequently damage tracking. The fixture used has a 15.09 mm span and the samples tested have dimensions of 0.5 mm thickness, ≈ 3.5 mm width and ≈ 20 mm length. Upon mechanical loading load-displacement curves were recorded and used to assess damage using the simplest damage model discussed in section I.2.4, equation (8).



Figure 29: In-situ imaging with miniature loading stage

Multiple regions on a specific sample were targeted and imaged after each cycle. As shown in Figure 30, each region targeted is marked and tracked after each cycle for imaging allowing to capture cyclic damage. Load was applied using a 100 lb load cell and the stage controlled from the computer using a software. Load-displacement curves were converted to stress-strain curves using the following relationships:

$$\sigma = \frac{3PL}{2bh^2} \tag{12}$$

$$\varepsilon = \frac{6\delta h}{L^2} \tag{13}$$

where P refers to load (N), L to span length (mm), b to width (mm), h to thickness (mm) and δ to displacement (mm).



Figure 30: 3-point bending fixture under in-situ imaging

III.2 Results and discussion

A monotonic test was performed by subjecting a sample to a compressive load varying with increasing strain until failure of the material occurred. In-situ imaging was carried out and damage tracked by taking successive images of a specific region during testing. Figure 31 shows the stress-strain curve of a typical monotonic test carried out. The first image (starting from the left side) shows the undamaged state of the material before the test is initiated at (0,0) (strain, stress). The second image represents the status of the material at 0.011 strain and 873 MPa stress corresponding to the onset of cracking. We can see from the image that a crack is formed at the outer ply of the laminate in the compression side where the load is applied. This crack further propagates as the strain is increased leading us to the third image where crack growth is observed at 0.013 strain and 938 MPa stress. Further increasing the strain results in crack propagation from the outer ply to inner plies at 0.017 strain and 908 MPa stress and subsequently to failure of the material.



Figure 31: 3-point compression bending monotonic test combined with in-situ imaging

Figure 32 presents the overall picture of the fractured material. The region circled in red refers to the region imaged during the test and corresponds to the crack initiation site on the composite laminate. This test allowed us to understand the cracking behaviour of a carbon fiber reinforced cyanate ester material under mechanical loading. It shows that damage initiates from microbuckling at the outer ply of the laminate and evolves in the form of delamination. As the outer ply initially cracks, the applied load is transferred to the inner plies which can sustain the associated level of stress until the crack propagates between the inner plies leading to the material's failure.



Figure 32: Overall picture of the fractured material following a monotonic 3-point compression bending test

Upon completion of monotonic tests, cycling tests were performed on a series of samples. Tests were carried out by increasing the strain amplitude with increasing number of cycles until failure (Figure 33).



Figure 33: Increasing displacement amplitude with time

Figure 34 shows a typical stress-strain curve obtained from the conversion of load-displacement data where stiffness decreases with increasing strain. A maximum stress of about 1.2 GPa is obtained at a strain of almost 0.02. Softening is observed from damage accumulation in the material.



Figure 34: Stress-strain curve obtained from a cyclic 3-point compression bending test

From the unloading segment of each cycle's stress-strain curve, the instantaneous modulus can be obtained from the slope. Those values are used to assess damage in the material using the simple model discussed earlier where D represents the damage variable. The models predicts no damage for a damage variable D = 0 whereas it predicts complete failure at D = 1. Those values are theoretical; in reality failure occurs at a critical damage variable $D_c < 1$.

Figure 35 shows a typical stress-strain curve for a composite and its constituents; fiber and matrix. It demonstrates how the slope of the fiber loading curve is quite sharper than the one for the matrix and that the stress-strain curve for a composite lies between those two curves. While cyclically loading a composite specimen to failure, cracks formation occurs leading to fibers failure and plastic deformation from the matrix. This plastic deformation in the matrix is responsible for the difference between loading and unloading curves. Following the unloading phase, there is a permanent elongation attributed to a certain amount of elastic recovery and residual strain.



Figure 35: Typical tress-strain curves for a composite, fiber and matrix [57]

Figure 36 shows combined results for a series of different tests performed on different samples. A threshold for damage was determined and occurs at an average stress and strain of respectively 577 MPa and 0.0085. Past this threshold, the modulus decreases continuously and damage accumulates with increasing applied strain until materials reaches failure at zero modulus.



Figure 36: Damage variable as a function of maximum strain in each cycle



Figure 37: Damage accumulation under cyclic loading

Figure 37 shows images of the accumulation of damage as a function of increasing maximum strain (left to right) up to failure. Similarly to monotonic tests, the first crack in cyclic tests appear on the outer ply on the compression side corresponding to microbuckling and causes delamination with increasing number of cycles as it propagates and grow.

PART IV THERMOMECHANICAL ANALYSIS

The purpose of a thermomechanical analysis was to determine if thermal cycling had an effect on thermal properties of the material. This has been achieved by monitoring dimensional change in the material with respect to temperature and allowed to determine if the coefficient of thermal expansion was temperature variant.

IV.1 Experimental procedure

Thermomechanical analyses were conducted using a TMA Q400 manufactured by TA Instruments as shown on Figure 38. This device can operate theoretically in a range of temperature varying between -150°C and 1000°C where the cold temperature that can be reached depends on the cooling medium used.



Figure 38: TA Q400 TMA [58]

A probe is applied on a material sample where the linear variable differential transducer (LVDT) generates an output signal that is directly proportional to the dimensional change encountered by the material over a range of temperature. The coefficient of thermal expansion (CTE) of the material can be obtained from a plot of dimensional change as a function of temperature where the CTE corresponds to the slope of the linear portion of the curve. Two series of varying thickness samples were tested with dimensions presented on Table 5.

	Thin sample	Thick sample
Thickness (mm)	0.5	2.0
Length (mm)	5.0 - 8.0	5.0 - 8.0
Width (mm)	5.0 - 6.0	5.0 - 6.0

Table 5: Sample dimensions for TMA testing

Those samples were subjected to a number of thermal cycles under temperatures reaching -70°C for the cold part of the cycle and 150°C for the hot part of the cycle.

IV.2 Results and discussion

The effect of thermal cycling on the CTE behaviour was studied for both thin (0.5 mm thickness) and thick laminates (2.0 mm thickness). Plots of dimensional change vs. temperature were obtained from TMA measurements (see Figure 39 for a typical plot). Those plots were used to determine the CTE value after each thermal cycle. Using the linear portion of the curve, that is between 50°C and 150°C, the CTE was calculated for each cycle (Figure 40).



Figure 39: Typical plot of dimensional change vs. temperature obtained from TMA measurements

Results show that after 16 cycles, no change in CTE was observed in a thin sample as shown on Figure 41. For a thick sample, we find a similar trend where no change in CTE is observed after four cycles. Comparing Figure 41 and Figure 42, we can see that sample thickness has a slight effect on the measure of CTE with a thick sample demonstrating a higher CTE. Those results agree with [34] where no change in CTE was found for woven composite materials as shown on Figure 17. It is important to mention that the purpose of comparing results for thin and thick samples was not to compare their thermal behaviour but rather to verify that the absence of changes in CTE with increasing number of cycles for thin samples was not attributed to geometry factors or misalignment of the sample under the probe (keeping thin samples of 0.5mm thickness aligned under the probe was quite a challenge).



Figure 40: Zoom on linear portion of the curve in Figure 39 to determine the CTE



Figure 41: CTE vs. Number of cycle for a thin sample



Figure 42: CTE vs. Number of cycle for a thick sample

PART V DYNAMIC MECHANICAL ANALYSIS UNDER THREE POINT BENDING

This section provides an overview of the results obtained through DMA testing which intends to detect the presence of cracks through the monitoring of the Young's modulus. Such test provides not only mechanical properties but also thermal properties such as the glass transition temperature and therefore, it was measured using this technique as it allowed us to obtain much information from one single test. Nevertheless, the objective of using this technique was to monitor the change in modulus with respect to temperature as the material undergoes thermal cycling.

V.1 Experimental procedure

Dynamic mechanical analyses were conducted using a DMA Q800 manufactured by TA Instruments as shown on Figure 43. This device can operate theoretically in a range of temperature varying between -150°C and 600°C where cold temperatures are obtained using liquid nitrogen evaporated to form cold nitrogen gas. This test allows to thermal cycle a sample while measuring

the storage and loss modulus as a function of temperature using a three point bending fixture. This test allows also to determine the glass transition temperature (T_g) of the material by plotting the storage modulus as a function of varying temperature where the T_g corresponds to the onset point of the curve. Dimensions of tested samples corresponding to a width, length and thickness of respectively 5 mm by 50 mm by 5 mm.



Figure 43: TA Q800 DMA [58]

Samples thermally cycled were imaged using an Olympus upright optical microscope connected to a high resolution CCD camera for microcracks observations.



Figure 44: Optical microscope connected to a high resolution CCD camera

V.1.1 Results and discussion

A series of tests were performed at varying frequencies of 0.1, 1 and 10 Hz in order to ensure that the effect of frequency was negligible on measurements. Combining values at those three different frequencies, the log of the storage modulus as a function of varying temperature was plotted in order to determine the T_g of the composite material (Figure 45). From this plot, we observe the onset of the curve corresponding to a T_g of ≈ 126 °C. This value of T_g corresponds to a carbon reinforced cyanate ester composite which has not been subjected to post-curing.



Figure 45: Log of storage modulus (log(E')) vs. temperature at frequencies of 0.1, 1 and 10 Hz.

Another series of samples were subjected to thermal cycling at temperatures varying between -120°C and 20°C in order to study the effect of cold cycling on the microcracking behavior of the material through modulus monitoring as well as imaging as shown on Figure 46.



Figure 46: Thermal cycling schedule: 8 cycles performed between 20 and -120°C

The modulus was recorded at 20°C and -120°C and compared in both cases to its initial value at each cycle in order to assess the effect of thermal cycling on the materials' modulus and to ensure the temperature at which the comparison is made do not affect conclusions. Results demonstrate no variation in modulus as a function of increasing number of thermal cycles as can be seen on Figure 47. This is attributed to the fact that there is no presence of microcracks from thermal cycling as proved by imaging.



Figure 47: Variation in modulus as a function of increasing number of thermal cycles

V.1.1.1 Imaging analysis

In order to confirm the absence of microcracks, three different approaches were used. The first attempt consisted of polishing samples and imaging them after thermal cycling but this approach was eliminated since the absence of microcracks could be attributed to the polishing particles filling the cracks that could be present. The second approach consisted of polishing the samples before thermal cycling in the DMA and imaging before and after thermal cycling to observe the potential presence of microcracks. Magnifications up to 1000X were used to ensure that microcracks were in fact absent and not so small that they could not be observed at lower magnifications. Figure 48 shows images taken at various regions on the sample at the highest magnification of 1000X on the optical microscope confirming the absence of microcracks.



10 µm

Figure 48: 1000X imaging following DMA testing demonstrating the absence of microcracks. Note: On some images the cross-sections of the fibers is an ellipse because polished surface and the axis of the fibers are not exactly perpendicular

The last approach consisted of using fluorescent dyes to help detect microcracks that could be so small that they would only be apparent by filling them with a fluorescent medium which under UV light would become visible. This last attempt has confirmed further the absence of microcracks

in this carbon reinforced cyanate ester composite subjected to 8 thermal cycles between 20°C and -120°C (Figure 49).



Figure 49: 1000X imaging using fluorescent dyes following DMA testing demonstrating the absence of microcracks

PART VITHERMAL CYCLING WITH A "FASTDIPPING" METHOD

The various detection methods we have used in the previous section failed to detect any damage due to thermal cycling with the DMA. Possible cause(s) include temperature amplitude at the sample which is actually lower than specified. In this next series of experiments we therefore subjected the samples to more extreme thermal treatments. A group was subjected to cold cycling by direct and fast dipping into liquid nitrogen (T \approx -210°C) and another was subjected to hot cycling by direct and fast dipping into boiling water (T=100°C). The objective of subjecting a series of sample to cold cycling and another to hot cycling only was to determine if both induce damage in the sample or if only one of the two does. Sample dimensions varied between 3.5- 25 mm for the width, 20-25 mm for the length and a constant thickness of 0.5mm. Damage was assessed by imaging and mechanical testing.

VI.1 Cold cycling

Cold cycling was carried out on a series of samples between 20°C and -210°C using liquid nitrogen as the cooling medium as shown on Figure 50. Samples were dipped in liquid nitrogen for a period of 10 minutes and directly transferred to room temperature water (20°C) for a period of 5 minutes.

This procedure was repeated until ten cycles were completed. Another series of samples were subjected to 5 cold cycles using the same procedure but in this case damage was assessed by performing a non-destructive 3-point compression bending test initially and after completion of the 5 cold cycles. The purpose of the bending test was to capture any possible softening of the material due to internal damage.



Figure 50: Thermal schedule for 10 cold cycles

Different regions in a single sample were imaged in order to track the damage in the entire sample and ensure the absence or presence of microcracks is not associated to a specific location only. We observed that damage accumulation was not uniform within the sample. Figure 51 shows an area of the sample taken before and after 10 thermal cycles showing no apparent damage. Figure 52 shows another region taken in the same sample where damage is observed after three cycles only. In this case cracks appeared in the form of delamination on the outer ply of the composite laminate. Another region is represented in Figure 53 showing crack initiation after two cycles only in a region initially containing flaws on the outer ply. After three cycles only delamination occurred on the outer ply of the laminate.

Before cycling

After 10 cycles





200 µm





Figure 52: Images taken before and after 3 cold cycles



Figure 53: Images taken before and after 2 and 3 cold cycles

Those images demonstrate the damage generated by extreme cold cycling for a cyanate ester composite:

- Delamination from the outer ply occurs but doesn't not propagate to the inner plies;
- No presence of transversal cracks has been observed during the various tests and analyses carried out.

A series of three point bending tests were also carried out on samples before and after five cold tests in order to evaluate the effect of microscopic damage on mechanical properties. Figure 54 shows the results for those tests where we see a detrimental decrease in mechanical properties following thermal cycling. An initial modulus of 97.2 ± 1.5 GPa was measured compared to a value of 51.3 ± 6.5 GPa for a damaged sample. This corresponds to a drop of almost 50% in bending stiffness after five cycles only. This result demonstrates that instantaneous stiffness of a composite structure or material can be used to monitor damage. The stiffness method presents several advantages over imaging: it is faster than imaging, does not require sectioning and polishing of the material, and it is non-destructive.



Figure 54: Three point bending test carried out on samples before and after five cold cycles

VI.2 Hot Cycling

Hot cycling was carried out between 20°C and 100°C using boiling water as the heating medium as shown on Figure 55. Samples were dipped in boiling water for a period of 10 minutes and directly transferred to room temperature water (20°C) for a period of 5 minutes. This procedure was repeated until ten cycles were completed.



Figure 55: Thermal schedule for 10 hot cycles

Figure 56 shows images taken before and after one and ten hot cycles. After only one cycle we observe delamination on the outer ply of the laminate. After ten cycles we observe more delamination on the other outer ply of the laminate.



Figure 56: Images taken before and after 1 and 10 hot cycles

Figure 57 shows images of another region on the same sample after five and eight cycles. After five cycles we observe a longitudinal crack in an inner ply, something we haven't observed from cold cycling. In this case delamination occurred not only in outer plies but also in an inner ply.



Figure 57: Images taken before and after 5 and 8 hot cycles. Red arrows indicate the location of cracks
Figure 58 also shows another region in the same sample after one, two and eight cycles. After one cycle we observe a longitudinal crack in the outer ply of the laminate. After two and eight cycles we observe significant damage in the outer ply of the laminate where a piece of material from the outer ply seems to be almost detached from the rest of the sample.



Figure 58: Images taken before and after 1, 2 and 8 hot cycles

Imaging allowed us to observe damage induced from hot cycling. We observed that:

- Delamination occurs both in outer and inner plies as observed from the propagation of longitudinal cracks from outer to inner plies;
- No presence of transversal cracks has been observed during the various tests and analyses carried out.

In summary, two main conclusions can be drawn from those series of tests: both cold and hot cycling induce damage in samples and transversal microcracks are absent from all samples.

PART VII THEORETICAL MODEL

PART II

This section intends to present three models developed as part of this study. The objective here is to determine:

- Maximum stresses at the interface between the a fiber and the matrix
- The effect of a coating applied on fibers and its impact on the reduction of maximum stresses
- The mechanical and thermal properties of the woven composite using a simplified model

VII.1 Model I: Fiber in infinite matrix

From the theory of elasticity, a stress analysis is performed in order to determine thermal stresses induced by thermal cycling and CTE mismatch at the interface between a fiber and an infinite matrix.

First of all, we start our analysis by assuming an axisymmetric plane stress problem in polar coordinates where:

- There is no dependence on θ (axisymmetry)
- ♦ A very thin section is assumed: stress independence with Z axis, that is:
 - $\circ \sigma_{rz} = 0 \text{ and } \sigma_{\theta z} = 0$
 - $\circ \quad \tau_{rz} = 0 \text{ and } \tau_{\theta z} = 0$



Figure 59: Stress analysis using polar coordinates

Assuming no body forces ($F_r = 0$; $F_{\theta} = 0$) and a quasi-steady state ($\sum F_r = 0$), we derive the following relation based on Figure 59:

$$-\sigma_{r}rd\theta + \left[\sigma_{r} + \frac{\partial\sigma_{r}}{\partial r}dr\right](r+dr)d\theta - \left[\sigma_{\theta} + \frac{\partial\sigma_{\theta}}{\partial\theta}d\theta\right]dr\sin\frac{d\theta}{2}$$
$$-\sigma_{\theta}dr\sin\frac{d\theta}{2} - \tau_{\theta r}dr\cos\frac{d\theta}{2} + \left[\tau_{\theta r} + \frac{\partial\tau_{\theta r}}{\partial\theta}d\theta\right]dr\cos\frac{d\theta}{2} + F_{r}rdrd\theta = 0$$

Assuming that the second order terms are negligible and making the following approximation: $sin\frac{d\theta}{2} \cong \frac{d\theta}{2}$; $cos\frac{d\theta}{2} = 1$, we obtain the following relationship (complete derivation can be found in Appendix I):

$$\therefore \frac{1}{r} \frac{\partial \sigma_{\theta}}{\partial \theta} + \frac{2 \partial \tau_{r\theta}}{r} + \frac{\partial \tau_{r\theta}}{\partial r} = 0$$
(14)

We pursue our analysis with strain-displacement relationships which we derive assuming a plane stress problem. Complete derivations can be found in Appendix II from which general equations for radial and tangential stresses are obtained:

$$\sigma_r = 2C + \frac{A}{r^2} \tag{15}$$

$$\therefore \sigma_{\theta} = 2C - \frac{A}{r^2} \tag{16}$$

For the case of a single fiber in an infinite matrix as shown on Figure 60, we solve equations (15) and (16)



Figure 60: Scheme for model of a fiber in an infinite matrix

For the matrix:

$$(\sigma_r)_m = 2C_m + \frac{A_m}{r^2} \tag{17}$$

For the fiber:

$$(\sigma_r)_f = 2C_f + \frac{A_f}{r^2} \tag{18}$$

Assuming perfect bonding between the fiber and the matrix at r = R, we consider stresses and displacements equal at the interface:

$$(\sigma_r)_m = (\sigma_r)_f$$
$$[(u_r)_{total}]_m = [(u_r)_{total}]_f$$

Since we assumed an axisymmetric displacement ($u_{\theta} = 0$) we have:

$$u_r = \frac{1}{E} \left[\frac{-A(1+\nu)}{r} + 2C(1-\nu)r \right]$$
(19)

At r = 0 (inside the fiber):

$$(\sigma_r)_f = 2C_f + \frac{A_f}{r^2} = 2C_f + \frac{A_f}{0} = \infty$$

Since the stress cannot be infinite in the fiber at r = 0, A_f should be equal to zero for this relation to be valid.

At
$$r = \infty$$
:

$$(\sigma_r)_m = 2C_m + \frac{A_m}{r^2} = 2C_m + \frac{A_f}{\infty} = 2C_m + 0 = C_m$$

Since at an infinite radius the matrix is subjected to no stresses, $(\sigma_r)_m = 0$:

$$(\sigma_r)_m = 0 = 2C_m$$
$$C_m = 0$$

Based on those constraints, the maximum stress in the matrix occurs at r = R and can be calculated from the following equation (see Appendix III for complete derivation):

$$\left(\sigma_{r}\right)_{m} = \frac{\Delta T(\alpha_{f} - \alpha_{m})}{\left[\frac{(1 + \nu_{m})}{E_{m}} - \frac{(1 - \nu_{f})}{E_{f}}\right]}$$
(20)

From selected properties in Table 4 and considering a change of temperature of 290 °C, the maximum hoop stress in the matrix $[(\sigma_{\theta})_m = -(\sigma_r)_m]$ occurring at the interface with the fibers is calculated and a value of 45.56 MPa is obtained.

VII.2 Model II: Coated fiber in infinite matrix

This model intends to determine conditions at which thermal stresses between the fiber and the matrix can be reduced using a coating serving as an intermediate media for load transfer between fiber and matrix as shown on Figure 61.



Figure 61: Scheme for model of a fiber coated within an infinite matrix

This model is also based on the theory of elasticity and is derived in the same fashion where:

$$(\sigma_r)_f = 2C_f + \frac{A_f}{r^2}$$
$$(\sigma_r)_m = 2C_m + \frac{A_m}{r^2}$$

.

And

$$(\sigma_r)_s = 2C_s + \frac{A_s}{r^2} \tag{21}$$

At r = a, the interface between the fiber and the coating, we have:

$$(\sigma_r)_f = (\sigma_r)_s$$
$$2C_f + \frac{A_f}{a^2} = 2C_s + \frac{A_s}{a^2}$$
$$C_f = C_s + \frac{A_s}{2a^2}$$

At r = b, the interface between the coating and the matrix, we have:

$$(\sigma_r)_s = (\sigma_r)_m$$
$$2C_s + \frac{A_s}{b^2} = \frac{A_m}{b^2}$$
$$C_s = \frac{1}{2b^2} [A_m - A_s]$$

Assuming perfect bonding between the interfaces we have:

$$\left[\left(u_{r}\right)_{total}\right]_{f}=\left[\left(u_{r}\right)_{total}\right]_{s}$$

And

$$\left[\left(u_{r}\right)_{total}\right]_{s}=\left[\left(u_{r}\right)_{total}\right]_{m}$$

Solving for the unknown constants in equations (17), (18) and (21) we can determine the hoop stress in the matrix using the following derived formula:

$$(\sigma_{\theta})_{m} = -\frac{b^{2}\Delta T}{r^{2}} \left\{ \frac{(\alpha_{s} - \alpha_{m})}{[\gamma + \beta]} + \frac{(\alpha_{f} - \alpha_{s})\omega - (\alpha_{s} - \alpha_{m})\frac{[\Omega - \beta]\omega}{[\gamma + \beta]}}{\omega[\Omega - \beta] - [\Omega - \beta][\gamma + \beta] + \frac{b^{2}}{a^{2}}[\Omega + \lambda][\gamma + \beta]} \right\}$$
(22)

Where

$$\gamma = \frac{\left(1 + \nu_m\right)}{E_m} \tag{23}$$

$$\beta = \frac{\left(1 - \nu_s\right)}{E_s} \tag{24}$$

$$\Omega = \frac{\left(1 - \nu_f\right)}{E_f} \tag{25}$$

$$\lambda = \frac{\left(1 + v_s\right)}{E_s} \tag{26}$$

And

$$\omega = \frac{2}{E_s} \tag{27}$$

In order to determine the best coating parameters to reduce maximal stresses in the matrix, the effect of different parameters have been studied based on the fiber and matrix properties along with fictive properties assumed for the coating.

VII.2.1.1 Effect of coating thickness

In order to study the effect of coating thickness, a plot of the maximum hoop stress in the matrix as a function of varying thicknesses is presented based on coating properties listed in the following table (where the subscript *s* refers to the coating):

E _s (GPa)	250
Vs	0.25
$\alpha_s(^{\circ}C^{-1})$	2.99E-05

 Table 6: Coating properties assumed for the study of the effect of coating thickness on matrix stresses reduction

Those coating properties were selected assuming a material with middle properties between fibers and matrix.





It can be seen from Figure 62 that the application of a coating, independently of its thickness reduces the stresses in the matrix. However, this effect plateaus as the coating's thickness reaches five times the radius of the fiber (b/a = 5). Furthermore, it is demonstrated that with a coating modulus of 250 GPa the variation of the coating thickness itself is not sufficient to reduce thermal stresses to a lower level than with the case where no coating is applied that is, 45.56 MPa.

VII.2.1.2 Effect of coating modulus

The effect of coating modulus on the reduction of maximal matrix stresses was studied for a coating with a thickness equal five times the radius of the fiber, since it was shown in the previous section that at such a value the effect of coating thickness reaches a plateau in terms of stress reduction.



Figure 63: Maximum hoop stress in the matrix as a function of varying coating modulus

As shown on Figure 63, in order to decrease stresses in the matrix, the selected coating should have a lower modulus than the one of the matrix. More specifically, its value should be:

$$E_{s} < 0.656E_{m}$$

VII.2.1.3 Effect of coating coefficient of thermal expansion

For a coating of thickness equal to five times the radius of the fiber, the CTE was varied between $\alpha_s = 0.01\alpha_m$ and $\alpha_s = 1.5\alpha_m$. Figure 64 shows the linear behavior of the variation of the maximal matrix stress with respect to a change in CTE. It can be seen that stresses in the matrix reaches zero for a value of CTE very close to $\alpha_s = \alpha_m$. Overall, these models show that using a fiber coating with tailored thermo-mechanical properties may provide an effective approach to minimizing thermal stresses in the matrix, thereby minimizing damage from thermal cycling.



Figure 64: Maximum hoop stress in the matrix as a function of varying coating CTE

VII.2.1.4 Summary of properties required for the selection of a coating

We discussed the effects of varying the coating thickness, modulus and CTE in order to decrease as much as possible the stresses in the matrix. Our analysis based on the developed model shows that those stresses can be significantly reduced for:

- ✤ A coating thickness close to five times the radius of the fiber
- ♦ A coating modulus smaller than the one of the matrix $(E_s < 0.656E_m)$
- ✤ A coating CTE almost equal to the one of the matrix

VII.3 Model III: Thermo-elastic response of laminates

This simple laminate model serves as the basis to predict the anisotropic elastic coefficients and coefficients of thermal expansion for the composite, with focus on in-plane properties. The model also captures the effect of thermal/stiffness mismatch between layers which can give rise to interlaminar fracture during thermal cycles.

VII.3.1 Elastic properties

A classical laminate analysis is used to derive the properties of the composite. For simplicity we ignore the waviness and interweave of the fibers (mosaic model [59]). Figure 65 shows the coordinate system associated to a single laminate.



Figure 65: Coordinate system associated with a single laminate [60]

The modulus along the fibers is given by (Voigt composite):

$$E_1 = \varphi E_f + (1 - \varphi) E_m \tag{28}$$

Where E_f and E_m are the moduli of fiber and matrix, and ϕ is the volume fraction of fibers. The modulus across the fibers is given by (Reuss composite):

$$\frac{1}{E_2} = \frac{\varphi}{E_f} + \frac{1-\varphi}{E_m}$$
(29)

Or

$$E_2 = \frac{E_m E_f}{\varphi E_m + (1 - \varphi) E_f} \tag{30}$$

The in-plane Poisson's ratio is given by:

$$v_{12} = \varphi v_f + (1 - \varphi) v_m \tag{31}$$

The in-plane shear modulus is given by:

$$\frac{1}{G_{12}} = \frac{\varphi}{G_f} + \frac{1-\varphi}{G_m}$$
(32)

Where

$$G_{f} = \frac{E_{f}}{2(1 + v_{f})}$$
(33)

And

$$G_m = \frac{E_m}{2(1+\nu_m)} \tag{34}$$

Or

$$G_{12} = \frac{G_f G_m}{\varphi G_m + (1 - \varphi) G_f}$$
(35)

Or

$$G_{12} = \frac{E_f E_m}{\varphi E_m (1 + v_f) + (1 - \varphi) E_f (1 + v_m)}$$
(36)

By way of transformation, the modulus along an axis x in the 1-2 plane and forming an angle with axis 1 is given by:

$$\frac{1}{E_x} = \frac{\cos^4 \theta}{E_1} + \frac{\sin^4 \theta}{E_2} + \left(\frac{1}{G_{12}} - \frac{2\nu_{12}}{E_1}\right)\cos^2 \theta \sin^2 \theta$$
(37)

For $\theta = 0^{\circ}$ one recovers $E_{0^{\circ}} = E_1$ and for $\theta = 90^{\circ}$ one recovers $E_{90^{\circ}} = E_2$. Of interest here is also the angle $\theta = 45^{\circ}$:

$$\frac{1}{E_{45'}} = \frac{1}{4} \left[\frac{1}{E_1} + \frac{1}{E_2} + \left(\frac{1}{G_{12}} - \frac{2\nu_{12}}{E_1} \right) \right]$$
(38)

Or

$$E_{45^{\circ}} = \frac{4E_1E_2G_{12}}{E_2G_{12} + E_1G_{12} + E_2\left(E_1 - 2\nu_{12}G_{12}\right)}$$
(39)

From these results the properties of individual plies can be recovered. A "0" ply is made of a $\theta = 0^{\circ}$ laminate and a $\theta = 90^{\circ}$ laminate of equal thickness. Therefore

$$E_0 = \frac{1}{2} \left[E_{0^\circ} + E_{90^\circ} \right] \tag{40}$$

A "45" ply is made of two $\theta = 45^{\circ}$ laminates of equal thickness. Therefore,

$$E_{45} = \frac{1}{2} \left[E_{45^{\circ}} + E_{45^{\circ}} \right] = E_{45^{\circ}}$$
(41)

Using selected properties found in Table 4, the following elastic properties are determined:

E 1	313.30	GPa
E ₂	8.05	GPa
V 12	0.24	
G12	6.20	GPa
$E_{0^{\circ}}(=E_{1})$	313.30	GPa
E90° (=E2)	8.05	GPa
E45°	13.92	GPa
Eo	160.07	GPa
E45	13.92	GPa

 Table 7: Elastic properties calculated for an YSH-50A-10S/EX-1515 composite based on selected properties from Table 4 and equations (28) to (41)

The modulus in the fiber direction is 313.30 GPa, the one in the matrix direction 8.05 GPa and the shear modulus 6.20 GPa. Moreover, for a "0" ply a modulus of 160.07 GPa is found whereas for a "45" ply a modulus of 13.92 GPa is obtained. In terms of elastic properties, a "0" ply behaves better than a "45" ply.

VII.3.2 Thermal properties

Using the same configuration as above, one can estimate the anisotropic coefficients of thermal expansion in each ply. A uniform change of temperature ΔT will give rise to axial strains in the fibers equal to:

$$\varepsilon_1^{(f)} = \frac{\sigma_1^{(f)}}{E_f} + \alpha_f \Delta T \tag{42}$$

Where $\sigma_1^{(f)}$ is the axial stress in the fibers and α_f is the coefficient of thermal expansion (CTE) of the fibers, which is assumed to be isotropic. Similarly the strain in the matrix, along the axis of the fibers, will be:

$$\varepsilon_1^{(m)} = \frac{\sigma_1^{(m)}}{E_m} + \alpha_m \Delta T \tag{43}$$

Where $\sigma_1^{(m)}$ is stress in the matrix along the direction of the fibers and α_m is the CTE of the matrix, also assumed to be isotropic. Thermoelastic mismatch of properties between fibers and matrix may give rise to internal stresses $\sigma_1^{(f)}$ and $\sigma_1^{(m)}$, respectively. Fibers and matrix deform by the same amount along axis 1, so that:

$$\varepsilon_1 = \varepsilon_1^{(f)} = \varepsilon_1^{(m)} \tag{44}$$

To obtain the effective CTE of the laminate along axis 1, we are interested for the case where the laminate is free to expand (i.e. no external loads are applied). In this case the internal stresses are self-balancing and:

$$\varphi \sigma_1^{(f)} + (1 - \varphi) \sigma_1^{(m)} = 0 \tag{45}$$

Equations (42) through (45) can be combined to yield:

$$\varepsilon_{1} = \left[\frac{\varphi E_{f} \alpha_{f} + (1 - \varphi) E_{m} \alpha_{m}}{\varphi E_{f} + (1 - \varphi) E_{m}}\right] \Delta T$$
(46)

The CTE of the laminate along axis 2 is therefore given by:

$$\alpha_1 = \frac{\varphi E_f \alpha_f + (1 - \varphi) E_m \alpha_m}{\varphi E_f + (1 - \varphi) E_m}$$
(47)

Along axis 2 both fibers and matrix are free of stress and therefore,

$$\varepsilon_2^{(f)} = \alpha_f \Delta T \tag{48}$$

And

$$\varepsilon_2^{(m)} = \alpha_m \Delta T \tag{49}$$

The total strain in the laminate is:

$$\varepsilon_2 = \varphi \varepsilon_2^{(f)} + (1 - \varphi) \varepsilon_2^{(m)} \tag{50}$$

Replacing:

$$\varepsilon_2 = \left[\varphi \alpha_f + (1 - \varphi) \alpha_m\right] \Delta T \tag{51}$$

And

$$\alpha_2 = \varphi \alpha_f + (1 - \varphi) \alpha_m \tag{52}$$

By way of transformation, the CTE along an axis x in the 1-2 plane and forming an angle with axis I is given by:

$$\alpha_x = \alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta \tag{53}$$

For $\theta = 0^{\circ}$ one recovers $\alpha_{0^{\circ}} = \alpha_1$ and for $\theta = 90^{\circ}$ one recovers $\alpha_{90^{\circ}} = \alpha_2$. Of interest here is also the angle $\theta = 45^{\circ}$:

$$\alpha_{45^\circ} = \frac{1}{2} \left(\alpha_1 + \alpha_2 \right) \tag{54}$$

From these results the properties of individual plies can be recovered. A "0" ply is made of a $\theta = 0^{\circ}$ laminate and a $\theta = 90^{\circ}$ laminate of equal thickness. A thermoelastic analysis leads to:

$$\alpha_0 = \frac{E_{0^\circ} \alpha_{0^\circ} + E_{90^\circ} \alpha_{90^\circ}}{E_{0^\circ} + E_{90^\circ}}$$
(55)

A "45" ply is made of two $\theta = 45^{\circ}$ laminates of equal thickness and thus,

$$\alpha_{45} = \frac{E_{45^{\circ}}\alpha_{45^{\circ}} + E_{45^{\circ}}\alpha_{45^{\circ}}}{E_{45^{\circ}} + E_{45^{\circ}}} = \alpha_{45^{\circ}}$$
(56)

Using selected properties from Table 4, the following thermal properties are obtained:

E 1	-3.31E-04	
£ 2	6.86E-03	
α1	-1.14E-06	
a 2	2.36E-05	°C-1
$\alpha_{0^{\circ}}(=\alpha_{1})$	-1.14E-06	°C-1
$\alpha_{90^{\circ}}(=\alpha_2)$	2.36E-05	°C-1
A45 °	1.12E-05	°C-1
αο	-5.20E-07	°C-1
0.45	1.12E-05	°C-1

 Table 8: Thermal properties calculated for an YSH-50A-10S/EX-1515 composite based on selected properties from Table 4 and equations (42) to (56)

Thermal strains in the fiber (ϵ_1) and matrix (ϵ_2) directions are provided. Coefficients of thermal expansion in the fiber and matrix directions were calculated and the following respective values were obtained: -1.14E-06 °C⁻¹ and 2.36E-05 °C⁻¹. Furthermore, coefficients of thermal expansion were calculated for a "0" and "45" ply where a value of -5.20E-07 °C⁻¹ was found for a "0" ply whereas a value of 1.12E-05 °C⁻¹ was found for a "45" ply. This shows that in terms of thermal properties a "0" ply behaves also better than a "45" ply.

VII.3.3 Edge effects

For a continuous bimaterial subjected to thermal stresses the stresses at the interfaces are zero, and only flexural stresses develop. However, for a bimaterial of finite width, edge effects stresses will occur, consisting of a shear stress [60]:

$$\tau(x) = \frac{\left[(1+\nu_1)\alpha_1 - (1+\nu_2)\alpha_2\right]\Delta T}{\sqrt{\lambda s}} \left(e^{-k(L-x)} + e^{-k(L+x)}\right)$$
(57)

And a transverse (or "peeling" stress) [60]:

$$p(x) = \frac{\left(\frac{E_2h_1h_2^3}{12(1-v_2)^2} - \frac{E_1h_2h_1^3}{12(1-v_1)^2}\right) \left[(1+v_1)\alpha_1 - (1+v_2)\alpha_2\right] \Delta T}{2s\left(\frac{E_1h_1^3}{12(1-v_1)^2} + \frac{E_2h_2^3}{12(1-v_2)^2}\right)}$$
(58)

Where

$$\lambda = \frac{\left(1 - v_1^2\right)}{E_1 h_1} + \frac{\left(1 - v_2^2\right)}{E_2 h_2} + \frac{\left(h_1 + h_2\right)^2}{4\left(\frac{E_1 h_1^3}{\left(1 - v_1^2\right)} + \frac{E_2 h_2^3}{\left(1 - v_2^2\right)}\right)}$$
(59)

And

$$s = \frac{2}{3} \left(\frac{(1+\nu_1)}{E_1} h_1 + \frac{(1+\nu_2)}{E_2} h_2 \right)$$
(60)

$$k = \sqrt{\frac{\lambda}{s}} \tag{61}$$

From selected properties (Table 4), the shear and transverse stresses are obtained from relations (57) to (61) for a sample of dimensions L = 10 mm and $h = h_1 = h_2 = 0.5 \text{ mm}$. Stresses are calculated for two cases: x = L and x = 0 respectively.

τ(x=L)	-10.22	MPa
τ(x=0)	0.00	MPa
p(x=L)	0.13	MPa
p(x=0)	0.13	MPa

Table 9: Shear and transverse stresses calculated for an YSH-50A-10S/EX-1515 composite based on selectedproperties from Table 4 and equations (57) to (61)

The shear stress was found to be null at the center of the sample (L = 0) whereas it was found to be maximal at the edges with values of ± 10.22 MPa calculated as shown on Figure 66. Considering a shear modulus of 6.20 GPa, such levels of stresses result in shear strains of 1.65E-03 mm/mm at

the sample's edges. The peeling stress was found to be the same both at the center and edge of the sample with a value of 0.13 MPa. Some of these stresses are significant, and could be responsible for the formation of cracks at the interfaces between laminates.



Figure 66: Shear and peel stresses as a function of x where x varies between 0 and 10 mm

PART VIII CONCLUSIONS

VIII.1 Thesis summary

This research led to five main outcomes resulting from experiment and modelling.

The five key outcomes of this work can be summarized as:

- Damage induced by external mechanical loading can be assessed using a simple three point bending test;
- 2. Thermal cycling using TMA does not result in reduction of thermal properties of the material;

- 3. Thermal cycling using DMA does not result in reduction of mechanical properties of the material;
- 4. Extreme thermal cycling using a "fast dipping" method induces microcracking and results in reduction of mechanical properties;
- 5. Thermoelasticity-based models allows to:
 - i. Determine thermal stresses at the interface induced by thermal cycling in the case of a fiber surrounded by an infinite matrix;
 - ii. Determine conditions under which a coating on a fiber can reduce maximum thermal stresses induced by thermal cycling at the interface;

iii. Determine mechanical and thermal properties in plies oriented in different directions These outcomes are discussed in more details below.

VIII.1.1 Damage induced by external mechanical loading can be assessed using a simple three point bending test

External mechanical loading induces damage in the material and the exact amount of damage can be assessed using a simple, non-destructive three point bending test. Such test demonstrated that the damage mechanism consist of microbuckling on the outer ply of the laminate, on the compression side, followed by delamination propagating on the inner plies of the material which eventually leads to its failure.

VIII.1.2 Thermal cycling using TMA or DMA does not result in reduction of thermal and mechanical properties of the material

Thermal cycling carried out between -70°C and 150°C using TMA demonstrate no apparent variation in CTE after 16 cycles which is attributed in part to the woven configuration of the laminate as reported in the literature.

Thermal cycling performed between 20°C and -120°C using DMA demonstrate no apparent damage on the material after eight cold cycles. Damage was assessed by monitoring the modulus during the tests and by taking before and after cycling images. Modulus values remained constant throughout the entire test and imaging showed no presence of microcracks which means that no

damage was induced by such thermal cycling and therefore, no change in mechanical properties could be recorded.

VIII.1.3 Extreme thermal cycling using a "fast dipping" method induces microcracking and results in reduction of mechanical properties

Extreme thermal cycling using a "fast dipping" method induced microcracking in the material in the form of longitudinal cracks causing delamination. Cold cycling was performed between 20°C and -210°C dipping quickly the material in liquid nitrogen and hot cycling between 20°C and 100°C dipping quickly the material in boiling water. Imaging before and after each cycle demonstrate the presence of damage in early cycles until completion of ten cycles. Mechanical testing in three point bending was carried out before and after five cycles on a cold cycled sample demonstrating almost 50% reduction in modulus after only five extreme cycles.

VIII.1.4 Thermoelasticity-based models

Based on the thermoelasticity-based theories, we developed a simple model consisting of a fiber in an infinite matrix allowing to determine the magnitude of thermal stresses at the interface induced by thermal cycling. For a temperature difference of 290°C, thermal stress of the order of 45 MPa were calculated, which is sufficient to induce damage in the composite. This model can be used in the future to optimize fibers, matrix, ply architecture and geometry of the component in order to minimize thermal stresses and damage. The models also suggest that the incorporation of a coating on the fiber with five times or greater the diameter of the fiber could significantly reduce thermal stresses. Performing an analysis on the effect of coating modulus on the reduction in thermal stresses based on a coating diameter of five times the one of the fiber, we found that a modulus of $E_s < 0.656E_m$ can further reduce stresses to a level of about 12.5 KPa. Finally, an analysis on the effect of the coating CTE on the reduction in thermal stresses allows us to conclude that a coating having a diameter of five times the one of the fiber, a modulus smaller than 0.656 times the one of the matrix and a CTE equal to the one of the matrix could almost eliminate thermally induced stresses.

PART IXRECOMMENDATIONS AND FUTURE WORK

From the conclusions drawn as part of this study, two recommendations for the design of composites for space applications can be made:

- Cyanate ester composites which have not been subjected to post-curing can act as a better candidate compared to its non-post-cured counterpart for applications where microcracking resistance has a greater priority than mechanical performance
- Simple mechanical tests can be used to assess damage from extreme thermal and mechanical loading

Based on our conclusions and recommendations, there are areas where future work remains to be done. Those main areas consist of the following:

- It is suggested that non post-cured material would behave better with respect to microcracking than post-cured material.
 - Thermal cycling on specimens post-cured at different temperatures should be carried out and the effect of curing temperature studied
- Thermal cycling should be conducted at different upper and lower temperatures in order to understand the effect of temperature difference on the microcracking behaviour and the onset of microcracking
- Thermal cycling should be conducted in different environments to determine the effect oxidizing environments such as air on the onset of microcracking

Finally, in order to reduce or eliminate thermally induced damage there are a few areas where work could be done:

- Determine the ideal layup configuration where stresses between plies would be minimal
- Determine if the 5-harness satin weave geometry is the best by looking at other woven patterns and compare their resistance to thermal damage
- Incorporate a coating with specifications as discussed in section VII.2 which demonstrated to reduce thermal stresses at the fiber/matrix interface level

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PART XI | APPENDICES

XI.1 Appendix I



Assuming no body forces and a quasi-steady state:

$$-\sigma_{r}rd\theta + \left[\sigma_{r} + \frac{\partial\sigma_{r}}{\partial r}dr\right](r+dr)d\theta - \left[\sigma_{\theta} + \frac{\partial\sigma_{\theta}}{\partial\theta}d\theta\right]dr\sin\frac{d\theta}{2}$$
$$-\sigma_{\theta}dr\sin\frac{d\theta}{2} - \tau_{\theta r}dr\cos\frac{d\theta}{2} + \left[\tau_{\theta r} + \frac{\partial\tau_{\theta r}}{\partial\theta}d\theta\right]dr\cos\frac{d\theta}{2} + F_{r}rdrd\theta = 0$$

Assuming second order terms are negligible and making the following approximation:

$$\sin\frac{d\theta}{2} \cong \frac{d\theta}{2} \quad \cos\frac{d\theta}{2} \cong 1$$

We obtain:

$$-\sigma_{r}rd\theta + \sigma_{r}rd\theta + \sigma_{r}drd\theta + \frac{\partial\sigma_{r}}{\partial r}rdrd\theta + \frac{\partial\sigma_{r}}{\partial r}dr^{2}d\theta$$
$$-\sigma_{\theta}dr\sin\frac{d\theta}{2} - \frac{\partial\sigma_{\theta}}{\partial\theta}d\theta dr\sin\frac{d\theta}{2} - \sigma_{\theta}dr\sin\frac{d\theta}{2} - \tau_{\theta r}dr\cos\frac{d\theta}{2}$$
$$+\tau_{\theta r}dr\cos\frac{d\theta}{2} + \frac{\partial\tau_{\theta r}}{\partial\theta}d\theta dr\cos\frac{d\theta}{2} + F_{r}rdrd\theta = 0$$

Dividing all terms by $rdrd\theta$ due to the axisymmetric assumption we obtain:

$$\frac{1}{r}\sigma_r - \frac{1}{r}\sigma_\theta + \frac{1}{r}\frac{\partial\tau_{\theta r}}{\partial\theta} + \frac{\partial\sigma_r}{\partial r} = 0$$
$$\frac{1}{r}\sigma_r - \frac{1}{r}\sigma_\theta + \frac{\partial\sigma_r}{\partial r} = 0$$
$$\therefore \frac{\partial\sigma_r}{\partial r} + \frac{\sigma_r - \sigma_\theta}{r} = 0$$

$$-\sigma_{\theta}dr\cos\frac{d\theta}{2} + \left[\sigma_{\theta} + \frac{\partial\sigma_{\theta}}{\partial\theta}d\theta\right]dr\cos\frac{d\theta}{2} - \tau_{\theta r}rd\theta + \tau_{\theta r}dr\sin\frac{d\theta}{2} + \left[\tau_{r\theta} + \frac{\partial\tau_{r\theta}}{\partial r}dr\right](r+dr)d\theta + \left[\tau_{\theta r} + \frac{\partial\tau_{\theta r}}{\partial\theta}d\theta\right]dr\sin\frac{d\theta}{2} + F_{\theta}rdrd\theta = 0$$

$$-\sigma_{\theta}dr + \sigma_{\theta}dr + \frac{\partial\sigma_{\theta}}{\partial\theta}drd\theta - \tau_{r\theta}rd\theta + \tau_{r\theta}rd\theta + \tau_{r\theta}drd\theta + \frac{\partial\tau_{r\theta}}{\partial r}rdrd\theta + \frac{\partial\tau_{r\theta}}{\partial r}rd\theta + \frac{\partial\tau_{$$

We finally obtain:

$$\therefore \frac{1}{r} \frac{\partial \sigma_{\theta}}{\partial \theta} + \frac{2 \partial \tau_{r\theta}}{r} + \frac{\partial \tau_{r\theta}}{\partial r} = 0$$









$$\therefore \varepsilon_r = \frac{1}{E} [\sigma_r - v\sigma_\theta]$$
$$\therefore \varepsilon_r = \frac{\partial u_r}{\partial r} \quad \varepsilon_\theta = \frac{u_r}{r} \quad \varepsilon_{r\theta} = 0$$
$$\therefore \varepsilon_r = \frac{E}{(1 - v^2)} [\varepsilon_r + v\varepsilon_\theta]$$
$$\therefore \varepsilon_r = \frac{1}{E} [\sigma_\theta - v\sigma_r]$$
$$\therefore \sigma_\theta = \frac{E}{(1 - v^2)} [\varepsilon_\theta + v\varepsilon_r]$$

Equilibrium equation:

$$\therefore \frac{\partial \sigma_r}{\partial r} + \frac{\sigma_r - \sigma_\theta}{r} = 0$$

For plane stress:

$$\therefore \sigma_r = \frac{E}{(1-v^2)} [\varepsilon_r + v\varepsilon_\theta]$$
$$\therefore \sigma_\theta = \frac{E}{(1-v^2)} [\varepsilon_\theta + v\varepsilon_r]$$

Substituting and rearranging terms, we obtain:

$$\frac{\partial^2 u}{\partial r} + \frac{1}{r} \frac{\partial u}{\partial r} - \frac{1}{r^2} = 0$$

$$\frac{\partial^2 u}{\partial r} + \frac{1}{r} \frac{\partial u}{\partial r} - \frac{1}{r^2} u = 0$$

Solving:

$$u = C_{1}r + C_{2}\frac{1}{r}$$

$$\varepsilon_{r} = \frac{\partial u_{r}}{\partial r} = C_{1} - \frac{C_{2}}{r^{2}}$$

$$\varepsilon_{\theta} = \frac{u_{r}}{r} = C_{1} + \frac{C_{2}}{r^{2}}$$

$$\sigma_{r} = \frac{E}{(1 - v^{2})} \left[(C_{1} - \frac{C_{2}}{r^{2}}) + v(C_{1} + \frac{C_{2}}{r^{2}}) \right]$$

$$\sigma_{r} = \frac{E}{(1 - v^{2})} \left[(1 + v) \left[C_{1} - \frac{C_{2}}{r^{2}} \right] \right]$$

$$\sigma_{r} = \frac{E(1 + v)}{(1 - v)(1 + v)} C_{1} - \frac{E(1 + v)}{(1 - v)(1 + v)} \frac{C_{2}}{r^{2}}$$

$$\sigma_{r} = \frac{E}{(1 - v)} C_{1} - \frac{E}{(1 - v)} \frac{C_{2}}{r^{2}}$$

$$A = \frac{-EC_{2}}{(1 - v)} C = \frac{EC_{1}}{2(1 - v)}$$

We obtain the general equation for radial stress:

$$\therefore \sigma_r = 2C + \frac{A}{r^2}$$

And the general equation for tangential stress:

$$\sigma_{\theta} = \frac{E}{(1-\nu^{2})} \left[(C_{1} + \frac{C_{2}}{r^{2}}) + \nu(C_{1} - \frac{C_{2}}{r^{2}}) \right]$$

$$\sigma_{\theta} = \frac{E}{(1-\nu^{2})} \left[(1+\nu)C_{1} + \frac{C_{2}}{r^{2}}(1-\nu) \right]$$

$$\sigma_{\theta} = \frac{E(1+\nu)}{(1-\nu)(1+\nu)}C_{1} + \frac{E(1-\nu)}{(1-\nu)(1+\nu)}\frac{C_{2}}{r^{2}}$$

$$\sigma_{\theta} = \frac{E}{(1-\nu)}C_{1} + \frac{E}{(1+\nu)}\frac{C_{2}}{r^{2}}$$

$$A = \frac{-EC_{2}}{(1+\nu)} \quad C = \frac{EC_{1}}{2(1-\nu)}$$

$$\therefore \sigma_{\theta} = 2C - \frac{A}{r^2}$$

XI.3 Appendix III

At r = R:

$$(\sigma_r)_m = (\sigma_r)_f$$
$$2C_m + \frac{A_m}{r^2} = 2C_f + \frac{A_f}{r^2}$$
$$\frac{A_m}{r^2} = 2C_f$$
$$C_f = \frac{A_m}{2r^2}$$

 A_m and C_f should be determined:

$$\begin{bmatrix} (u_r)_{total} \end{bmatrix}_m = \begin{bmatrix} (u_r)_{total} \end{bmatrix}_f$$

$$u_r = \Delta r = R\alpha\Delta T = \frac{1}{E} \begin{bmatrix} \frac{-A(1+\nu)}{r} + 2C(1-\nu)r \end{bmatrix}$$

$$R\alpha\Delta T - \frac{1}{E} \begin{bmatrix} \frac{-A(1+\nu)}{r} + 2C(1-\nu)r \end{bmatrix} = 0$$

$$R\alpha_f \Delta T - \frac{1}{E_f} \begin{bmatrix} \frac{-A_f(1+\nu_f)}{R} + 2C_f(1-\nu_f)R \end{bmatrix} = 0$$

$$R\alpha_m \Delta T - \frac{1}{E_m} \begin{bmatrix} \frac{-A_m(1+\nu_m)}{R} + 2C_m(1-\nu_m)R \end{bmatrix} = 0$$

$$R\Delta T(\alpha_f - \alpha_m) + \frac{2C_f(1-\nu_f)R}{E_f} = \frac{1}{E_m} \begin{bmatrix} \frac{A_m(1+\nu_m)}{R} \end{bmatrix}$$

$$C_f = \frac{A_m}{2r^2}$$

$$R\Delta T(\alpha_f - \alpha_m) + \frac{2(1 - \nu_f)R}{E_f}C_f = \frac{1}{E_m} \left[\frac{A_m(1 + \nu_m)}{R}\right]$$
$$\Delta T(\alpha_f - \alpha_m) + \frac{2(1 - \nu_f)}{E_f}\frac{A_m}{2R^2} = \frac{1}{E_m} \left[\frac{A_m(1 + \nu_m)}{R^2}\right]$$
$$A_m \left[\frac{1}{R^2} \left[\frac{(1 + \nu_m)}{E_m} - \frac{(1 - \nu_f)}{E_f}\right]\right] = \Delta T(\alpha_f - \alpha_m)$$

$$A_{m} = \frac{\Delta T(\alpha_{f} - \alpha_{m})}{\frac{1}{R^{2}} \left[\frac{(1 + \nu_{m})}{E_{m}} - \frac{(1 - \nu_{f})}{E_{f}} \right]}$$
$$A_{m} = \frac{\Delta T(\alpha_{f} - \alpha_{m})}{\frac{1}{R^{2}} \left[\frac{(1 + \nu_{m})}{E_{m}} - \frac{(1 - \nu_{f})}{E_{f}} \right]}$$
$$\left(\sigma_{r}\right)_{m} = \frac{A_{m}}{r^{2}} = \frac{\Delta T(\alpha_{f} - \alpha_{m})}{\frac{r^{2}}{R^{2}} \left[\frac{(1 + \nu_{m})}{E_{m}} - \frac{(1 - \nu_{f})}{E_{f}} \right]} = \frac{R^{2}}{r^{2}} \frac{\Delta T(\alpha_{f} - \alpha_{m})}{\left[\frac{(1 + \nu_{m})}{E_{m}} - \frac{(1 - \nu_{f})}{E_{f}} \right]}$$

Maximum stress in the matrix occurs at r = R:

$$\left(\sigma_{r}\right)_{m} = \frac{\Delta T(\alpha_{f} - \alpha_{m})}{\left[\frac{(1 + \nu_{m})}{E_{m}} - \frac{(1 - \nu_{f})}{E_{f}}\right]}$$