Structural integrity of reinforced polymer matrix composites subjected to hygrothermal conditioning

Zhong, Yucheng

2015

Zhong, Y. (2015). Structural integrity of reinforced polymer matrix composites subjected to hygrothermal conditioning. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/65209>

<https://doi.org/10.32657/10356/65209>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**STRUCTURAL INTEGRITY OF REINFORCED POLYMER
MATRIX COMPOSITES SUBJECTED TO
HYGROTHERMAL CONDITIONING**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2015

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HYGROTHERMAL CONDITIONING**

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2015

Acknowledgements

Firstly, I would especially like to express my foremost sense of gratitude to my supervisor, Assoc. Professor Sunil Chandrakant Joshi, not only because of the opportunity of studying a PhD in NTU he provided with me, but for the patient guidance, the way of supervising and the learning atmosphere he has offered to me.

Secondly, thanks are due to my seniors in our research group, Arthanareswaran Dineshkumar, Mubarak Ali Mohamed Ali and Vishwesh Dixit for their valuable help in almost every part of my PhD life in Singapore.

I am honored to be able to join the NTU community. I am delightful to be part of School of Mechanical and Aerospace Engineering. I would like to thank NTU and MAE for the learning environment provided to me.

Special thanks shall be given to staffs and lab technicians of MAE, Mr. Lim Yong Seng, Mrs. Chia Hwee Lang et al. and technicians in Materials Lab 1 and 2 for their help and support during my experiments and study. I also would like to express my thanks to Mr. Lew Sui Leung Thomas and Mrs. Yong Mei Yoke.

Finally, I would like to give my hearted thanks to my parents, my sister and my wife, Huang Zaohua, for all the things they have done for me throughout my life. Also, thanks to all my friends in NTU and Singapore for making my life happier and easier.

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Abstract

The mechanical properties of polymer matrix composites (PMCs) are prone to the attack of hygrothermal environment. Much effort has been devoted to the investigation of the behavior of laminated composites under combined hygrothermal environments. In most of the published research work on the durability of PMCs under hygrothermal environments, the various properties of composite structures were reported to degrade after hygrothermal conditioning. However, positive effects of hygrothermal ageing were also reported. Therefore, more and rigorous investigation is crucial to solve the contradictions existing in the literature. Hygrothermal environments attack composite materials through two principal mechanisms, microstructure degradation and moisture uptake. Structural defects including matrix cracking, delamination, weakening of the fiber/matrix interface may be triggered by hygrothermal conditioning. The absorbed moisture in PMCs is reported to act as plasticizers and reduce the glass transition temperature of the epoxy resin, which consequently affects the mechanical properties of the material at elevated temperatures. However, in many cases hygrothermal ageing induced structural defects and the effects of moisture may coexist and have different influences on specific properties of composite materials. This fact was frequently ignored in the literature. In recognition of this phenomenon, this Ph.D. thesis is devoted to the durability of materials made from PMCs under hygrothermal environments with full consideration of both hygrothermal ageing induced damages and the effects brought about by the moisture absorbed during hygrothermal ageing.

Experimental work began with the characterization of the response of hygrothermally aged CFRP (carbon fiber reinforced polymer) unidirectional (UD)-prepreg and woven-prepreg laminates to low-velocity impact. The hygrothermal conditionings designed included immersion in water at constant temperatures, including 60°C and 80°, and exposure to hygrothermal cycles. Each hygrothermal cycle consisted of 12 hours in water at 60°C or 80°C and 12h in a freezer at -30°C. It was found that both CFRP UD-prepreg and woven-prepreg laminates did not have any visible damages formed during conditioning. Instead, their impact resistance was improved by the absorbed moisture. The moisture residing in the CFRP laminates delayed the impact induced damages and preserved their strength up to larger projectile deflections. Consequently, CFRP laminates with higher moisture contents exhibited higher impact resistance and experienced lighter impact damage. Hygrothermal conditioning of this category was defined as short-term hygrothermal conditioning, which did not cause damages but mainly incurred moisture uptake in composite materials.

Long-term conditioning on CFRP UD-prepreg laminates was therefore conducted to identify the durability of the CFRP laminates under prolonged hygrothermal conditioning. It was found that as the sample was continuously immersed in water, individual plies of a UD-prepreg laminate were squeezed out under the combined action of ply swelling and interlaminar shear stress, causing the formation of delamination between plies of different fiber orientations. Delamination or wrinkles began to take place at the end of Stage II of the moisture absorption process. These damages in turn provided extra free spaces for moisture absorption. Consequently,

after the saturation level was reached the laminates continued to absorb moisture, resulting in the Stage III moisture uptake state. A three-stage moisture absorption behavior of CFRP UD-prepreg laminates exposed to long-term conditioning was therefore identified. Hygrothermal conditioning induced damages caused the reduction in the strength and modulus of the laminates. Consequently, the impact resistance of CFRP UD-prepreg laminates also declined.

The mechanical properties of 7781 E-glass fabric reinforced epoxy composite laminates after hygrothermal ageing were also evaluated. It was found that the tensile elongation and strength of the GFRP (glass fiber reinforced polymer) laminates decreased remarkably after hygrothermal drying. Upon the removal of the absorbed moisture, only a small percentage (less than 5%) of recovery in the tensile strength was obtained. It was proposed that the strength of the E-glass fiber was negatively affected by hygrothermal ageing, leading to the degradation in the tensile properties of the GFRP composite materials. Due to the reduction in the tensile strength, the impact resistance of the GFRP laminates decreased after hygrothermal ageing. The absorbed moisture did not alleviate the impact damage in GFRP laminates but rather reduced their contact stiffness under low-velocity impact. Core-shell polymer (CSP) particles have been proved to be effective impact resistance modifier. However, it was found that the advantage brought about by the CSP particles diminished after hygrothermal ageing since these particles absorbed moisture and experienced evident property degradation under hygrothermal environments.

Research thrust was then focused on the durability of fiber metal laminates. Water immersion conditioning was conducted on GLARE (glass laminate aluminum

reinforced epoxy) 4A laminates, which had S2 glass fiber as the reinforcement in the composite layer. The decrease in the tensile strain and strength of GLARE 4A laminates after hygrothermal conditioning was remarkable. Upon removal of the absorbed moisture, only minor recovery in the tensile strain and strength was observed. It was proposed that the ultimate tensile strength of the S2 glass fiber in the GLARE 4A laminates might decrease upon exposure to hygrothermal ageing, which consequently led to the decrease in the tensile strength of the composite layer in the GLARE 4A laminates. Due to the degradation in the tensile strength, a pronounced decrease in the fatigue life of GLARE 4A laminates happened.

List of Publications

1. Zhong Y and Joshi SC. Impact resistance of hygrothermally conditioned composite laminates with different lay-ups. *Journal of Composite Materials* 2015; 49(7): 829-841.
2. Zhong Y and Joshi SC. Impact behavior and damage characteristics of hygrothermally conditioned carbon epoxy composite laminates. *Materials and Design* 2015; 65: 254-264.
3. Zhong Y and Joshi SC. Improved Impact Response of Hygrothermally Conditioned Carbon/Epoxy Woven Composites. *Science and Engineering of Composite Materials*, 2015.
4. Zhong Y and Joshi SC. Initiation of structural defects in CFRP composites under hygrothermal environments. *Journal of Composite Materials*, 2015.

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List of Abbreviations and Symbols

Abbreviations

CFRP	- Carbon fiber reinforced polymer composite
CSP	- Core-shell polymer particles
CTE	- coefficients of thermal expansion
DCB	- Double-cantilever beam
DETA	- Diethylenetriamine
DGEBA	- Diglycidyl ether of bisphenol A
FESEM	- Field emission scanning electron microscope
FML	- Fiber-metal laminates
GFRP	- Glass fiber reinforced polymer composite
GLARE	- Glass Laminate Aluminum Reinforced Epoxy
PMC	- Polymeric matrix composite
RH	- Relative humidity
SEM	- Scanning electron microscope
UD	- unidirectional

Symbols

A	- Area of a plate
C	- Concentration of the diffusing substance
C_i	- Initial concentration of the diffusing substance
C_m	- Concentration at the surface of the material
D_i	- Projectile deflection corresponding to incipient damage point
D_{max}	- Maximum projectile deflection
D_p	- Projectile deflection corresponding to peak load point
D_z	- Diffusion coefficient or diffusivity in the through-thickness direction
DI	- Damage index

E_d	- Impact energy absorbed through plastic deformation and damage creation and propagation or actual impact energy absorbed
E_{d1}	- Actual impact energy absorbed before peak load point
E_{d2}	- Actual impact energy absorbed after peak load point
E_{el}	- Impact energy absorbed through elastic deformation
E_i	- Total energy absorbed corresponding to incipient damage point
E_p	- Total energy absorbed corresponding to peak load point
E_{total}	- Total impact energy or actual impact energy exerted on specimens
F_i	- Incipient damage load or load corresponding to incipient damage point
F_p	- Peak contact force between the impactor and the specimen
h	- Thickness of a plate
J	- The flux of the diffusing substance
m	- Weight of the diffusing substance in the material
M_{final}	- Final moisture content of specimens
M_m	- Effective equilibrium moisture content
M_1	- Moisture content at time t_1
M_2	- Moisture content at time t_2
n	- Number of samples in one group
S_p^2	- Pooled variance estimate
s^2	- Sample variance
t	- <i>Student's t distribution (t statistic)</i>
$Time$	- Hygrothermal conditioning time duration
τ	- Interlaminar shear stress
W	- Weight of a moist specimen
W_b	- Baseline weight of specimens or weight before hygrothermal conditioning
W_{dry}	- Dry weight of specimens
W_{final}	- Final weight of specimens or weight before impact testing
W_i	- Initial weight of specimens
$\bar{Y}$	- Average value of one group

Chapter 1 Introduction

1.1 Introduction

Laminated composites, which are competitive counterparts of metallic materials, are often subjected to combined hygro-thermo-mechanical environments including changing temperatures, humidity and cyclic service loads. Although they are being used in various fields because of their high strength- and stiffness-to-weight ratios as well as superb corrosive resistance (Cândido et al. 1993; Rikards, 2000; Hillermeier and Seferis, 2001; Almeida and Awruch, 2009; Benkhedda et al. 2008; Daniewicz and Frantziskonis, 1992), composite parts have been reported to get damaged or degraded by these environmental factors (Céline, 2006; Potter and Purslow, 1983; Mezghani, 2012; Zainuddin et al. 2010; Sun et al. 2011; Shen et al. 2000), which makes the study of the effects of hygro-thermo-mechanical environments on composites crucial.

The effects of hygrothermal conditioning on the properties of polymeric matrix composites have been studied extensively. However, substantial contradictions exist among the results in the literature. Both, positive and negative effects of hygrothermal ageing have been reported. This forms the impetus for the current thesis. The susceptibility to impact is a common disadvantage of composite materials with a brittle matrix. However, only limited information on the effects of hygrothermal conditioning on the impact resistance of composites is found in

academic publications. Therefore, effect of hygrothermal conditioning on the impact properties of composites materials was chosen in this work first for study.

Hygrothermal environments attack composite materials through two principal mechanisms-microstructure degradation and plasticization. However, in many cases hygrothermal ageing induced structural defects and plasticization may coexist and have different influences on specific properties of composite materials. This fact was frequently ignored in the literature. Therefore, in the current study, microstructural observation on samples exposed to hygrothermal conditioning using techniques such as scanning electron microscope and optical microscope was contemplated.

Accelerated hygrothermal conditioning simulating real in-service environments were designed for the purpose of investigating the effects of moisture and hygrothermal ageing on the microstructures and impact resistance of CFRP UD-prepreg and woven-prepreg laminates. Due to the lack of relevant experimental data on this material system, CFRP UD-prepreg and woven-prepreg materials are selected as the target material for investigation. Several fundamental mechanical tests were planned to achieve a deeper understanding of the role played by moisture in CFRP laminates and epoxy resin. These tests included tensile tests on pure epoxy resin and CFRP woven-prepreg laminates, Mode I fracture toughness test on CFRP woven-prepreg laminates. Long-term hygrothermal conditioning was planned on laminates to verify whether the impact resistance of the laminates would change after prolonged hygrothermal conditioning.

Later, hygrothermal conditioning study was performed on GFRP laminates to check the genericity of the conclusions drawn for CFRP laminates. Dispersion of

core-shell polymer (CSP) particles at the interlaminar interface has been found to be an effective technique to improve the resistance of both, GFRP and CFRP laminates, to low-velocity impact (Ali and Joshi, 2012 and 2013). This being relatively new but a promising solution, hygrothermal ageing to identify the durability of CSP particles dispersed GFRP laminates was considered important.

Glass laminate aluminum reinforced epoxy (GLARE), which is a type of fiber metal laminates (FML), is composed of several very thin layers of aluminum interspersed with glass fiber prepreg layers, bonded together with a matrix such as epoxy. The major advantages of GLARE over conventional aluminum include better damage tolerance, better corrosion resistance and lower specific weight (Khan et al. 2011). It has been attracting more and more attention from academic field as it is a representative of the next generation structural materials. However, the potential effects of hygrothermal conditioning on the fatigue behavior of GLARE laminates was rarely investigated. It was also thought important to conduct some fatigue studies on hygrothermally aged GLARE laminates with the purpose of experimentally characterizing their fatigue behavior.

Thus, this thesis first looked at the existing lack of understanding and some sort of supporting data and built its premise with the intension of filling those gaps.

1.2 Scope and objective

The objective of this thesis is to investigate the durability of polymer matrix composites under combined hygrothermal environments. The actual phenomena associated with hygrothermal exposure including moisture uptake and possible

microstructure degradation are to be identified. The major purpose of the present research is to study the effects of hygrothermal exposure on the mechanical properties of PMCs, and to identify the relevant degradation mechanisms.

The scope of the present study is listed as follows:

(1) Durability of CFRP composite materials

The materials studied included laminates fabricated from CFRP UD-prepreg and woven-prepreg materials. Several types of hygrothermal conditions were particularly designed to simulate in-service environments. The impact response and tensile behavior of hygrothermally-aged CFRP composites were investigated. Related mechanisms, which are responsible for the change in the mechanical properties of hygrothermally-aged CFRP composite materials are proposed.

(2) Durability of CSP particle-reinforced GFRP composites

CSP particles were added into all the 7 inter-ply interfaces with the dispersion density of 30 g/m^2 to improve the impact response of the GFRP composites. These GFRP laminates were fabricated to explore the effects of CSP particles on the moisture uptake behavior and their environmental durability. The GFRP composites thus prepared were immersed in water at elevated temperature for different durations. Low-velocity impact tests and tensile tests were then conducted on the hygrothermally-aged GFRP laminates to investigate the effects of the hygrothermal ageing on their mechanical performance.

(3) Durability of GLARE laminates

The material under investigation was GLARE 4A laminates, which were procured commercially. These laminates were immersed in water at 80°C for 120 days. The durability of GLARE 4A laminates under hygrothermal environment was evaluated at two aspects. The structures of the samples were observed at both macro and micro levels to identify possible structural defects formed under the combined attack of moisture and elevated temperature. Tensile tests and tension-tension fatigue tests were conducted on the hygrothermally-aged GLARE 4A laminates to explore their mechanical properties after the exposure to the hygrothermal surrounding.

1.3 Method and approach

The research work of this thesis mainly dealt with the experimental characterization of the microstructure and mechanical properties of hygrothermally aged composite materials and GLARE laminates. The research approach undertaken can generally be divided into four parts: sample preparation, hygrothermal conditioning, mechanical testing, and structural observation.

1.3.1 Specimen preparation

For laminates made from prepreg materials, prepreg materials were firstly cut into required dimensions according to the mechanical test to be performed. The plies were then stacked manually into laminates and cured in either a convection oven or an autoclave with proper curing conditions. GLARE 4A laminates were cut from plates of GLARE 4A using water-jet cutting technique in order to achieve better edge quality.

1.3.2 Conditioning of specimens

Specimens were immersed in a water bath at different temperatures for different time duration to achieve different hygrothermal conditioning. Other typical hygrothermal conditions encountered by composite parts during service were also reproduced, including, for instance, cold/dry environment provided by a freezer.

1.3.3 Mechanical testing

The mechanical testing performed included a number of:

- (1) Low-velocity impact tests on CFRP unidirectional laminates, CFRP woven laminates, and GFRP laminates dispersed with CSP particles.
- (2) Tensile tests on CFRP woven-prepreg laminates, GFRP laminates, pure epoxy resin tensile samples and GLARE 4A laminates.
- (3) Mode I fracture toughness tests on CFRP woven laminates.
- (4) Tension-tension fatigue test studies on GLARE laminates.

1.3.4 Micro-structural observation

The micro-structural observations and the techniques used in this thesis included:

- (1) Scanning electron microscope (SEM): SEM can effectively observe micro-structure of laminates before and after conditioning, including individual fibers, matrix resin, voids, various damage modes of laminated composites, etc.

(2) Field emission scanning electron microscope (FESEM): FESEM can be used to observe the microstructure of PMCs specimens with higher magnification than SEM.

(3) Optical Microscope: optical microscope allows low-magnification observation of features such as the pitting corrosion at the outer aluminum layers of GLARE 4A laminates, surface cracks formed at CFRP laminates during hygrothermal ageing, etc.

1.4 Thesis outline

The entire thesis is suitably divided into 8 chapters. Chapter 1 introduces the background and objectives of current thesis as well as methods and approaches used. Chapter 2 summarizes research work that has already been done by various researchers on hygrothermal effects on composite materials. Details of the experimental process of the current study are presented in Chapter 3. Discussed in Chapter 4 are the results of hygrothermal conditioning and impact testing on CFRP woven and UD laminates. Chapter 5 discusses the effects of long-term hygrothermal conditioning on the microstructure and impact resistance of CFRP UD laminates. Chapter 6 discusses the low-velocity impact response of GFRP laminates dispersed with CSP particles. Chapter 7 discusses the effects of moisture and hygrothermal environment on the microstructure and fatigue behavior of GLARE 4A laminates. Major conclusions and contributions are enumerated in Chapter 8.

Chapter 2 Literature review

2.1 Composites

A composite is a structural material that consists of two or more constituents which are combined at a macroscopic level and are not soluble in each other. Generally, a composite has two phases, matrix phase and reinforcing phase. Based on the types of matrix phase of composites, there are three categories of composites; namely, polymeric matrix composites (PMCs), metal matrix composites and ceramics matrix composites (Daniel and Steven, 2001). Common reinforcements include fibers, particles and flakes. The type of composites that is involved in this thesis is fiber reinforced polymeric matrix composites.

2.1.1 Laminated composites

The most common form in which fiber-reinforced composites are used in industry is called a laminate. It is obtained by stacking a number of thin layers of fibers and matrix resin and consolidating them into the desired thickness. A single layer is called a lamina, which is formed by imbedding a large number of fibers or a fiber fabric in polymer matrix. The thickness of a lamina is usually in the range of 0.1-1mm. Several laminae form a laminate. Figure 2-1 shows typical laminae arrangement and a composite laminate.

For laminated composites, the fibers can be continuous (endless fibers) and discontinuous (short fibers). Therefore, there are several types of lamina classified according to types and orientations of the fiber. In Figure 2-1(a), the names of the

four types of lamina are unidirectional continuous lamina, bidirectional continuous lamina, unidirectional discontinuous lamina and random discontinuous lamina, respectively from top till bottom. The physical and mechanical properties of a composite laminate can be tailored by controlling the fiber orientation and thickness of each lamina as well as the stacking sequence of various layers, which is an outstanding advantage of laminated composites.

Figure 2-1 Typical laminae and a composite laminate

2.1.2 Constituents of composites

Major constituents of a lamina include reinforcement fibers, matrix resin, coupling agents, fillers or coatings and so on. Details of common fibers and matrices used in industry are presented below.

2.1.2.1 Reinforcement

Fibers are the principal constituent in fiber-reinforced composite materials. They occupy the largest volume fraction and take the major portion of the load exerting on a composite part. There are mainly four types of fiber in industry: carbon fiber, glass fiber, boron fiber and aramid fibers.

Glass fibers are based on silica (SiO_2) melted with oxides. Glass fibers are the most common and cheapest type of fibers. There are two types of glass fibers used for structural applications, E-Glass and S-Glass. Compared to other standard forms of glass fiber, E-glass has high electrical resistivity and low dielectric constant. S-glass has high strength and stiffness. The manufacturing process of glass fibers is shown schematically in Figure 2-2.

Figure 2-2 Schematic illustration of the process used to fabricate glass fiber (Alan et al. 2004)

Carbon fibers are a class of fibers with high strength and stiffness. Compared to glass fibers, carbon fibers are much more expensive. Structure of carbon fiber is shown in Figure 2-3. Fabrication of graphite fibers involves thermal decomposition (pyrolysis) of a precursor material, which is either PAN (polyacrylonitrile) or pitch. The manufacturing process of carbon fiber is schematically illustrated in Figure 2-4.

Figure 2-3 Schematic illustration of the structure of carbon fiber (Weibull, 1951)

Figure 2-4 Schematic illustration of processing of carbon fibers (Alan et al. 2004)

Boron fibers (Frankline and Wawner, 2000) are large monofilaments around 125-140 μm in diameter, compared with around 10 μm for carbon fibers. Because boron is almost as hard as diamond, PMCs based on it are difficult to drill and machine. Boron fibers are made by chemical vapor deposition (CVD) of boron onto fine incandescent tungsten or a pitch-based carbon fiber. The manufacturing process of boron fibers is illustrated in Figure 2-5.

Figure 2-5 Schematic representation of the process used to manufacture boron fibers (Alan et al. 2004)

Aramid fibers are organic fibers with sufficient strength and stiffness for use in PMCs suitable for aerospace applications. The structure of aramid fibers is shown in Figure 2-6. These organic polymer fibers are produced by an extrusion or spinning process. One point worth mentioning is that, unlike inorganic fibers, aramid fibers have a high tendency to absorb moisture (Keinath and Morgan, 1990).

Figure 2-6 The polymeric structure of aramid fibers (Chawla, 1987)

2.1.2.2 Matrix resins

Matrix resin in a fiber-reinforced composite serves four functions: (1) transferring load into and out of fibers; (2) stabilizing fibers; (3) providing a barrier against an adverse environment; (4) protecting the surface of the fibers from mechanical abrasion. There are two types of matrix resins, thermoplastics and thermosets. For the curing of thermosetting resins, chemical reaction will occur and a cross-linked 3D network will be formed, while during fabrication of composite parts based on thermoplastics, no chemical reaction occurs and the process is reversible. Therefore, the curing temperature of thermosets is relatively low because they have low viscosity before curing, but the curing time is longer than thermoplastics. Thermoplastics have higher processing temperature because of the high viscosity of larger molecules but need a shorter processing time.

Within the family of thermosetting resins, epoxy resins are the most widely used in aircraft structures. Epoxies have excellent chemical and mechanical properties.

Starting materials for epoxy usually contain a number of epoxide groups, which are three-atom rings of one oxygen atom and two carbon atoms. For example, the starting material of the epoxy used in the current study is diglycidyl ether of bisphenol A (DGEBA), which contains two epoxide groups with one at each end of the molecule. Generally epoxies falls into two categories, 120°C curing group and 180°C curing group. Those with higher curing temperature usually allow higher service temperature.

Bismaleimide resins, which also have excellent processibility and good mechanical properties, are another group of thermosetting resins that are used in aerospace industry. Most importantly, BMI resins can operate at higher temperatures than epoxies. Generally, BMI resins cured at around 200°C allow an operating temperature over 180°C. However, because of their high cost, they are usually selected only when the service temperatures exceed the capability of epoxies.

Other thermosetting polymers used in industry include polyester, the starting material of which is an unsaturated polyester resin that contains a number of C=C double bonds, vinyl ester, which is cured from unsaturated vinyl ester resin. Both polyester and vinyl ester form cross-links at the carbon-carbon double bonds. Their properties depend strongly on the cross-link density. The modulus, glass transition temperature and thermal stability of cured thermosetting resins are improved by increasing the cross-linking density, but the strain-to-failure and impact resistance are reduced. The major factors influencing the cross-link density are the number of instauration points of the starting material and degree of curing. The first one can be controlled by varying the weight ratio of various ingredients used for making

unsaturated starting material. The second one is controlled by curing parameters such as curing temperature and curing time. Proper curing temperature and curing time should be set before curing in order to obtain fully cured specimens.

Polyether ether ketone (PEEK), polyphenylene sulfide (PPS), thermoplastic polyimides, etc. are generic thermoplastics used in PMCs. Thermoplastic polymers can be very broadly classified as amorphous or semi-crystalline. Most thermoplastics, suitable for use as matrices of PMCs, exhibit some degree of crystallinity because they offer better resistance to chemical attack by fuels, hydraulic oil, and paint stripper. Compared with thermosets, thermoplastics absorb less moisture. Thermoplastics also have better interlaminar strength and impact resistance because they are tougher than thermosetting polymers. Another major advantage inherent with thermoplastics is that defects in matrix can be healed by welding. The processing time of thermoplastics is shorter because no chemical reaction is required. But the requirement for crystallization temperature and pressure is more stringent, which in turn increases the manufacturing cost.

2.1.3 General characteristics

The strength and modulus of many fiber-reinforced composite materials are either comparable to or better than many traditional metallic materials. However, the specific gravities of composites are quite low. Therefore, the strength-weight and modulus-weight ratios of these materials are markedly superior to that of metallic materials. In addition, many composite laminates also possess excellent fatigue strength as well as fatigue damage tolerances. For these reasons, fiber-reinforced

composite materials have emerged as important alternatives to metallic materials in many weight-critical components.

Unlike traditional structural materials, such as steel and aluminum which are considered isotropic because they exhibit nearly equal properties irrespective of the direction of measurement, laminated composites are usually orthotropic (in some cases anisotropic) materials. In general, physical and mechanical properties of fiber-reinforced composites depend strongly on the measurement direction. For example, the tensile strength and modulus of a unidirectional lamina are the maximum when the direction of measurement is the same as the fiber orientation. At other angles of measurement, these properties will be lower; the minimum value will be observed when measured transverse to the fibers.

As mentioned earlier, the orientation of each layer as well as the stacking sequence of the laminate can be varied to control the physical and mechanical properties of it. Thus, another advantage of laminated composites is design flexibility which can be utilized to optimize the structure under certain requirements.

There are a number of other differences between metallic materials and PMCs. For instance, metals generally can deform plastically, while fiber-reinforced composites fail as soon as the elastic limit is reached even though the whole structure will not break catastrophically. There are a number of other advantages of PMCs, such as good corrosion resistance and low coefficients of thermal expansion which is crucial for dimensional stability of the structure.

However, the weakness or disadvantages of fiber-reinforced composites are also evident and inevitable. The difference in physical properties of fibers and matrix

resin often results in not only thermal stresses after curing but also internal stresses upon absorbing moisture. The failure of metals is usually visible. However, for PMCs, some damages are internal in nature. For example, when struck by foreign object, even if there are no apparent damages on the surface, there are probably damages such as matrix cracking, fiber debonding and breakage inside the structure which have detrimental effects on residual strength of the material. Thus, the impact properties of laminated composites are always of great interest to the researchers in this field (Richardson and Wisheart, 1996; Geubelle and Baylor, 1998; Choi et al. 1991; Schoeppner and Abrate, 2000; Sanchez-Saez et al. 2005). Polymer resins usually absorb moisture even in the air. Preliminary experimental results showed that moisture has positive effects on CFRP laminates. But whether the long term effects of moisture are positive or not is not guaranteed. The properties of PMCs are also usually affected by environmental factors such as elevated temperature, corrosive fluids and ultraviolet rays, which are especially important for space applications.

2.1.4 Manufacturing of composites

In the early stages of applications, laminated composites parts were made by a hand lay-up technique, which is slow and labor intensive and not suitable for mass production and producing large composite structural parts, though is a reliable process. Fortunately, there are several types of manufacturing methods that can support mass production rates and meet the requirements of the consumers. Among them, compression molding, pultrusion, filament winding, automated tape lay-up process, and autoclave techniques are popular in both, industry and academic world. Different manufacturing methods are suited for the fabrication of composite parts of

different shapes, thicknesses, and volumes. The raw materials of different fabrication methods are also different in some cases.

The quality of components depends strongly on the proper control of the process parameters of their manufacturing process. For laminated composite parts, high temperature and pressure, and appropriate curing time are crucial for their quality.

2.1.4.1 Bag molding process

The bag molding process is used predominantly in aerospace industry where high production rate is not an important consideration. It allows curing of the laminates with perfect quality. All unidirectional-prepreg specimens used in this study were cured by this method and the details of this method can be found in the later chapter. A common starting material for bag molding process is a prepreg that contains fibers impregnated with partially cured (B-staged) epoxy resin. Firstly, a vacuum bag assembly with ply lay-ups for laminates inside is prepared. Then the entire assembly is placed inside an autoclave where process parameters such as pressure, temperature and vacuum are well controlled as function of time to consolidate and densify the number of prepreg layers into a solid laminate.

2.1.4.2 Compression Molding

Compression molding (Dumont et al. 2007) is a mass production manufacturing method, which is used for transforming sheet molding compounds (SMC) into finished products in a predesigned mold which has a cavity of the same shape of the desired part. It has two principal advantages. Firstly, it has the capability of producing parts of complex geometry in short periods of time. Non-uniform

thickness, ribs, flanges, holes and shoulders, for instance, can all be incorporated during the compression molding process. Secondly, the entire curing process, including mold preparation and SMC placement, as well as parts removal after curing, can be automated. Thus, it is a method that can produce composite parts with complex geometry continuously. During the compression molding process, the charge, which is usually a stack of several rectangular plies of certain shapes and thickness, is placed onto the bottom part of the mold which is preheated. The mold is closed quickly and the top half mold is lowered at a constant rate until a predetermined pressure is exerted onto the specimen.

2.1.4.3 Automated tape lay-up process

For the fabrication of large composite components such as stabilizer skins, automated tape lay-up (ATL) is preferred to hand lay-up. Automated tape layers normally consist of a gantry with a dispensing head that is free to move over the surface of the tool. Unidirectional prepreg rolls are loaded on the head of ATL machines. As the tape is placed on the surface, the protecting film is stripped away; the tape is pressed against the part surface and is cut when reaches the edges. Figure 2-7 shows a typical ATL process and a product made by this technique. Normally, prepreg tapes for automated ATL process have three types of width, 75mm, 150mm and 300mm.

Figure 2-7 Schematic diagram of automatic tape laying process (left) and a typical product (Alan et al. 2004)

Tape layer systems can lay prepreg tape materials on a variety of tool configurations with exceptional consistency and accuracy and provide a significant cost reduction over hand lay- up processes (Grimshaw et al. 2001). Many companies or institutes have purchased tape layer systems, such as Boeing, NASA, and DaimlerChrysler Airbus. It have been widely adopted to manufacture large components such as the horizontal stabilizer skins of Boeing 777 Commercial Aircraft, wing of Air Force F22 Raptor, flap skins of A330/A340 and so on. Figure 2-8 shows the manufacturing of Boeing 777 empennage skins using an ATL machine.

Figure 2-8 Fabrication of Boeing 777 empennage skins (Grimshaw et al. 2001)

2.1.4.4 Other manufacturing processes

Various other manufacturing techniques include pultrusion, filament winding (Shen, 1995), resin transfer molding and so forth. Pultrusion (Jacob, 2006) is suitable for manufacturing of long, straight parts which have constant cross-sectional area. During filament winding process (Lossie and Brussel, 1994), a band of continuous fibers which are impregnated by resin is wrapped around a rotating mandrel and cured to produce an axisymmetric part. Therefore, filament winding technique is used to fabricate components such as pressure vessels, pipelines etc. In resin transfer molding (Joshi, 2012; Mallick, 1993; Kendall et al. 1992), fibers, fabrics, woven roving or continuous strand mats of predetermined volume and dimension are placed in a mold cavity, which is then closed and liquid resin with catalysts is injected into it.

2.1.5 Applications of composites

Nowadays, composites are widely used, from the outer space to the ocean, from civil engineering to aerospace engineering. It is impossible to list all the applications of PMCs. In this section, several of the major fields where composites are used are briefly introduced.

2.1.5.1 Aircraft applications

Military and commercial aircrafts, where weight reduction is crucial for higher speed, increased payloads and reduced consumption of fuels, represent the first and principal area where composites are used intensively, from secondary structures to even some of the primary structures (Lewis, 1994). Examples of the applications of

composites on various aircrafts are well known and numerous, such as the fuselage, wing skins, floors, stabilizers, ailerons and so on (Soutis, 2005).

2.1.5.2 Space applications

As the same for aircrafts, weight reduction is the driven force for using fiber-reinforced composites in space vehicles. Fiber-reinforced composites are widely used for space applications, such as solar arrays, antennas, optical platforms and supports for cryogenic tanks (Bansemir and Haider, 1998). For example, composites have been used on the solar arrays of the Chinese communication satellite Dong Fang Hong 3 (DFH3). Moreover, Bansemir (1998) reported that the design flexibility of composites can be utilized to optimize the structure with the purpose of reducing thermal conductivity which finally has played a crucial role in increasing the lifetime of a satellite.

Another advantage of using PMCs in spacecrafts is their dimensional stability over a wide temperature range (Mallick, 1993). Many carbon fiber-reinforced epoxy laminates can be designed to produce a coefficient of thermal expansion (CTE) close to zero.

2.1.5.3 Land transportation applications

Composites are also widely used in automobiles (Lee et al. 2004). Glass fiber reinforced polyester body panels on the 1953 Corvette was the first major application of composites in the automotive industry (Peters, 1998). Applications of PMCs in the automotive industry generally fall into three categories: body components, chassis components and engine components. Body components include exterior

panels and doors. Typical chassis components of composites are composite leaf springs. Composites have also been used to manufacture intake manifolds, pulleys, torque converter reactors and valve covers and so on (Peters, 1998). Figure 2-9 shows the various phenolic composite parts for automobile engines.

Figure 2-9 Various phenolic composites parts for engine applications (Peters, 1998)

2.1.5.4 Other applications

Composites have also been used for making sport goods, such as tennis rackets, golf shafts (Slater et al. 2010), fishing rods and bicycles (Lessard et al. 1995). Application areas such as boat hulls, decks, bulk heads, masts and spars have also chosen composites (Mallick, 1993) over other materials.

2.1.6 In-service environmental conditions

The environmental conditions to which composite parts are subjected in service are as diverse as the applications of composites. For composite parts on airplane, both high and low temperatures are possible even for a single flight. For instance, when heated directly under sunlight on ground, the temperature of a composite part

can reach as high as 55°C, while during flight the temperatures may go below -55°C. In addition, during flight, temperatures of composites near hot spots such as engine mounts etc. may go even higher whereas at other places they may drop even lower depending on the altitude of the flight (Patel and Case, 2002). Changing humidity, cycling temperature conditions usually affect the properties of composites. For spacecraft applications, composite parts are often attacked by ultraviolet (UV) rays and atoms of oxygen, which generally cause chemical degradation of the matrix resin (Grossman and Gouzman, 2003). For applications such as automobiles and marine applications, corrosive fluids also attack composite parts if improperly protected (Prehn et al. 2005). The current research, however, is focussed on environmental effects on laminated composites.

2.2 Impact testing of composites

Composites are prone to impact damage and impact related issues for composites are exceptionally important. As recognized in preceding sections, PMCs are brittle in nature. They behave in an elastic manner in the stress versus strain curves under tensile tests. Metals usually have yielding and subsequent plastic deformation. Therefore, when struck by a foreign object (an impact event), metallic materials may yield or even show some degree of plastic deformation, but the whole structure will not be affected. For composite parts, when struck by foreign objects, damage modes such as matrix cracking, fiber debonding and breakage are likely to occur because PMCs do not have plastic deformation. Moreover, these damages are not evident in many cases even though they can affect the residual strength of the structure to a large extent.

Common causes of impact damage can be listed according to the various stages of composite parts, namely, production, service, repair and maintenance. In the production and repair stage, dropping tools, accidental collision with other equipments or tools are the possible sources of impact damage. In service stage, causes may include hailstone impact, runaway debris, bird strike, lightning strike, shock waves, ice released from the edge of a propeller blade and so on.

2.2.1 Comparison of impact response of polymer composites

Impact properties of PMCs have been investigated intensively by researchers all over the world. Aleszka (1978) had conducted impact testing on graphite/epoxy laminates and found that the load and absorbed energy corresponding to incipient and full penetration damage were independent of the impact energy exerted. Thus F_i , E_i , F_p and E_p can be used to compare the impact properties of different laminates. Feraboli (2006) stated that the incipient damage point corresponds to a point on the load versus time curve after which there is an evident sharp drop due to loss of out-of-plane stiffness because of damages such as delamination. Feraboli (2004) also summarized that impact events can be divided into three categories, subcritical impact event, critical impact event, supercritical impact event as shown in Figure 2-10. Therefore, the impact properties of different composite specimens can be compared by examining the load and energy versus time curves of them. A parameter named *Damping Index* is often used to characterize the extent of impact damage of impact tested specimens (Walker et al. 2002; Bledzki et al. 1999). In this report,

damping index is renamed to *Damage Index*. Higher value of *damage index* implies more severe damage generated during an impact event.

2.2.2 Impact response of hygrothermally conditioned composites

Results about impact testing of hygrothermally conditioned PMCs are rarely found in the literature. Karasek et al. (1995a, 1995b) studied the effects of moisture and temperature on the impact behavior of graphite/epoxy composites. IM7 carbon fiber and four types of resins were selected to make composite samples. Both dry and sea water saturated samples of each material were tested at three temperatures, -21°C, room temperature and 66°C. It was concluded that when tested at 21°C (ambient temperature) moisture had little effect on the damage initiation energy and impact energy dissipation process. They concluded that moisture saturation had occurred prior to impact testing. However, according to the data presented it is confident to claim that the samples were actually not saturated. The maximum average moisture content was merely 0.80%. The samples were relatively thick laminates with a thickness of 6.35mm. Therefore, the effects of moisture might not be fully reflected. Considering the possible large scatter in the mechanical properties of PMCs, the reliability of their conclusion is questionable.

Figure 2-10 Force and energy versus time for subcritical, critical and supercritical impact events (Feraboli, 2004)

The effect of water immersion ageing on low-velocity impact behavior of aramid–glass fiber/epoxy composites were also investigated (Imielińska and Guillaumat, 2004). It was reported that the absorbed moisture did not affect the delamination threshold load and impact energy absorption significantly. However,

the authors failed to apply higher impact energy level to the laminate which might reveal the potential effects of absorbed moisture on the impact resistance of aramid-glass fiber/epoxy composites. Therefore, more vigorous investigation is required to further explore the effects of hygrothermal conditioning and moisture on the impact response of PMCs.

2.2.3 Impact response of CSP particle reinforced composites

Core-shell polymer particles, which are in the form of fine white powder and appear as discrete particles without any agglomeration, have been reported to be effective impact modifier by Ali and Joshi (2012 and 2013). They have a soft rubber (PBA) core and a transparent shell of poly (methyl methacrylate) (PMMA) with an epoxy functional group grafted to the shell to improve the interfacial bond of the particles with epoxy matrix. Ali and Joshi (2012) first investigated the effects of incorporating CSP particles within interply interfaces on the impact response of CFRP prepreg laminates. 51g/m² of CSP particles were dispersed at all the 7 ply interfaces of an 8-ply CFRP woven laminate. After the addition of CSP particles, the peak contact force during impact improved by 41%. Consequently, the extent of impact damage decreased dramatically. They proposed that CSP particles in the interplay regions reinforced the resin-rich regions, making these regions ductile and leading to higher peak load under impact. Moreover, CSP particles deformed compressively when the impact load was applied, absorbing part of the impact energy. These mechanisms explained the improved impact response of CFRP

laminates with particles. Ali and Joshi (2013) also investigated the effects of CSP particles on the damage evolution of fiberglass fabric epoxy prepreg laminates under different energy levels of impact. CSP particles did not change the predominant damage modes but delayed and mitigated the damage creation. The deformation of the CSP particles and the tearing of their outer shells consumed part of the impact energy. CSP particles ahead of crack tips impeded crack propagation by requiring the cracks to follow a more tortuous path. In summary, CSP particles provide a promising solution for the enhancement of the impact damage resistance of fiber reinforced polymer composites. A comprehensive understanding of the effects of CSP particles on the various aspects of composite materials is the prerequisite for their practical application. In this thesis, the durability of CSP particle reinforced GFRP laminates to a hygrothermal environment is particularly addressed.

2.3 Hygrothermal conditioning of composites

It is common that composite parts are working under various hygrothermal conditions or combinations of various conditions. Composite parts usually have a service life of more than 10 years, such as those used on airplanes. In service, they are usually subjected to moisture absorption/desorption cycles, and thermal cycling (cycling between low and high temperatures). These cyclings do have effects on the properties and internal structures of composites. However, as promising alternatives to metallic materials, composites usually can stand the negative or detrimental effects of environmental factors. Thus, on the one hand, environmental factors such as temperature, moisture, sunlight radiation, chemicals in the atmosphere, usually degrade the structures of composites and their properties. On the other hand,

composites, which are light but strong materials, can bear the effects of environmental factors and provide service for many years.

However, there are a number of cases in which composite parts are severely damaged by environmental factors (Joseph et al. 2002; Li, 2000; McMillan et al. 1998). Therefore, it is important to identify environmental factors that degrade composite materials and the mechanism of degradation. Only then one would know why composites degrade, and could find out ways of improving them to make composites stronger, more durable and more reliable.

Numerous works on the hygrothermal effects of composites can be found from the literature, which are far beyond enumeration. The general process adopted for studying the effects of hygrothermal conditioning is the fabrication of specimens, conditioning and subsequent mechanical testing. Thus, research work on hygrothermal effects already published is briefly introduced below considering four aspects, materials involved, structures involved, conditions used and properties tested.

2.3.1 Materials involved

The effects of moisture and temperature on various types of composite materials have been reported. Some of the materials studied are very exotic and have never been used commercially, while others have already occupied an established position in the market.

Among all the composites materials, epoxy based composites have attracted the most interest. Zhang et al. (1993) fabricated double cantilever beam (DCB)

specimens with T300/914C graphite/epoxy unidirectional prepregs to study the influence of temperature and moisture on the interlaminar fracture toughness of the material. Specimens were either conditioned in an environment at a temperature of 70°C and a relative humidity of 100 until saturation, or dried at 50°C to constant weight, or stored in normal laboratory environment. After that, specimens were subjected to fatigue test. It has been reported that interlaminar fracture toughness increased with moisture and the growth rate of fatigue crack was lower for hydrothermally conditioned specimens as compared to the dried ones.

Patel et al. (2000) studied the effects of moisture, temperature and combined hygrothermal conditions on the strength and life of a graphite/epoxy woven composite material system by combining mechanical fatigue and changing environment. They found that initial and residual tensile properties and fatigue life of the materials were only minimally affected by any of the imposed environmental conditions for the fatigue stress levels considered in their study. But low temperature was not considered in that investigation.

Mishra et al. (2010) studied the effects of thermal and cryogenic treatment on hydrothermally conditioned glass fiber reinforced epoxy matrix composite and the impact on its mechanical properties with change in percentage of individual constituents of the laminates. The author reported that the hygrothermal treatment prior to the exposure to thermal or cryogenic conditioning is the major attribute to the variations in the interlaminar shear strength values.

Bao et al. (2002a, 2002b) systematically studied moisture diffusion and hygrothermal aging in uni-weave, woven and woven/uni-weave bismaleimide

composites. They reported that both, the neat resin and uni-weave composites, displayed similar two-stage diffusion behavior, with the first and second stages being diffusion- and relaxation-controlled, respectively, while the short term diffusion in the woven composite is non-Fickian and should be fitted with a dual-diffusivity model. The authors also found that during the prolonged moisture absorption, the swelling stresses eventually caused the formation of interfacial cracks in the composite.

Zhou and Zhong (2004) performed hygrothermal freeze–thaw cycling exposures on glass–vinyl ester composite to simulate harsh temperature and moisture conditions that the composite might encounter during their lifetime in services. The cycling conditions used were 80°C/saturated steam/48 h<->-17.8°C/dry/24 h. Compression tests were conducted to investigate hygrothermal cycling effects on mechanical properties of the composite. The results showed that the degradation in compression strength for hygrothermally cycled composites was less significant than that of samples exposed to isothermal conditioning at the same temperature and with the same exposure duration.

Chung et al. (2002) investigated hygrothermal cycling effects on the durability of carbon fiber/phenolic resin composites. A hygrothermal cycle with changing temperature and relative humidity was used. Interlaminar fracture toughness tests were conducted on conditioned specimens. The researchers found that both, type I and type II fracture toughness, decreased after numbers of cycles of conditioning and that the fracture performance of a phenolic composite modified with a silicone-based

additive decreased after fewer hygrothermal cycles than unmodified phenolic and epoxy composites.

2.3.2 Different structures

Except for simple laminates, special structures such as stitched laminates, bolted joints have also been studied.

Cheng et al. (2011) investigated the hygrothermal properties of uni-weave stitched and unstitched T300/QY9512 (carbon fiber-reinforced BMI) laminates experimentally and analytically. Specimens were dipped in $71\pm 10^{\circ}\text{C}$ distilled water for 7 days. Moisture content of unstitched laminates reached up to 1-1.1% and that of stitched laminates up to 1.1-1.2% approximately. Later, BMI laminates were subjected to compression tests at three conditions, 20°C /dry, 150°C /dry, 150°C /wet. Test results have shown that hygrothermal environment condition had a severe effect on compressive strength of the laminates and the reduction in compression strength of the stitched laminates reached up to 50%.

Chen (2001) examined the effects of hygrothermal cycling upon the performance of bolted composite joints. The specimens of IM 6/3501-6 (brittle) and IM7/8552 (toughened) were repeatedly subjected to elevated temperature/humidity for 12 h, and then were subjected to room temperature dry conditions for the next 12h. Two hot/wet environmental cycles were chosen: 32.2°C , 98% RH and 48.9°C , 98% RH. Specimens were exposed to the environmental cycling for one, two, three and four months until fatigue testing. He found that the bolt torque relaxed as the number of environmental cycles increased. Fatigue tests of specimens exposed to hygrothermal

cycling exhibited greater hole elongation than those not exposed. The author also reported that the tests run on IM6/3501-6 material specimens with hygrothermal cycling have shown reasonable declines in fatigue life.

Botelho et al. (2007a) investigated the influence of hygrothermal conditioning on mechanical properties of fiber-metal laminates (Carall) by tensile and compression tests. Carall is a hybrid material, which consists of thin aluminium metal sheets bonded together with alternating carbon fiber/epoxy layers. Carall specimens were exposed to an atmosphere with a combination of 80°C and 90% relative humidity (RH) in an environmental conditioning chamber to an effective moisture equilibrium state. Later, compression and tensile tests were performed on conditioned specimens. The results showed that for carbon fiber/epoxy composites tensile and compression values decreased after hygrothermal conditioning, while the changes in mechanical properties of Carall were negligible, regardless the hygrothermal conditioning.

2.3.3 Hygro-thermo-mechanical conditions

Reynolds and McManus (2000) designed various hygrothermal conditions based on the baseline condition shown in Figure 2-11, which is the hygrothermal condition of a supersonic aircraft provided by Boeing. The baseline environment has been observed to cause micro-cracking damage in a variety of candidate materials and layups. Therefore the author has managed to isolate the effects of different damage mechanisms and accelerate them. Later, specimens of IM7/PETI-5 and IM7/PIXA-M were conditioned under the various conditions designed by the author, including time at moisture, moisture cycling, and time at temperature and thermal cycling to

study their effects on the properties of the materials. Results suggested that for the IM7/PETI-5 and IM7/PIXA-M materials tested, time at moisture was the most important cause of micro-cracking damage, with thermal cycling playing some role. Moisture cycling has also played a role in the distribution of damage.

Figure 2-11 Baseline hygrothermal cycle of a supersonic aircraft (Reynolds and McManus, 2000)

Generally, the real thermal conditioning encountered in service is impossible to simulate with experimental methods because of the limit on time and equipments, so usually accelerated testing should be used. Jedidi et al. (2005) designed accelerated testing scheme to study the drying effects of supersonic flight at high temperature, around 130°C , on the durability of the polymeric matrix composites. This phenomenon constituted an entirely new situation for these materials in contrast with a classical subsonic flight at low temperature. The author first characterized the in-service material state during the supersonic flight cycles and after the maintenance operations. Later, the material geometry and environmental conditions were defined to meet the in-service material state in short time. Finally, different accelerated

cycles adapted to the new situation of supersonic flights, i.e. focusing on the cyclical drying of the material, were proposed.

Composite parts are often subjected to the combined effects of mechanical loading and environmental factors. In most papers, mechanical loading was not considered, which has been reported to not only influence the moisture diffusion behavior of composites, but also accelerate the structural degradation of composites. Beckery et al. (2005) included mechanical loading during conditioning in his work. Specimens of E-glass/epoxy were immersed in distilled water at room temperature or 65°C, and were tested after time durations of 500, 1000, and 3000 h. Samples were stressed in tension at 20% of the ultimate strength of the material when immersed in water. Tensile tests were conducted on both, conditioned and control specimens. Experimental results showed that the modulus, strength, and strain of the E-glass/epoxy composite material were affected by the presence of moisture and mechanical loading when compared to control specimens. At shorter durations of conditioning at room temperature, a slight increase in strength and a slight decrease in modulus were observed; and at longer durations, 3000 h, a noticeable reduction in strength and strain-to-failure was observed. The author speculated that constant stress may have a positive effect in short-term.

Li et al. (2000) performed impact tests and tension after impact tests on hygrothermally conditioned and unconditioned E-glass/epoxy laminates. Hygrothermal cycle used was 24 h in a box with distilled water, and 24 h in dry oven which had the same temperature of the water. Three temperatures have been used, 50°C, 75°C and 100°C. The maximum number of cycles used was 8. The author

found that both impact properties and the tension after impact strength of GFRP laminates decreased as the number of moisture cycles increased and that with the increase of the conditioning temperatures, impact properties and the tension after impact strength decreased at an accelerated speed.

2.3.4 Properties

The properties can be divided into two groups, fiber-dominated properties and matrix-dominated properties. The effects of environmental conditions on matrix dominated properties are generally more pronounced than on fiber-dominated properties (Pavlidou and Papaspyrides, 2003; Collings and Stone, 1985; Tsai et al. 2009; Kellas et al. 1990; Wosu et al. 2012).

Cunha et al. (2008) investigated the influence of the hygrothermal effects on the compression strength of carbon unidirectional tape/epoxy 8552 composites. Specimens were either conditioned in a humidity-controlled chamber at 80°C and 95% RH for 9 weeks until saturation, tested at room temperature or conditioned in a salt spray chamber at 36°C and 95% RH for 9 weeks until saturation. Compression strength tests have been performed on conditioned specimens at two temperatures, room temperature ($22 \pm 3^\circ\text{C}$) and high temperature ($82 \pm 1^\circ\text{C}$). Degradation in compression strength has been observed for specimens conditioned in both environments. For instance, samples tested at high temperature and submitted to the humidity-controlled chamber presented a decrease of 25.7% in the compression strength, when compared with non-conditioned samples.

Ray (2006) reported results about temperature effects during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites. Both E-glass/epoxy and carbon/epoxy specimens were exposed in climatic chamber at certain temperature and relative humidity for a long period of time. Later, interlaminar shear strength (ILSS) of specimens of both material systems was tested. The author made a conclusion that the higher temperature during hygrothermal ageing not only increased the moisture uptake rate but modified the local stress threshold required for delamination nucleation. Specimens conditioned at higher temperature had less value of ILSS even when the moisture content was actually same. The reduction in ILSS values was significant in both systems for the same level of absorbed moisture at a higher conditioning temperature.

Kumar and Sridhar (2008) investigated moisture absorption behaviour and its effects on mechanical properties of carbon fiber-reinforced epoxy composite laminates. Specimens of certain dimensions were immersed into distilled water until mechanical testing. Longitudinal tensile, transverse tensile and in-plane shear properties were measured for $[0]_8$, $[90]_{10}$ and $[\pm 45]_{10}$ laminates as a function of moisture absorption. The author found that the longitudinal tensile strength dropped by 25-30% during first month of the exposure period and remained constant during rest of the exposure time; while the transverse tensile strength showed decreasing trend during exposure period and that an increasing–decreasing trend was observed for in-plane shear strength during the exposure period.

Buck et al. (1998) also studied the effects of the combination of sustained load, elevated temperature, and moisture on the durability of an E-glass/vinyl ester

composite material. Ultimate tensile strength of samples which were environmentally conditioned under different combinations of sustained load, elevated temperature and moisture exposure were measured to evaluate the durability of the material. The results have confirmed that moisture at elevated temperatures reduced the strength of the material. More importantly, the researcher reported that the sustained load which was applied to samples during the conditioning process had been found to further reduce the composite durability.

2.3.5 Moisture in polymer resin and composites

The interaction between water molecules and polymer resin is the most important and fundamental for understanding hygrothermal effects. Even though considerable research work has been focused on water molecules-polymer resin interaction, water diffusion mode and related mechanisms in polymer resin are still not fully understood and substantial disagreement still persists. Two mechanistic approaches that generally characterize the nature of water in epoxy have emerged (Zhou and Lucas, 1999). One is the interaction concept which suggests that water molecules couple strongly with certain hydrophilic functional groups such as hydroxyl or amine in epoxy resin (Zhou and Lucas, 1999a, 1999b; Adamson, 1980; Bellenger et al. 1989). The other approach is the free volume approach which presumes that water diffuses into epoxy resin and resides in the free volume of the material. For this approach bonding between water molecule and epoxy resin network is deemed negligible (Woo and Piggott, 1987; Gupta et al. 1985).

Zhou and Lucas (1999a, 1999b) assessed the nature of sorbed water and the related hygrothermal effects in three types of epoxy systems. Solid state nuclear magnetic resonance (NMR) was conducted to determine the mobility of water in epoxy. He concluded that water molecules bound with epoxy resins through hydrogen bonding. Two types of bound water were proposed by Zhou. Type I bonding corresponded to a water molecule which formed single hydrogen bond with the epoxy resin network, while Type II bonding was the result of a water molecule forming multiple hydrogen bonds with the resin network.

Woo and Piggott (1987) carried out water absorption experiments on three types of DGEBA epoxy resins. They found that the water did not appear to be bound to polar groups in the resin or hydrogen bonding sites although water inside did not behave as free water. They also reported that there was some clustering of the water molecules in the polymer rather than complete separation of the molecules.

Apicella and Nicolais (1985) investigated effects of water on the properties of epoxy matrix and composite and assumed that there were three modes of moisture absorption: (1) dilution of the free volume in the network, (2) hydrogen bonding involving hydrophilic groups of the polymer and (3) adsorption onto the surfaces of "holes" which define the excess free volume of the glassy structure. They also reported that actual modes of moisture absorption may differ from one type of material to another.

2.4 Fatigue test of composites and aluminum alloy

2.4.1 Fatigue test of composites

Polymeric matrix composites are widely used in areas such as sporting goods, aircrafts and automobiles, where cyclic and/or fluctuating loads are common and often inevitable. These loading conditions may eventually cause the failure of composite structures. Understanding and observation of the response of fiber reinforced composites under fatigue loading are crucial for both the selection of material according specific applications and the development of new composite materials for better fatigue resistance.

According to the characteristic of the peak and valley load, fatigue test on polymer composites can be divided into three categories, tension-tension fatigue, tension-compression fatigue and compression-compression fatigue. Within the scope of this study, tension-tension fatigue test will be particularly emphasized. The test control parameter can be either the strain or the stress. Prior to tension-tension fatigue test, the static properties of the material to be tested should be obtained through tensile test. For a stress-controlled constant amplitude fatigue test, the peak fatigue stress can be determined by the fatigue stress level.

$$\sigma_{peak} = S_{max} \times \sigma_{ult} \quad (2-1)$$

Where,

σ_{peak} = peak fatigue stress;

S_{max} = fatigue stress level;

σ_{ult} = ultimate tensile strength of the material to be tested.

The valley fatigue stress (σ_{valley}) is generally determined by fatigue ratio R :

$$\sigma_{valley} = \sigma_{peak} \times R \quad (2-2)$$

The fatigue life of composite laminates generally decreases rapidly with peak fatigue stress. An S-N curve can be obtained to predict the fatigue life of a certain material under a specified peak fatigue stress. Figure 2-12 shows typical S-N curves of composite materials under tension-tension fatigue test.

In a composite material under fatigue test, global damage accumulation of various forms including matrix cracking and fiber breakage generally occurs reducing the strength and stiffness of the sample. Once the residual strength is lower than the applied peak fatigue test, the sample will failed instantly. What essentially occurs during fatigue test is damage accumulation and decrease in the strength of the sample.

Figure 2-12 The S-N curves (fatigue stress vs. fatigue life) of glass fiber/epoxy laminate and GLARE laminates (Da Silva et al. 2008)

It is commonly believed that damage modes in composite laminates under fatigue loading include fiber failure and matrix failure (Wicaksono and Chai, 2013). The damage accumulation process in composite materials under fatigue loading is uniquely complicated. For metals under cyclic loading, failure begins with the

initiation of localized single crack, which gradually propagates leading to the catastrophic failure of the material (Patton et al. 1998). In contrast to homogeneous materials such as metals, composite materials generally have two distinct constituents, fibers and resin, making the occurrence of more damage mechanisms possible. These damage mechanisms include matrix cracking, delamination, fiber/matrix debonding and fiber breakage (Colombo et al. 2012; Aono et al. 2008; Schmidt et al. 2012). These damage mechanisms may occur independently or interactively depending on materials properties and loading conditions. However, a common trend is observed that composites under fatigue loading exhibit global and gradual accumulation of damage of various types, including matrix related damage and fiber fracture (Dzenis, 2003).

Understanding the fatigue damage development process is apparently crucial not only for the characterization of the fatigue behavior of composite materials but for the development of new composite materials for better fatigue resistance. All the damage mechanisms common for composite materials are likely to occur. However, the sequence of occurrence as well as the density of these damages modes is usually a function of the combination of materials properties and loading conditions (Konur and Matthews, 1989). Much research effort has been devoted to the modeling and observation of the fatigue damage development of composites (Naik et al. 2001; Wu and Yao, 2010; Mao and Mahadevan, 2002; Irving and Thiagarajan, 1998; Fruehmann et al. 2010; Montesano et al. 2014). Naik (2003) proposed a damage development mechanism of a cross-ply laminate during tension-tension fatigue (Figure 2-13). During fatigue loading, fiber breakage occurs because of over-

straining or over-stressing. Since fibers are the major load-bearing elements, only until certain percentage of fibers fractures the ultimate failure of the laminate would occur. Fiber breakage can be incurred by several reasons. Weak fibers in the laminate generally break earlier under cyclic loading. The stress redistribution caused by damages such as matrix cracking, delamination and fiber breakage will lead to higher stress in the fibers at the vicinity of these damage forms, which further contributes to the breakage of fibers. The damage development depicted in Figure 2-13 essentially presents a multi-stepped fatigue damage process. At the first step, micro matrix cracks are initiated along the fibers in the 90° ply and moderate fiber breakage also occurs. Later, matrix cracks propagate while other types of failure such as fiber/matrix debonding and delamination are also initiated and further propagate. The existence of these damages weakens the laminate and increases the load shared by the fibers in the 0° ply, which increases the volume of fiber breakage rapidly and the final rupture of the laminate is expected.

The corresponding damage accumulation profile is shown in Figure 2-14. The damage accumulation of laminates made from unidirectional prepreg materials under cyclic loading usually has three stages. Rapid damage accumulation occurs at the beginning of fatigue test, leading to fast reduction in residual strength of the material. The following stage usually manifests a damage buildup in a gradual manner. Rapid damage accumulation takes place again during the last stage of fatigue test leading to the ultimate failure of material.

Figure 2-13 Damage development in a cross-ply laminate subjected to tension-tension cyclic loading

(Naik, 2003)

Figure 2-14 Fatigue damage accumulation in laminated composites during fatigue life (Naik, 2003)

Both destructive and nondestructive methods are potential tools to observe damage in advanced composites under fatigue loading. However, it is impractical to adopt destructive techniques to observe the continuous damage evolution in a composite during fatigue test. A number of non-destructive evaluation (NDE) methods have been reported in the literature as effective techniques for the damage analysis of laminate composites. Infrared thermography was used by Montesano et al. (2014) to assess the fatigue behavior and the corresponding damage states of a textile polymeric composite plate. They found that the thermographs were capable of establishing local high temperature regions that corresponded to damage within the braider yarns. Takeda et al. (1995) studied the damage progress in cross-ply CFRP laminates under tensile fatigue loading using the replica technique. During the fatigue tests, the test was periodically stopped and the polished edge surface of the specimen under test was replicated on a replica film (acetyl cellulose film). The replica film was then observed by optical microscopy to identify the transverse cracks and delamination formed during fatigue loading. Thermography, microscopy and optical fracture analysis with high-speed photography were used by Schmidt et al. (2012) for the monitoring of the void formation, multiaxial fatigue damage mechanisms and final failure process in glass-fiber reinforced composites. As an on-line monitoring tool, acoustic emission (AE) is ideally suited for the for damage analysis of composite materials (Bhat et al. 1994; Dzenis, 2003; Bourchak et al. 2007; Philippidis and Assimakopoulou, 2008; Tsamtsakis et al. 1998; Reis et al. 2011). An important step is to identify and establish the AE characteristics of individual failure mechanisms in order to using this technique to understand fatigue damage in

composite materials. Other techniques for detecting fatigue damage include, for example, electrical resistance (R) measurement (Wang and Chung, 1998; Irving and Thiagarajan, 1998), ultrasonic resonance and acoustic microscopy (Dzenis, 2003).

In general, the modulus and strength of the material are sensitive to fatigue damage accumulation. The loss in stiffness during fatigue test and the residual properties of composites after cyclic loading has attracted much attention for decades. Daniel and Charewicz (1986) reported experimental results on the stiffness and residual strength reductions in cross-ply graphite/epoxy laminates under tensile fatigue loading. It was reported that the residual modulus manifested a sharp reduction initially, followed by a moderate decrease up to the final failure of the sample. Change of the residual strength with fatigue cycles showed evident three stages (Figure 2-15). A sharp reduction was observed initially, followed by a plateau in the middle part of the fatigue test. A rapid decrease in residual strength appeared in the last session of the fatigue life. O'Brien and Reifsnider (1981) measured the reductions in stiffness resulted from fatigue damage for boron/epoxy laminates. Uniaxial tension, rail shear and flexure tests were conducted to measure the degradation in E_{xx} , E_{yy} and G_{xy} . The loss of dynamic stiffness as a function of fatigue cycles was found. All the three types of in-plane stiffness decreased after cyclic fatigue loading with the percentage of change in individual stiffness depended on the layup of the laminate.

Figure 2-15 Degradation in residual strength of laminated composites during fatigue test featured by evident three stages (Daniel and Charewicz, 1986)

2.4.2 Fatigue crack development in aluminum alloy

For aluminum alloy, fatigue is also a phenomenon in which cracks develop and propagate under cyclic loading leading to the eventual failure of the structure. In metallic materials, the fatigue process is commonly divided into three stages prior to fracture: crack initiation, stage I crack propagation and stage II crack growth (Forsyth, 1963; Plumbridge, 1972). Plumbridge (1972) summarized the fatigue-crack propagation in metallic materials. Once a stress in excess of the yield value of the material is applied, the production and movement of dislocations will take place, which subsequently produce slip bands or slip lines. The slip bands become broader and deeper under repeated stressing. A micro-crack eventually initiates. There are several other common crack initiation mechanisms which include, for example, crack initiated by the fracture of second-phase particles (Patton et al. 1998),

cracks initiated at surface inclusions (Pearson, 1975). Stage I growth is technically the enlargement of initiated micro-cracks. Therefore, it is impractical to distinguish between crack initiation and stage I growth. Several mechanisms were proposed for the elucidation of stage II fatigue-crack propagation and striation formation as outlined by Plumbridge (1972). For instance, Forsyth and Ryder (1961) suggested that cleave fracture occurred ahead of the crack tip in a precipitation hardened alloy and the striation profile was formed by the necking of the intermediate material. Another potential mechanism proposed stated that the formation of sub-grains would help with absorbing deformation and arresting the crack (Grosskreutz, 1963). The dominant factor for crack growth generally depends upon the microstructure of the specific material. The various mechanisms developed may be valid under different circumstances.

2.5 GLARE

GLARE belongs to FML, a group of composites that offer significant improvements compared to current materials used for aircraft structures due to weight reduction and improved damage tolerance characteristics (Botelho et al. 2006; Botelho et al. 2004; Vogelesang and Vlot, 2000; Sinmazçelik et al. 2011). Nowadays, several types of FML laminates are being studied such as GLARE (glass fiber/epoxy/aluminum) (Botelho et al. 2006; Botelho et al. 2004; Sinmazçelik et al. 2011), Arall (aramid/epoxy/aluminum) (Botelho et al. 2006; Botelho et al. 2004; Sinmazçelik et al. 2011) and Carall (carbon fiber/epoxy/aluminum) (Vogelesang and Vlot, 2000).

2.5.1 Introduction

GLARE consists of several layers of thin aluminum sheets interspersed with layers of glass fiber reinforced polymeric matrix composite materials. GLARE was originally developed at Delft University of Technology at the beginning of 1980 (Lin and Kao, 1995; Castrodeza et al. 2002; Soprano et al. 1996; Vlot, 1993, 1996). Later, a partnership between AKZO and ALCOA started to operate in 1991 to produce and commercialize GLARE (Kawai and Hachinohe, 2002; Castrodeza et al. 2006). Figure 2-16 shows an example of a cross-ply GLARE laminate. It takes advantages of metal and fiber-reinforced composites, providing superior mechanical properties that cannot be achieved by either of its constituents (Chang et al. 2008). Major advantages of GLARE include low density, high fracture toughness and strength, high impact and fatigue resistance, excellent moisture and corrosion resistance, and so on (Castrodeza et al. 2003; Asundi and Choi, 1997). Due to the advantages listed above, GLARE is sought after for more and more applications in aerospace industry. For instance, GLARE is selected for the Boeing 777 impact resistant bulk cargo floor and the upper fuselage panels of Airbus A380 (Sinmazçelik et al. 2011).

2.5.2 Hygrothermal effects on GLARE

Publications on the hygrothermal effects of laminated composites are abundant in the literature, while the investigation of the various hygrothermal effects on fiber-metal laminates is relatively a new field of research. As aforementioned, polymeric matrix composites usually absorb moisture when held in humid environment or immersed in water, and their properties are affected consequently. The moisture

absorption in FML composites is slower when compared with polymer composites, even under the relatively harsh conditions, due to the barrier of the aluminium outer layers. For polymer composites, the moisture absorption mainly takes place on the top and bottom surfaces of the laminate, while the free edges usually contribute a much lower portion to moisture transportation. In FML, basically only the outer aluminium layers are exposed as a result of its lay-up design. The prepreg layers are only exposed through the free edges of the laminate and holes, if any (Botelho et al. 2007b).

Figure 2-16 Schematic illustration of a cross-ply GLARE laminates (Bellenger, 1989)

Moisture and chemicals however can penetrate the composite lamina at free edges. Thus, moisture can still be a threat to GLARE laminates. On the other hand, the hybrid nature of GLARE laminates may make the environmental degradation process much more complicated since epoxy resins generally absorb moisture when exposed to humid environments and metals are prone to surface corrosion (Botelho et al. 2005). For instance, how moisture and other environmental conditions affect

the metal/prepreg lamina interface is unknown. Thus the investigation of the hygrothermal effects of GLARE laminates is crucial for the understanding of the behaviour this material under various environmental conditions.

Botelho et al. (2005) investigated hygrothermal effects on damping behaviour of GLARE composites. The experimental results of their work indicated that the E' modulus of the glass fiber/epoxy (G/E) composites decreased during hygrothermal conditioning. However, for GLARE laminates the E' modulus remained unchanged during the cycle of hygrothermal conditioning. He concluded that the outer aluminium sheets in the GLARE laminate shielded the G/E composite laminae from moisture absorption, which in turn prevented, to a certain extent, the material from hygrothermal degradation. Botelho et al. (2007c) also studied the elastic properties of hygrothermally conditioned GLARE laminates. He found that while the tensile and compression values of glass/fiber epoxy composites reduced after hygrothermal conditioning, no changes in mechanical properties (tensile and compression strength) were observed for GLARE laminates, regardless the hygrothermal conditioning.

While plenty of experimental data on the fatigue behaviour of GLARE laminates can be found in the literature (Takamatsu et al. 1999; Young et al. 1994; Miyata et al. 1996), results concerning the effects of hygrothermal conditioning on the fatigue life of GLARE laminates are limited. For the fatigue test of GLARE laminates, fatigue crack initiation generally occurs in the aluminium layer first. Fatigue life to the detection of the first crack at the aluminium layers is defined as the fatigue initiation life. Homan (2006) investigated the effect of exposure to a combination of moisture and elevated temperature (85% humidity, 70 °C, 3000 h) on the fatigue

initiation life of GLARE laminates. It turned out that the exposure did not affect the initiation behaviour of fibre metal laminates. However, whether hygrothermal exposure would affect the total fatigue life of GLARE laminates was not considered in their investigation. Research work by DA SILVA et al. (2009), however, did resolve this aspect. Aluminum alloy 2024-T3 sheets and prepreg materials made of glass fiber in plain weave fabric form and epoxy were used to fabricate GLARE laminates. As fabricated GLARE samples were placed into an environmental conditioning chamber in which a hygrothermal environment with a temperature of 80°C and a relative humidity of 90% was maintained. Prior to tension-tension fatigue testing, 0.3% increase in weight because of moisture uptake in GLARE laminates was achieved. The phenomenon observed was that the fatigue life of hygrothermally conditioned GLARE laminates was shorter when compared to unconditioned samples. However, the change in microstructure associated with hygrothermal conditioning was not taken into consideration in this publication.

2.6 Conclusions

In this chapter, basic information about laminated composites and their applications and manufacturing processes is briefly presented followed by the introduction of the impact properties as well as low-velocity impact tests of polymeric matrix composite materials. Research work already been conducted on hygrothermal effects on composites are specially reviewed in details. An introduction of the fatigue behaviour of both PMCs and aluminium alloy was particularly added. A short introduction about GLARE laminates is also included.

Most importantly, shortcomings in the research work reported in the literature are identified to build up the scope for the current thesis. Results about impact testing on hygrothermally conditioned PMCs are rarely found in the literature. This gave impetus to study the impact response of hygrothermally conditioned CFRP composites. While CSP particles have proved earlier to be effective impact modifier, the durability of CSP particle-reinforced GFRP laminates under hygrothermal environments has not been investigated. GLARE laminates are relatively new but promising aerospace materials. However, results concerning the effects of hygrothermal conditioning on the fatigue life of GLARE laminates are very limited. Further investigations are therefore necessary to fill in these gaps identified through the literature review.

Chapter 3 Experiment details

In this chapter, the materials and equipment involved in the various experiments planned in this study are enumerated. Details about each mechanical test or experiment are also introduced in this chapter.

3.1 Specimen preparation

3.1.1 Impact test samples

3.1.1.1 CFRP unidirectional-prepreg laminates

CFRP unidirectional (UD)-prepreg laminates are referred to as laminates made from unidirectional carbon fiber epoxy prepreg materials in this thesis. In order to study the effects of staggered lay-up structures which result from automated tape lay-up process on the properties of laminated composites, two types of laminates were fabricated; namely, normal and staggered lay-up laminates from CFRP unidirectional prepreg materials.

The material used was L-930HT (GT700) solution coated unidirectional epoxy prepreg (CFRP) material manufactured by J.D. Lincoln Inc., suitable for applications with a service temperature beyond 82°C. The epoxy resin in this prepreg material is diglycidyl ether of bisphenol A (DGEBA). Physical properties of the GT700 carbon fiber used in the prepreg material are listed in Table 3-1. L-930HT (GT700) is a flame retardant unidirectional modified epoxy prepreg with excellent mechanical properties. It is a versatile general-purpose prepreg material which can be cured over a broad range of temperatures and pressures. It performs well in aerospace, sporting

goods, automotive and other commercial applications. The prepreg materials were stored in a freezer where the temperature is maintained at around -30°C .

The stacking sequence used for both, normal and staggered lay-up laminates, was [45/90/-45/0]_s. During the course of fabrication of both, normal and staggered, laminates, unidirectional prepregs were first cut with care into 0° and 45° lamina of $10 \times 10 \text{ cm}^2$, which is the allowable specimen size for impact test. After being exposed to the lab conditions (23°C and RH around 50%) overnight, the laminae were stacked into a laminate according to the above-mentioned stacking sequence for curing. A roller was used to roll the plies during the lamination process in order to make void-free adhesion between laminae.

Table 3-1 Physical properties of GT700 carbon fiber (extracted from the datasheet provided by the manufacturer, J.D. Lincoln Inc.)

Fiber Areal Weight	150 g/m ²
Standard Resin Content	40% by weight
Volatile Content	2% max
Standard Tack	Medium
Cured Ply Thickness	0.165-0.178 mm

Compared to normal laminates, the fabrication of staggered laminates necessitated an extra step. During the preparation of staggered laminates, each lamina was cut into smaller strips (3 strips for 0° and 90° laminae, and 4 strips for $\pm 45^{\circ}$ laminae) along the direction of the fibers before stacking into a laminate (Figure 3-1).

The curing equipment used was an autoclave manufactured by Bondtech Corporation, which is a pressure vessel that provides good control of the curing parameters for composites, including heat-up rate, curing temperature, pressure and

vacuum. Shown in Figure 3-2 is the curing program for all the laminates made from prepreg materials including CFRP prepreg materials and GFRP prepreg materials. The values of curing parameters are listed in Table 3.2. The actual curing temperature is approximately 121.5°C, which is within the recommended curing temperature range (121-135°C) for the prepreg material used. The heating rate is 1.62°C/min, which is slow enough to guarantee uniform temperature distribution on the tooling and the laminates. The curing time was 1 hour longer than that recommended by the manufacturer in order to obtain fully cured specimens.

Figure 3-1 Lamination of staggered laminates: (a) Cutting methodology for 0° lamina; (b) Cutting methodology for 45° lamina; (c) A staggered laminate after lamination

Figure 3-2 Curing program for autoclave curing

Table 3-2 Curing parameters of the curing program adopted

Curing Parameters	Value
curing temperature	122°C
actual curing temperature	~121.5°C
curing time	2 hours
pressure	606.7kPa
vacuum	-84kPa

Prior to autoclave curing, a vacuum bag assembly was made, which included specimens waiting for curing, a mold and other curing related accessories. Figure 3-3 is the schematic representation of the vacuum bag assembly for autoclave curing while a real vacuum assembly used in this experiment is shown in Figure 3-4. Vacuum is very important for autoclave curing. It serves to suck out gases, volatiles and extra resin out of specimens. Figure 3-5 shows the differences between samples cured with vacuum and without vacuum during curing. It is evident that the samples cured with vacuum during curing tended to have smoother surface when compared with those cured under non-vacuum conditions. Generally, the weight of the samples

cured with vacuum is lower than that of the samples cured without vacuum. Table 3-3 shows the details of the vacuum bag lay-up accessories.

Figure 3-3 Schematic representation of a vacuum bag lay-up

Figure 3-4 Vacuum bag assembly for autoclave curing

Once finished, the vacuum bag assembly was put into the chamber of the autoclave for curing (as shown in Figure 3-6). Figure 3-7 shows the autoclave used in this study. Specimens were taken out from the autoclave after the curing process was completed and the autoclave was cooled down to room temperature.

Table 3-3 Brief introduction of various accessories used in vacuum bag assembly

Item	Brief Introduction
Aluminum plate	It is used to hold the whole vacuum bag assembly.
Non-porous peel ply	It prevents matrix resin from flowing away or further to the aluminum plate.
Bleeder material	It absorbs the extra resin flowing from the specimen during curing.
Porous peel ply	It allows free passage for volatiles and excess resin during curing and ensure smooth surface of laminates.
Aluminum top plate	It is a part of the aluminum mold which ensures uniform pressure exerted on laminates.
Aluminum mold	It plays a crucial role in autoclave curing by ensuring the dimensional stability of specimens which are pressed by high pressure during curing. Also mold release agent should be applied prior to curing in order to prevent matrix resin from sticking to the mold.
Vacuum bag films	It is used to form a vacuum bag.
Sealant tape	It provides perfect seal between the vacuum bag film and aluminum plate
Thermal couple	It is used to detect the temperature within the vacuum bag.

Figure 3-5 Comparison between samples cured with and without vacuum: (a) A sample cured with vacuum; (b) a sample cured without vacuum

Figure 3-6 A vacuum assembly in autoclave chamber

Figure 3-7 Autoclave and vacuum pump used in this study

The weight of the specimens which was defined as their initial weight in this report was measured after they were taken out from the autoclave. An analytical

balance which is precise to 0.1mg for coupons weighing less than 50g and 1mg for coupons heavier than 50g was used to measure the weight of specimens. Figure 3-8 shows the balance used in this experiment.

Figure 3-8 Analytical balance used in this study

In order to prevent specimens from absorbing large amount of moisture in the lab condition in which the relative humidity is around 50%, all specimens were stored in a dry cabinet (Figure 3-9) for subsequent conditioning or mechanical testing. The relative humidity and temperature inside the dry cabinet were 22% and 23°C, respectively.

Figure 3-9 Dry cabinet used in current study

3.1.1.2 CFRP woven-prepreg laminates

CFRP woven-prepreg laminates for low-velocity impact test were fabricated using a 3K carbon/epoxy woven prepreg that had a standard resin content of 40% by weight before curing. The preregs were L-930HT (GT700) in woven form manufactured by J.D. Lincoln Inc. The woven preregs were cut into laminae of size 100mm×100mm after being defrosting in the lab condition for 4 to 5 hours. The laminae were then stacked into laminates consisting of 8 layers according to a stacking sequence of $[0/90]_8$. A roller was used to compact the plies during stacking in order to achieve void-free adhesion between adjacent layers. The laminated lay-ups were cured in a convection oven at 130°C for 4 hours. A pressure measuring 5kPa was applied to the laminates by placing dead weights on to the specimens. Figure 3-10 shows the convection oven used for the curing of CFRP woven impact laminates. The oven allows a temperature up to 300°C and provides digital temperature and time setting. Similar to autoclave curing, porous peel ply, bleeder material, non-porous peel ply and aluminum plates were placed on the two surfaces of specimens as shown in Figure 3-10 (b).

Figure 3-10 Convection oven used in this study: (a) chamber of convection oven; (b) Oven loaded with specimens

For curing in oven, there are three major factors that should be considered, that is, temperature, time and pressure, which is usually exerted by the metallic blocks. Temperature influences the mobility of epoxy resin by decreasing its viscosity. So, more resin would flow out during the curing process at higher temperatures. The pressure is also an important factor which served to decrease the density of voids inside specimens and increased the amount of resin flowing out of specimens. Preliminary experiments showed that if there was little resin coming out of composite laminates, the quality of specimen surface would be affected. Enough curing time is required in order to get fully cured coupons.

3.1.1.3 GFRP laminates dispersed with CSP particles

The prepreg materials used for the fabrication of GFRP laminates was L-530 (7781) prepreg material manufactured by J. D. Lincoln Inc. It is a solution coated epoxy prepreg material which has been modified to increase its flame resistance. The L-530 epoxy resin in this prepreg material is also diglycidyl ether of bisphenol A (DGEBA). The reinforcement used in this prepreg material is 7781 fiberglass fabric. Listed in Table 3-4 are the properties of 7781 glass fabric.

Table 3-4 Physical properties of 7781 glass fabric (extracted from the datasheet provided by the manufacturer, J.D. Lincoln Inc.)

Standard Weight	488 g/m ²
Standard Resin Content	38% by weight
Volatile Content	2% by weight
Standard Tack	Medium
Cured Ply Thickness	0.254 mm

Pregregs of L-530 (7781), which were previously stored in a freezer at -30°C , were cut into laminae of $10 \times 10 \text{ cm}^2$ after being defrosted in lab condition for 4~5 hours. Later, Laminae were stacked into laminates of 8 plies for curing. Except that the prepreg materials used were different, GFRP laminates were fabricated under the same conditions as CFRP laminates made from unidirectional prepregs, that is, they were cured by the autoclave with the same curing program.

The CSP particles (PARALOID EXL-2314) used as impact modifier in GFRP laminates were supplied by the Dow Chemical company, Singapore. These particles were in the form of fine white powder and appear as discrete particles without any agglomeration. They have a soft rubber (PBA) core and a transparent shell of poly (methyl methacrylate) (PMMA) with an epoxy functional group grafted to the shell to improve the interfacial bond of the particles with epoxy matrix. The morphology of as received CSP particles is shown in Figure 3-11.

Figure 3-11 Morphology of as received CSP particles observed under SEM

During the fabrication of GFRP laminates dispersed with CSP particles, CSP particles were dispersed manually at all the 7 inter-ply interfaces as schematically shown in Figure 3-12. The lamination process of GFRP laminates with CSP particles

is shown in Figure 3-13. In order to achieve a more uniform distribution of CSP particles at the interfaces of GFRP laminates, CSP particles were firstly dispersed onto a peel ply (Teflon release film) with an areal density of 30g/m^2 (Figure 3-13). Later, CSP particles on the peel ply were successfully transferred to the GFRP ply by placing the GFRP ply on the top of the peel ply.

Figure 3-12 Schematic representation of a GFRP laminate with CSP particles dispersed at all the 7 interfaces

Figure 3-13 Lamination process of CFRP laminates with CSP particles

3.1.2 Tensile test samples

3.1.2.1 CFRP woven tensile samples

CFRP tensile sample was made from L-930HT (GT700) woven prepreg materials. It had 8 layers following a stacking sequence of $[0^\circ/90^\circ]_8$. The dimension of the samples was 252mm×26mm×1.322mm. CFRP woven tensile samples were cured in the autoclave with the curing program shown in Figure 3-2. An aluminum mold (Figure 3-14) was used during curing in order to improve the quality of cured laminates. The mold has six cavities with a dimension of 252mm×26mm. The same vacuum bag assembly was used as shown in Figure 3-3.

Figure 3-14 Aluminum mold used for the curing of CFRP woven and GFRP tensile samples

3.1.2.2 GFRP tensile samples

GFRP prepreg materials, L-530 (7781), were used to fabricate GFRP tensile samples, which were cured from 8 plies of prepreg materials. The dimension of GFRP tensile samples was also 252mm×26mm. The same curing methodology as CFRP woven tensile samples was selected for the curing of GFRP tensile samples.

3.1.2.3 Pure epoxy tensile samples

Results of short-term hygrothermal conditioning indicated that moisture served to improve the elastic deformation ability of CFRP laminates under low-velocity impact. Therefore, it has been planned to study the effects of moisture on the static properties of pure epoxy resin. The epoxy resin and curing agent (hardener) selected were diglycidyl ether bisphenol A (DGEBA), diethylenetriamine (DETA), respectively, supplied by Sigma-Aldrich Corporation. The dimensions of the epoxy specimen are shown in Figure 3-15. The thickness of the specimen is 3.2mm. All the dimensions of the pure epoxy specimen tensile sample were determined according to ASTM D638. Epoxy tensile samples were fabricated by pouring a mixture of the epoxy resin and hardener into a rubber mold. The preparation process of the rubber mold assembly is shown in Figure 3-16. Firstly, an aluminum mold was made from aluminum steel 6061 alloy. The rubber mold was then made by pouring silicone mold making material into the aluminum mold.

Figure 3-15 Geometry of the pure epoxy tensile specimen (top view and side view)

DGEBA and DETA were mixed according to a stoichiometric ratio of 100:12 and stirred manually to achieve a uniform mixture of these two components. Stirred resin was de-gassed in a vacuum oven to remove the air trapped inside the resin for 10 minutes. Vacuum degassed resin was then poured into the rubber mold. The epoxy

resin was kept in the rubber mold at room temperature for 2days. Later, epoxy specimens were cured in an oven at 100°C for 2hours.

Step I: fabricate an aluminum mold.

Step II: fabricate the rubber mold using the aluminum mold.

Step III: Prepare the rubber mold assembly for curing.

Figure 3-16 Preparation of the rubber mold assembly for the fabrication of epoxy tensile sample

3.1.3 Double cantilever beam samples

Delamination is one of the major damage modes of laminated composite materials. Therefore, the investigation of the effects of hygrothermal conditioning on the interlaminar fracture toughness was carried out in this project.

Double cantilever beam (DCB) specimen for Mode I interlaminar fracture toughness test was made from carbon fiber reinforced epoxy woven prepreg material, L-930HT(GT700) in woven form, manufactured by J. D. Lincoln Inc. Prepreg materials were first cut into lamina of 252×26mm and then laminated according to

the stacking sequence $[0/90]_{14}$. A PTFE thin film with a thickness of $30\mu\text{m}$ was placed at each side of the laminated plies during lamination in order to introduce an initial crack to the DCB specimen (Figure 3-17). Laminated plies were then cured in the autoclave with the curing program shown in Figure 3-2. In order to maintain the dimensions of the cured samples, laminated plies were put into the aluminum mold shown in Figure 3-14 during curing. The cured laminate with PTFE films was cut at the center using a diamond saw. Two DCB samples having a dimension of $126 \times 26\text{mm}$ were therefore obtained. An aluminum block with the same width as the DCB sample was bonded to each side of the DCB sample using epoxy glue. The geometry of as prepared DCB sample is shown in Figure 3-18(a).

Figure 3-17 Schematic representation of laminated plies before curing

Figure 3-18 Geometries of the DCB specimen and the loading block

3.1.4 GLARE laminates

The GLARE materials investigated were plates of GLARE 4A material (GLARE 4A-4/3-0.3) provided by Delft University of Technology. The construction of the GLARE 4A plates is illustrated in Figure 3-19. The stacking sequence of the glass/epoxy layer is [0/90/0]. GLARE 4A plates of 200mm×200mm×2.317mm were cut into samples of 200mm×12mm×2.317mm for tensile and fatigue tests via water jet cutting. GLARE 4A coupons were dried in a vacuum oven at 45°C for 48hours to remove the moisture absorbed during water jet cutting.

Figure 3-19 Schematic representation of the construction of GLARE 4A laminate

3.2 Conditioning of samples

In this project, two types of hygrothermal conditions were designed. The first type of hygrothermal ageing was water immersion conditioning during which samples were immersed in water at constant temperatures such as 60°C and 80°C. These temperatures represented possible in-service temperature of composite

materials. Two water bathes (Figure 3-20) were used for water immersion conditioning. Water bath A is Julabo TW20 which is integrated with a microprocessor and purchased from Julabo Singapore Pte. Ltd. Its technical specifications are listed in Table 3-5. Water bath B is a circulating thermostat manufactured by Peter Huber Kältemaschinenbau GmbH of Germany. It is an assembly of Compatible Control CC3 and K20. Compatible Control CC3 is the controller of this device, which is programmable and provides over-temperature protection. When filled with certain thermofluid and connected to an external cooler, it allows a working temperature range of -30°C to 200°C. K20 is the cooling bath. The temperature stability of both water bathes is ± 0.3 °C.

Table 3-5 Technical Specifications of Julabo TW 20

Working temperature range	20~99.9°C
Temperature control	PID
Temperature stability	± 0.2 °C
Integrated programmer	not available
Heater capacity	2000 W

The second type of hygrothermal conditioning required samples to be exposed to a number of hygrothermal cycles, which was generally a combination of cold/dry and hot/wet environments. Two types of such hygrothermal cycles were designed. The first type of hygrothermal cycle was composed of 12 hour in water at 60°C and 12 hour in a freezer at -30°C, while the second one consisted of 12 hour in water at 80°C and 12 hour in a freezer at -30°C. The freezer used to provide cold/dry condition was shown in Figure 3-21.

3.3 Impact test of samples

The impact damage resistance of as-processed specimens and hygrothermally conditioned specimens was determined by an instrumented impact testing machine, Instron Dynatup 8250 drop tower impact tester, which is shown in Figure 3-22.

Figure 3-20 Water bathes used in this study: (a) Julabo TW 20; (b) Circulating Thermostat CC3-K20

Figure 3-21 Freezer used for conditioning and keeping prepreg materials

The Instron Dynatup 8250 drop tower impact tester applies impact forces to materials and structures, measures the loads generated as the material absorbs the impact energy, and performs calculations on data collected. The weight and height of the impactor can be set to desired values in order to achieve required impact energy or velocity. It is fitted with an instrumented tup that can measure the loads generated during the impact event. The system operates in conjunction with the Instron Dynatup Impulse data acquisition software and Impulse signal conditioning unit. It captures the load data at high frequency, thereby capturing the behavior of the specimen or structure as they deform and/or fail under impact. The data acquisition software is very convenient as it calculates test results and graphs the data. Load, time, deflection, velocity and energy, which are crucial for the characterization of impact properties of specimens, are all generated during impact testing event.

The first step of testing a specimen by an impact tester is to determine the impact energy, weight and height of the impactor according to ASTM D7136.

$$E = C_E \times h \quad (3-1)$$

where:

E = potential energy of impactor prior to drop, J,

C_E = specified ratio of impact energy to specimen thickness, 6.7 J/mm, and

h = nominal thickness of specimen, mm.

$$H = \frac{E}{mg} \quad (3-2)$$

where:

H = drop height of impactor, m,

m = mass of impactor for drop height calculation, kg, and

g = acceleration due to gravity, 9.81 m/s^2 .

Figure 3-22 Drop tower impact tester used in current study

There are two types of impactor weight that can be chosen for impact testing, namely, 2.735kg and 5.505 kg. An appropriate impactor mass must be chosen so that

the drop height is not less than 300mm. The drop height can be set by adjusting the position of the white sensor mounted on the bracket located on the left-hand side of the drop tower (as shown in Figure 3-23). Once the white sensor is secured, the system will raise the drop weight assembly to the desired height automatically after each of previous impact testing.

Velocity of the striking impactor is measured through a velocity detector assembly which operates in conjunction with a flag mounted on the drop weight assembly as shown in Figure 3-24. Whenever there is significant difference between the thicknesses of two consecutive coupons, the position of the velocity detector should be adjusted prior to impact testing so that it detects the velocity of the impactor immediately before contacting with the specimen. Move the velocity detector so that the bottom edge of the detector aligns with the bottom edge of the flag as shown in Figure 3-25.

Figure 3-23 Impact height setting by adjusting the position of the white sensor

Figure 3-24 Velocity detector assemblies

The third step is to create a testing profile suited for present requirements under the Instron Dynatup Impulse data acquisition software. In order to obtain correct impact energy values calculated by the system automatically, the impactor mass defined in the testing profile should be consistent with the actual impactor weight applied during an impact test.

Figure 3-25 Velocity detector position setting (extracted from Instron operation manual)

Only after finishing the above-mentioned three steps, the course of impact testing can be started and normal impact testing data such as deflection and energy can be

expected. Place the specimen between two aluminum plates of the pneumatic clamping fixture, both of which have a circular hole of 76mm in diameter. Once the coupon is fully secured between the aluminum plates by pneumatic force, release the drop weight assembly from predefined height and the impact tup which is placed between two guide columns will fall freely under gravity and hit the center of specimen. The impact process is started and the process data such as contact force and deflection will be collected by the data acquisition system simultaneously.

3.4 Tensile test of samples

All the tensile tests in the current investigation were performed using an MTS 810 Elastomer Test System (Figure 3-26a) at a crosshead speed of 1 mm/minute according to ASTM D3039. An axial extensometer was attached to the laminate during the tensile test to measure the strain in the laminate (Figure 3-26c). The specimen was clamped by a hydraulic force, which could be adjusted using the control panel shown in Figure 3-26b. The magnitude of the gripping force was determined by the peak load during tensile test. Table 3-6 summarized the gripping force for different types of samples.

Table 3-6 Gripping force for different samples during tensile test

Type of sample	Gripping force (MPa)
CFRP woven sample	7.5
GFRP sample	5.0
Pure epoxy tensile sample	0.7
GLARE 4A laminate	5.0

(a) MTS 810 Elastomer Test System

(b) Gripping force control panel

(c) Extensometer for strain measurement (gauge length 25mm)

Figure 3-26 The test system for tensile test in the current investigation

3.5 Mode I fracture toughness test

Mode I fracture toughness test was performed using an Instron universal mechanical tester series 5574, material testing machine, as shown in Figure 3-27. The testing rate (rate of cross-head displacement) was 2mm/minute. The displacement and load during the course of testing was measured by machine. The observation of crack propagation was assisted by painting the edge of the DCB sample with white typewriter correction fluid. A paper ruler was attached to the DCB sample as shown in Figure 3-28. The total crack length was calculated by Equation (3-3):

$$\text{Crack length} = \text{reading of the paper ruler} + a_0 \quad (3-3)$$

Figure 3-27 Instron 5574 for Mode I fracture toughness test

Figure 3-28 Mode I fracture toughness test set-up for DCB specimens

3.6 Tension-tension fatigue test

The fatigue behavior of GLARE 4A laminates were tested using the MTS 810 Elastomer Test System shown in Figure 3-26. The load (stress) was the test control parameter during the course of constant amplitude fatigue test. Three fatigue stress levels ($\frac{\text{Maximum fatigue stress}}{\text{Ultimate tensile strength}}$) were chosen for both unconditioned and conditioned

GLARE 4A laminates. During the tension-tension fatigue test, the change of the load exerted on the sample against the time followed a sine wave. The frequency was 5Hz. A fatigue ratio $R \left(\frac{\text{Valley load}}{\text{Peak load}} \right)$ of 0.1 was maintained throughout the fatigue test of both dry and aged groups.

3.7 Microstructure characterization & damage observation

The microstructures of the reference and conditioned specimens were characterized using SEM (JEOL SEM 5600LV) and FESEM (JEOL FESEM JSM 7600). In the meanwhile, the damage induced by mechanical testing such as low-velocity impact were observed using SEM.

The sample preparation method for SEM and FESEM observation was similar except that the gold coating time required was different. Prior to observation with FESEM/SEM, coupons cut from the intended area of a sample to be observed using a diamond saw were firstly polished by 800 grit, 1200 grit and 2400 grit SiC paper followed by polishing them using a polishing cloth sprayed with 0.3 μm alumina powder. The coupons thus prepared were gold coated for 20 seconds via a sputter coating machine to make them conductive for FESEM/SEM observation. The gold coating time required for SEM was 60 seconds instead.

OLYMPUS SZX7 zoom stereo microscope, a type of optical microscope, was also used for structure and damage observation. No extra sample preparation action was required prior to observation under optical microscope.

3.8 Concluding remarks

In this chapter, the materials tested, experiments conducted and relevant equipment used in this investigation has been introduced and discussed in sufficient details. It may be noted that due attention is given to the specifications of the materials chosen as well as the standard fabrication procedures. All tests were planned according to the recommended testing standards. The facilities chosen were also well calibrated and maintained. Thus, all necessary facilities were sourced and utilized in this study.

Chapter 4 Short-term ageing on CFRP laminates

4.1 Introduction

A comprehensive and in depth experimental plan was carried out with the main purpose of investigating the effects of hygrothermal conditioning on the microstructure and low-velocity impact response of carbon fiber reinforced epoxy composite materials. CFRP unidirectional (UD)-prepreg laminates, CFRP woven-prepreg laminates were firstly cured in either the autoclave or the convection oven, then immersed in a water bath at different temperatures or exposed to hygrothermal cycles, finally tested under impact at different energy levels. The moisture absorption behavior of these two types of materials under various environments has been studied. Microstructure of the laminates before and after hygrothermal ageing was observed using a scanning electron microscope (SEM). Impact testing was conducted to study the effects of moisture and hygrothermal ageing on the impact resistance of laminated composites. Also, the differences in the moisture absorption behavior and impact properties of normal and staggered lay-up laminates are discussed.

More importantly, in order to further understand the role played by absorbed moisture in laminated composites, tensile tests on CFRP woven laminates, Mode I fracture toughness tests on CFRP woven laminates and tensile tests on pure epoxy

resin samples were conducted to establish the relationship between the various mechanical properties of composites and the moisture residing inside the epoxy resin.

4.2 CFRP UD-prepreg laminates

The results of short-term hygrothermal conditioning study on CFRP UD-prepreg laminates are presented in this session. Laminated composite specimens were firstly fabricated from unidirectional CFRP prepreg materials, L-930HT (GT700) and then exposed to isothermal conditioning or cyclic hygrothermal environments. Impact testing was then carried out on specimens of different moisture contents and the microstructures of the laminates were examined using scanning electron microscope (SEM). The aim of this study is to discern the relationship between moisture contents and impact resistance of laminated composites and the mechanism on how moisture influences the impact properties of carbon fiber reinforced polymer (CFRP) laminates.

4.2.1 80°C Group

Three groups of CFRP UD-prepreg quasi-isotropic laminates (Groups 2~4) were immersed in a circulating water bath at 80°C, which allows a more uniform temperature profile within the water bath. They were immersed in water for different durations resulting in different moisture levels in the laminates. After the desired moisture content in these specimens had been achieved, they were tested by low-velocity drop tower tester together with unconditioned specimens, specimens of Group 1.

Automated tape lay-up technology (ATL) (Dirk et al. 2012) is widely employed today to manufacture advanced composite structures from unidirectional preregs. ATL machine delivers wide prepreg tapes onto a surface whilst automatically removing the ply protecting films. Each layer of laminates fabricated by this technology usually consists of numbers of prepreg tapes with gaps between individual tapes prior to curing. Therefore, staggered lay-up laminates simulating structures made from ATL were fabricated in order to study the effects of such gaps on the moisture absorption behavior and impact resistance of carbon/epoxy laminates.

4.2.1.1 Specimen fabrication

Four groups of samples were fabricated. Within each group, there were three normal and three staggered lay-up laminates. The stacking sequence was $[45/90/-45/0]_s$. The dimension of the cured laminates was $100\text{mm} \times 100\text{mm} \times 1.275\text{mm}$, which were cured in the autoclave and had an average resin content of 25.15 wt.% .

4.2.1.2 Hygrothermal conditioning scheme

Cured laminates were then immersed in water at 80°C for different durations to achieve different moisture contents. An analytical balance which is precise to 0.1mg for coupons weighing less than 50g was used to measure the weight of specimens periodically during conditioning. Three groups of CFRP UD-prepreg laminates (Groups 2, 3 and 4) were immersed in water at 80°C . The hygrothermal conditioning scheme for CFRP UD-prepreg laminates 80°C Group is summarized in Table 4-1. In this article, specimens with ID containing ‘N’ are normal laminates and those with

‘S’ in the IDs are staggered lay-up laminates. The first number indicates the group of the specimen whereas the second number refers to the specimen itself; for example, N41 represents normal specimen No. 1 of Group 4.

Table 4-1 Hygrothermal conditioning scheme for CFRP UD-prepreg laminates 80°C Group

Group	Immersion Time (h)	Specimen ID
Group 1	-	N11, N12, N13, S11, S12, S13
Group 2	39.00	N21, N22, N23, S21, S22, S23
Group 3	121.72	N31, N32, N33, S31, S32, S33
Group 4	1144.50	N41, N42, N43, S41, S42, S43

Before discussing the moisture absorption behavior of CFRP UD laminates, one important principle about diffusion has to be introduced, that is, Fick’s law. Fick’s first law states that the diffusion flux in the through-thickness direction z is proportional to the concentration gradient of the diffusing substance:

$$J = -D_z \cdot \frac{\partial C}{\partial z} \quad (4-1)$$

In many real situations the concentration profile and the concentration gradient $\frac{\partial C}{\partial z}$ are changing with time. The changes of the concentration profile can be described by a differential equation, Fick’s second law:

$$\frac{\partial C}{\partial t} = D_z \cdot \frac{\partial^2 C}{\partial z^2} \quad (4-2)$$

Solution of Equation (4-2) is concentration profile as a function of time, $C(z, t)$. Consider a plate of thickness h exposed on both sides to the same moist environment. The solution of Equation (4-2) is given by Jost (1960):

$$\frac{C - C_i}{C_m - C_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j+1)} \sin \frac{(2j+1)\pi z}{h} \exp\left[-\frac{(2j+1)^2 \pi^2 D_z t}{h^2}\right] \quad (4-3)$$

The total weight of the diffusing substance in the material is obtained by integrating Equation (4-3) over the plate thickness:

$$m = A \cdot \int_0^h C(z, t) dz \quad (4-4)$$

It is obvious that m is function of t . The result of this integration is (Jost, 1960):

$$G \equiv \frac{m-m_i}{m_m-m_i} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-(2j+1)^2 \pi^2 (\frac{D_z t}{h^2})]}{(2j+1)^2} \quad (4-5)$$

$$m = G(m_m - m_i) + m_i \quad (4-6)$$

m_i is the initial weight of the moisture in the plate and m_m is the weight of the diffusing substance in the plate when the material is fully saturated, in equilibrium with its environment (Springer, 1981). Both m_m and m_i can be treated as constants under given conditions.

For short times, the parameter G can be approximated as (Mallick, 1993):

$$G = 4 \left(\frac{D_z t}{\pi^2 h^2} \right)^{\frac{1}{2}} \quad (4-7)$$

For sufficiently large values of t , G can be approximated as (Mallick, 1993):

$$G \approx 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 D_z t}{h^2}\right) \quad (4-8)$$

From Equations (4-7) and (4-8), if the diffusion of moisture in a material follows Fick's law, moisture content of it will increase linearly with $t^{\frac{1}{2}}$ at the beginning. Moreover, the weight of a plate exposed to a humid environment on both sides can be expressed as:

$$W = W_{dry} + m \quad (4-9)$$

Thus, the weight of a Fickian specimen also increases linearly with $t^{\frac{1}{2}}$ initially when immersed in water or exposed to a moist environment. In summary, in case of Fickian diffusion, the moisture content and the weight of the material increase linearly with $t^{\frac{1}{2}}$ initially, and after a long period of time the m and W versus $\sqrt{t}$ curves approach asymptotically the maximum moisture content m_m and W_m , respectively, as shown in Figure 4-1.

Figure 4-2a shows the weight changing history of specimens of Group 4 as a result of moisture uptake when immersed in water. From the curves in Figure 4-2a, two conclusions can be drawn with certainty. First, the curves for all the six samples in this group are linear up to a point till which each specimen had absorbed 56% of its final moisture content, though, the aspect ratio of the composite specimens discussed here was $\frac{Width}{Thickness} = 81$, which is smaller than 100. Therefore, according to ASTM D5229, it was concluded that the diffusion of moisture inside CFRP laminates in the current study belongs to Fickian diffusion and edges effects could be neglected. Second, the slopes of the different curves are approximately the same at any point in time. The relative change in moisture contents in the samples of different groups is presented in Figure 4-2b, in which each point represented the average value of 6 specimens of each group.

The hygrothermal conditioning results of all the four groups of samples are summarized in Table 4-2. Each datum in Table 4-2 is the average value of 6 specimens of the same group. Specimens of Group 1 were stored in the dry cabinet and were not subjected to isothermal conditioning. Before impact testing, they were

dried again in the vacuum oven at 50°C in order to remove the moisture absorbed when stored in the cabinet. For specimens of Group 1, M_{final} is the moisture content after drying and is larger than zero because there was still certain amount of moisture residing inside the specimens. According to the conclusion made by Zhou and Lucas (1999), temperature that is not less than the glass transition temperature is required to remove the residual water. In the current work, such a high drying temperature was not used in order to prevent the effect of high temperature on the properties of laminates.

Figure 4-1 Schematic illustration of the weight of a specimen versus $\sqrt{t}$ under constant humidity and temperature conditions for Fickian diffusion behavior

Figure 4-2 Moisture absorption behavior of CFRP laminates in water at 80°C: (a) Weight change history of specimens of Group 4; (b) Average change in moisture content in samples as function of immersion time

Table 4-2 Summary of the hygrothermal conditioning result of CFRP UD-prepreg laminates 80°C

Group

Group	Number of specimens	W_{dry} (g)	Immersion Time (h)	M_{final} (%)	Thickness (mm)	Diffusivity D_z (mm ² /s)
Group 1	6	20.21669	-	0.060	1.275	-
Group 2	6	20.15508	39.00	1.110	1.277	4.044×10^{-7}
Group 3	6	20.21811	121.72	1.594	1.286	4.109×10^{-7}
Group 4	6	20.20884	1144.50	2.404	1.304	3.914×10^{-7}

M_{final} in Table 4-2 were calculated as follows:

$$M_{final} = \frac{W_{final} - W_{dry}}{W_{dry}} \times 100\% \quad (4-10)$$

In Table 4-2, D_z is calculated as follows according to ASTM D5229:

$$D_z = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (4-11)$$

where,

$$\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} = \text{slope of moisture absorption plot in the initial linear portion of the curve.}$$

As seen in Table 4-2, the average dry weight of Groups 1, 3 and 4 was approximately the same while the average dry weight of Group 2 was around 0.3% smaller than that of the other three groups. In Table 4-2, *Thickness* is the average thickness of each group measured before impact testing (Group 1) or after hygrothermal conditioning (Groups 2, 3, 4). As seen in Table 4-2, average thickness increased monotonically with average moisture content, indicating evident volumetric expansion resulted from moisture absorption.

4.2.1.3 Moisture uptake behavior of normal and staggered lay-up laminates

Normal and staggered lay-up laminates had the same stacking sequence and were cured under the same conditions. Within each group, normal and staggered lay-up laminates were subjected to the same period of hygrothermal conditioning. The t distribution was used to compare the difference in average dry weight and average diffusivity constant of the two types of laminates:

$$t = \frac{\bar{Y}_1 - \bar{Y}_2}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad (4-12)$$

and,

$$S_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \quad (4-13)$$

The null hypothesis H_0 is that the means of the two populations (normal and staggered lay-up laminates for the current case), μ_1 and μ_2 , are the same. Under the null hypothesis, Equation (4-12) follows the t distribution. If $|t| > t_{\frac{\alpha}{2}}(n_1 + n_2 - 2)$, then the null hypothesis should be rejected and one can claim with a confidence coefficient of $1 - \alpha$ that the two populations have different means ($\mu_1 \neq \mu_2$) and that the two groups of samples are taken from two populations that have different means. Details about the procedures of using the t statistic can also be found in Appendix X1. The results of the statistical analysis about the dry weight and diffusivity of the two types of laminates are summarized in Table 4-3. In Table 4-3, quantities with

subscript 1 represent the quantity of the normal laminates, and those with subscript 2 represent the quantity of the staggered laminates; the confidence level is $1-\alpha=0.95$.

From Table 4-3, on the one hand, it is concluded that average dry weight of the normal laminates was higher than that of the staggered laminates. On the other hand, the difference in the average diffusivities of the normal and staggered lay-up laminates was not significant even though the average diffusivity of the staggered laminates was higher than that of the normal laminates. From statistical point of view, it cannot be concluded that moisture diffuses faster in the staggered lay-up laminates than in the normal laminates.

Table 4-3 Statistical analysis results about initial weight and diffusivity of normal and staggered laminates

Statistics	n_1	n_2	$\bar{Y}_1$	$\bar{Y}_2$	s_1^2	s_2^2	t	$t_{\frac{\alpha}{2}}$
W_{dry}	12	12	20.26494	20.13442	0.02164	0.01285	2.434	2.074
D_z	9	9	3.995×10^{-7}	4.050×10^{-7}	0.059×10^{-14}	0.066×10^{-14}	-0.471	2.120

According to experimental data, the average weight of the staggered laminates before curing was approximately the same as that of normal laminates. However, after curing, the average weight of the staggered laminates was lower than that of the normal laminates. The fabrication process of the staggered lay-up laminates involved the cutting of each lamina into strips, which provided extra paths for the liquid resin to flow out during curing. Thus, more resin came out during curing resulting in the lower average weight of the staggered laminates.

At the same time, the gaps between prepreg strips were filled by resin. Since cured under the same conditions, it is assumed that these two types of laminates had

the same microstructure and cross-link density. Therefore, on the one hand, staggered lay-up laminates had slightly higher average diffusivity than normal laminates because that even though the gaps between prepreg strips were filled by the resin during curing, these gaps represented areas in which there was only resin but no fibers which usually served as barriers for the diffusing water molecules. On the other hand, these gaps were small in dimension and scarce in density in the laminates. Therefore, there was no substantial difference between the moisture absorption rates of the two types of structures.

4.2.1.4 Microstructure after isothermal water immersion

The cross section of the laminates of Group 4 was observed using the scanning electron microscope (SEM). Typical SEM images of unconditioned and conditioned laminate are shown in Figure 4-3. As shown in Figure 4-3, fiber/matrix debonding, matrix cracking and delamination were not identified in the SEM image of the conditioned laminate, proving that the current duration of hygrothermal exposure (1144.50h) did not bring about visible structural defects to CFRP UD laminates.

Figure 4-3 SEM images of the cross sections of laminates of different hygrothermal groups showing that exposure to water at 80°C for 1144.50h did not affect the microstructure of CFRP UD laminates

4.2.1.5 Impact properties of normal and staggered lay-up laminates

The impact damage resistance of as-processed specimens and hygrothermally conditioned specimens was examined by an instrumented impact testing machine, Instron Dynatup 8250 drop tower impact tester. For all the specimens in this experiment, the impactor weight and height chosen for impact testing was 2.735kg and 335mm, respectively, resulting in an impact energy level of 6J.

The parameters which are frequently used for the characterization of the impact resistance properties of composite materials include F_i , D_i , F_p , D_p , E_p , D_{max} , E_{el} and E_d . The way of defining these parameters and the relationships between them can be found in the studies by Karasek et al. (1995a, 1995b), Feraboli and Kedward (2004), Feraboli (2006). Figure 4-4 shows a typical load/energy-time curve of a low-velocity impact testing. On the Load/Energy-time curves, quantities such as incipient damage load F_i , peak load F_p , total energy absorbed E_{total} , damage generation energy E_d , and elastic energy E_{el} , etc., can be found.

Figure 4-4 Typical impact force/energy versus time curves during a low-velocity impact test

Another two characteristic impact parameters, E_{d2} and DI were also adopted in the discussion of impact properties in this study. The damage generation energy, E_d , consists of two parts; namely, E_d up to peak load point (E_{d1}) and E_d beyond peak load point (E_{d2}). Under the assumption that after peak load point most impact energy is devoted to the formation of damage, E_{d2} is calculated as:

$$E_{d2} = E_{total} - E_p \quad (4-14)$$

Lower values of E_{d2} indicate that less impact damage has been imparted to the test specimen by the impactor after peak load point. Damage index DI is calculated as:

$$DI = E_d / E_{el} \quad (4-15)$$

It has been proved to be a usefully parameter to characterize quantitatively the impact induced damage of composite laminates. Higher value of DI implies more damage generated and the materials with lower values of DI have better impact properties.

Statistical method was applied again to compare the impact resistance properties of the normal and staggered lay-up laminates. Details about the t statistic can be found at Appendix 1. The results of the analysis are presented in Table 4-4. In Table 4-4, F_i , F_p , E_{el} are the parameters that directly reflect the impact resistance of the specimens, while DI and E_{d2} are quantities that show the severity of impact damage.

Table 4-4 Statistical analysis results about impact properties of normal and staggered laminates

Statistics	n_1	n_2	$\bar{Y}_1$	$\bar{Y}_2$	s_1^2	s_2^2	t	$t_{\frac{\alpha}{2}}(22)$
F_i	12	12	2.578	2.570	0.093	0.078	0.071	2.074
F_p	12	12	2.699	2.737	0.042	0.029	-0.506	2.074
E_{el}	12	12	1.674	1.445	0.304	0.206	1.107	2.074
DI	12	12	2.654	3.156	1.049	0.919	-1.241	2.074
E_{d2}	12	12	0.967	0.829	0.392	0.313	0.567	2.074

It is noted that all the t values of the five parameters are smaller than the critical value $t_{\alpha/2}(22)$, indicating that based on the current experimental data it is hardly to determine which type of laminates had better impact resistance properties. Firstly, the average dry weight of the normal laminates was approximately 0.65% higher than that of the staggered lay-up laminates and the difference in dry weight was mainly resulted from the lower resin content of the staggered laminates. Fortunately, fibers have played a major role in carrying the impact load. Secondly, though there were gaps between prepreg strips of each ply before curing, these gaps were filled by flowing resin during curing and the prepreg strips joined together into a whole ply, which was the same as those uncut plies in the normal laminates. Therefore, normal laminates did not have better impact resistance than the staggered laminates from a statistical point of view.

4.2.1.6 Effects of moisture on the impact resistance of CFRP laminate

As calculated, the average actual impact energy for all the samples was 5.606J, and the coefficient of variation was 0.12%. Therefore, it is reasonable to conclude that all the specimens were subjected to the same level of impact loading.

In order to compare the impact resistance properties of specimens with different moisture contents, Specimens N11, N21, N31 and N41 were chosen from their individual groups. Their moisture contents were 0.075%, 1.130%, 1.620% and 2.433%, respectively. Figure 4-5 shows the load versus time curves of the four specimens. Because of the moisture absorbed, the characteristics of the impact event

had changed from supercritical impact event for N11 to critical impact event for N41 (Feraboli and Kedward, 2004). As seen in Figure 4-5, the time corresponding to incipient damage point (Feraboli, 2006) increased with moisture content, implying that the occurrence of incipient damage or the first significant damage was delayed. As seen in Figure 4-5, the curve of Specimen N41 is more symmetrical than that of Specimen N11 because the contact force trace of Specimen N41 has less oscillations and sharp load drops. Generally, oscillations or sharp load drops beyond the incipient damage point are indication of the initiation of damage forms such as fiber breakage, delamination, etc. Most importantly, as the moisture content increased, the sharp load drop occurred at later time of impact contact.

The contact duration between the impactor and the laminates decreased from N11 with the longest contact duration to N41 with the shortest duration. During impact testing, elastic deformation generally takes less time than damage propagation process such as delamination and fiber breakage, etc. Thus, it is concluded that the impact event was more elastic in nature for N41 than that of N11.

Figure 4-5 Typical load versus time curves of CFRP laminates of different moisture level

Figure 4-6 shows the load versus deflection curves of the four specimens. The initial parts of the four curves are approximately the same. There is no evident difference between the slopes of the linear parts of the curves, which indicates that the moisture had not affected the out-of-plane stiffness (Feraboli, 2006) of CFRP laminates. This is because the majority of the impact load was taken by the fibers and it is assumed that short-term moisture absorption at current temperature has minimal effect on fibers. As moisture content increased, the sharp load drop appeared at larger deflections. Therefore, specimens with higher moisture level could retain their resistance to the impact loading up to higher projectile deflections. The area under the load versus deflection curve is an indication of damage generation energy, E_d . Larger area implies that more impact energy is dissipated through damage creation. It is apparent that this area decreased as the moisture content increased.

Figure 4-6 Typical load versus deflection curves of CFRP laminates of different moisture level

As discussed earlier, the actual impact energy for each sample was approximately the same. As seen in Figure 4-7, specimen with higher moisture content had higher elastic deformation energy E_{el} and lower damage generation energy E_d , which proves that for conditioned laminates more of the impact energy was absorbed through elastic deformation and less impact energy was dissipated by damage mechanisms as compared to unconditioned specimens.

The impact testing results of the four groups of specimens are plotted in Figures 4-8 to 4-12. Except Figure 4-9, each datum in the following figures represents the average value of one group of specimens.

In Figure 4-8a, both D_i and D_p increased monotonically with average moisture level of each group. The increase in D_i implies that the first significant damage occurred at larger deflection for specimens exposed to water immersion, while the increase in D_p proved that laminates with higher moisture content could retain their resistance or mechanical strength to the impactor to higher projectile deflections. Before the incipient damage point, the test specimen generally behaves in an elastic manner and the strain in both the fibers and epoxy resin of the laminate is determined by the projectile deflection. For the same point in the laminate higher strain corresponds to larger deflection of the laminate under impact loading. Therefore, for laminates with higher moisture content, incipient damage occurred at higher strain level. The increase in D_i with moisture content served to prove that the absorbed moisture extended the elastic limit of the CFRP laminates under impact.

Figure 4-7 Typical energy versus time curves of CFRP laminates of different moisture level

As shown in Figure 4-8b, F_i and F_p also increased monotonically with moisture content. Before incipient damage point, materials would deform elastically. Within this period of impact, the contact force would increase consistently with deflection as seen in Figure 4-6. Therefore, specimens with larger D_i had larger incipient damage load F_i . This postulation is verified by Figure 4-9, which shows the values of D_i and F_i of all the 24 specimens tested. Figure 4-9 also proves that absorbed moisture had little effect on the contact stiffness of CFRP laminates as F_i increased almost linearly with D_i . As seen in Figure 4-10, it is convincible to conclude that F_p increased with D_p . In summary, moisture inside CFRP laminates increased D_i and D_p by extending the elastic limit of the material under impact, which in turn resulted in higher values of F_i and F_p .

Figure 4-8a shows that D_{max} of hygrothermally unconditioned specimens was higher than that of the conditioned specimens. For critical and supercritical impact events, higher maximum projectile deflection is indicative of the occurrence of more

severe impact damage. Therefore, the curve of D_{max} proves that degree of damage decreased with average moisture content. As shown in Figure 4-8a, the absorbed moisture led to an increase in D_i values while caused reduction in D_{max} . This can be attributed to the improved the elastic response of the laminate due to the absorbed moisture, which in turn made the incipient damage initiate at higher projectile deflections. Therefore, D_i increased with the moisture content.

However, the maximum projectile deflection D_{max} during an impact test event is related to the contact stiffness of the testing material. When attacking a laminate of higher contact stiffness, the speed of the impactor would be reduced to zero within a shorter time of contact, resulting in a shorter projectile deflection consequently. It also means lower contact stiffness would bring about larger projectile deflection during impact test. As discussed previously, specimens of different moisture contents had the same level of contact stiffness before the impact attack. However, the contact stiffness of the laminate would generally be reduced as damages such as fiber breakage and delamination were initiating and propagating in to the laminate. Specimens with higher moisture content experienced a lower extent of impact damage, which implies that these specimens had a less percentage of loss in the contact stiffness. Therefore, the maximum deflection was lower in the same proportion; hence D_{max} values decreased with the average moisture content in Figure 4-8a.

a) Between average moisture content and deflections, where D_i = deflection at incipient damage point, D_p = deflection at peak load point, and D_{max} = maximum deflection;

b) Between average moisture content and contact force, where F_i = incipient damage load, F_p = peak contact force.

Figure 4-8 Relationship between average moisture content and various impact property parameters

In Figure 4-11, average elastic deformation energy E_{el} of each group of specimens increased steadily with average moisture content, while E_d changed in opposite way because the average total impact energy E_{total} was approximately the same for each group. As the moisture content increased, more of the impact energy was absorbed by the specimen through elastic deformation and less impact energy was dissipated by damage mechanisms. Therefore, E_{el} increased while E_d decreased and at the same time specimens of higher moisture content had lower extent of impact damage. E_{d2} also decreased with the average moisture content. The change in E_{el} and E_d with M_{final} further proved that the elastic deformation capability of the laminates under impact was improved after moisture absorption.

Figure 4-9 Relationship between F_i and D_i of CFRP laminates

Figure 4-10 Relationship between average D_p and F_p of each group

Figure 4-11 Relationship between average moisture content and E_d (energy devoted to damage creation), E_{el} (energy dissipated by elastic deformation) and E_{d2} (E_d after peak load point) of CFRP laminates

Damage index DI decreased with M_{final} in Figure 4-12, which proved that the severity of impact damage decreased with moisture content. The rate of decrease is approximately constant initially, however increases at higher moisture content.

Figure 4-12 Relationship between average moisture content and damage index of CFRP laminates

4.2.1.7 Post-impact damage observation

Figure 4-13 presents the photographs of the damaged sites of representative laminates from each group. Strips of materials were found to be detached from the

laminate (Figure 4-13a). The damages shown in Figure 4-13 are actually delamination caused by the impact. It is not difficult to find that the extent of delamination decreased with the moisture content in the CFRP UD laminates. N11 experienced the most severe delamination, while the damage on the surface of N41 was merely discernable. Therefore, it is concluded that impact imparted delamination to CFRP unidirectional laminates and the magnitude of delamination decreased with moisture content for the duration for which the study is conducted.

Figure 4-13 Photographs of the damage sites of the impact tested laminates showing that the extent of delamination decreased with the moisture content of CFRP UD laminates

In summary, experimental data showed that the impact properties of CFRP UD-prepreg laminates improved after absorbing moisture. For specimens of Group 4, with an average increase in weight by 2.404% because of moisture absorption, F_i , F_p

and E_{el} increased by 30.87%, 16.45% and 76.69%, respectively, while average E_d and *damage index DI* decreased by 26.66% and 56.06%, respectively. Moisture improved the elastic deformation ability of the laminates under impact. Therefore, specimens with higher moisture contents behaved in an elastic manner up to larger deflections and their resistance to the impactor was also preserved to larger deflections. More impact energy was dissipated through elastic deformation and less impact damage was initiated. Correspondingly, the extent of impact induced damage decreased with the moisture content of the laminates.

4.2.2 60°C Group

The results of 80°C Group showed that isothermal water immersion conditioning for 1144.50 hours did not cause visible structural defects in CFRP UD-prepreg laminates. Instead, the impact resistance improved after hygrothermal conditioning. In order to verify the genericness of this finding, a hygrothermal cycle was particularly designed to identify possible degradation in structural integrity and impact response of CFRP UD-prepreg laminates under changing hygrothermal environments.

4.2.2.1 Specimen fabrication

Three groups of samples were fabricated from carbon/epoxy unidirectional prepreg materials, L-930HT (GT700), following a stacking sequence of [45/90/-45/0]_s. Details about the specimen fabrication process can be referred to Chapter 3. The dimension of the cured laminates was 100mm×100mm×1.274mm, which were cured in the autoclave and had an average resin content of 25.15 wt.% .

4.2.2.2 Hygrothermal conditioning scheme

Though stored in a dry cabinet, the specimens still adsorbed substantial amount of moisture. Therefore, prior to conditioning, specimens were dried in a vacuum oven at 50°C for 48 hours. Subsequently, vacuum oven-dried specimens were immersed in water at 60°C or subjected to cyclic hygrothermal conditions. The hygrothermal conditions adopted in this study were designed according to the possible temperature and humidity conditions encountered by composite parts in service. The hygrothermal conditions employed in the current investigation are shown in Table 4-5.

Table 4-5 Summary of the hygrothermal conditioning result of CFRP UD-prepreg laminates 60°C Group

Group	Specimen Identification	Conditioning	W_i (g)	Ageing Time (days)	M_f (%)	D_z (mm ² /s)	Thickness ^a (mm)
Group 1	Specimen 1~5	unconditioned	20.21796	0	0.056	--	1.274
Group 2	Specimen 6~10	Hygrothermal cycles	20.31544	78	1.379	--	1.290
Group 3	Specimen 11~15	60°C in water	20.04525	77	1.687	1.450×10^{-7}	1.273

^aThickness - thickness of specimens measured before impact testing.

In Table 4-5, each datum is the average value of 5 specimens. As shown in Table 4-5, specimens of Group 3 (isothermally conditioned group) were immersed in water at 60°C until saturation, while specimens of Group 2 (cyclically hygrothermally conditioned group) were subjected to a number of hygrothermal cycles; each cycle consisted of 12h in water at 60°C and 12h in freezer at -30°C. Values of M_f in Table 4-5 were calculated as follows:

$$M_f = \frac{W_f - W_i}{W_i} \times 100\% \quad (4-16)$$

Specimens of Group 1 (control group) were stored in the dry cabinet after curing. Prior to impact testing, they were dried in the vacuum oven at 50°C for 48 hours. However, there was still a small amount of moisture staying inside the laminates. Therefore, in Table 4-5, the average M_f of Group 1 is non-zero.

The weight of specimens of Group 2 was recorded each time after being conditioned in either water bath or freezer. During the course of experiments, it was found that CFRP specimens did not lose weight when kept in freezer. The reason should be that the moisture inside composites was at frozen state and lost their ability of transporting out of the specimen. Therefore, even though the relative humidity in the freezer was exceptionally low, specimens did not lose moisture inside the freezer. This also implies that moisture will stay in the composite parts made of CFRP at low temperature. After being cycled for 78 days, the average moisture content of Group 2 reached 1.379%.

Specimens of Group 3 were constantly immersed in water at 60°C until saturation. The moisture uptake behavior of CFRP laminates made from unidirectional prepreg materials when immersed in water at 60°C was plotted in Figure 4-14. The moisture content in the specimen increased linearly initially with respect to the square root of time. Upon the linear stage, the rate of moisture absorption decreased gradually. Finally, the increase in moisture content was negligible with respect to time. In the last 17 days of conditioning, the weight of the specimen varied by only 0.06%. It is therefore concluded that the diffusion of moisture in CFRP unidirectional laminates

studied in the current study followed Fick's law. This finding is similar to the conclusion from other investigations (Ray, 2006).

Figure 4-14 Moisture uptake profile of CFRP unidirectional laminates exposed to water at 60°C

The major difference in hygrothermal conditions between Group 2 and Group 3 includes two aspects. Firstly, specimens of Group 3 were isothermally conditioned in water at 60°C, while specimens of Group 2 were subjected to changing temperature and humidity conditions. Secondly, the final average moisture content of Group 3 was higher than that of Group 2.

4.2.2.3 Microstructures after hygrothermal conditioning

Besides moisture uptake, specimens of the cyclically conditioned group also experienced temperature cycling (60°C to -30°C) and possible volumetric expansion related to water-to-ice transition if absorbed moisture turned to ice crystals at -30°C. Since the fiber and matrix resin had different coefficients of thermal expansion (CTE), once a change in temperature was raised, the matrix resin could not expand or contract freely, resulting in a thermal stress in both the fibers and the matrix. Furthermore, a single lamina generally expands or contracts more along the direction transverse to the fiber orientation due to the presence of continuous matrix phase between the fibers. Thermal stress gets induced in the interlaminar region between

adjacent layers with different fiber orientations. Temperature cycling would bring about thermal stress cycling in the laminate. Therefore, interlaminar failure is likely to occur. The interface, which is responsible for transferring load between the fiber and the matrix resin, is also likely to be damaged by thermal stress cycling. The repeated volumetric expansion associated with the water-to-ice transition might also cause micro-cracks in the matrix. As reported in the literature (Liotier et al. 2011; Yavuz et al. 2006; Botelho et al. 2006), evident surface micro-cracks, fiber debonding from the matrix and delamination are generally found from composite laminates exposed to various hygrothermal conditions.

After hygrothermal conditioning, the microstructure of the CFRP laminates from different groups was observed using a scanning electron microscope (SEM). Figure 4-15 presents the typical microstructure of laminates exposed to different hygrothermal conditions. Two layers of the laminate with different fiber orientation were involved in all the three SEM graphs. In this study, the microstructure of the CFRP laminates from different hygrothermal groups was compared in four aspects, which include fiber, matrix, and fiber/matrix interface and interface connecting two adjacent layers.

After being compared with the fibers in Figure 4-15a, it is easily noticed that the fibers of the hygrothermally aged laminates remained intact after hygrothermal conditioning (Figures 4-15b and 4-15c). When exposed to water immersion conditioning at elevated temperature and/or cycled between hot/wet and dry/cold conditions within limited period of time, which represented harsh environments in service, the carbon fibers successfully maintained their structural integrity. No

visible holes or cavities were found in all the three SEM graphs of Figure 4-15, which not only showed that laminates cured by the autoclave had low void density, but proved that the epoxy resin was not affected by the two hygrothermal conditions chosen in this study.

Figure 4-15 SEM images of the cross sections of laminates of different hygrothermal groups: a) Control Group; b) Cyclically hygrothermally conditioned Group; c) Isothermally conditioned Group

No crack between fibers and matrix resin was found in the SEM graphs of cyclically and isothermally conditioned group (Figures 4-15b and 4-15c), indicating that the fiber/matrix interface was not damaged by the harsh hygrothermal conditions adopted in the current investigation. Most significantly, the interfacial area of both group remained intact after hygrothermal conditioning (Figures 4-15b and 4-15c). Both the cyclic hygrothermal conditioning and isothermal water immersion

conditioning showed no effects on the interlaminar interface of CFRP laminates. In contrast to the results reported in the literature, the hygrothermal conditioning conducted in this study did not bring about visible structural defects to the carbon fiber/epoxy composite laminates, proving that this material had good environmental durability.

4.2.2.4 Damage characteristics under low-velocity impact

As concluded in the previous section, specimens that had been exposed to different harsh hygrothermal environments had the same microstructures as specimens of the control group. The principal difference between specimens of the three groups was that they had different levels of moisture content. Specimens from different groups were subjected to low-velocity impact attack of the same magnitude. The damage characteristics of CFRP laminates after the impact attack were analyzed in terms of both the photographs of the two surfaces of the laminates and the internal microstructure of the damaged site of the laminate.

Figure 4-16 presents the photographs of the damaged sites of representative laminates from the three hygrothermal groups. The size of the indentation at the top surface (surface that had direct contact with the impactor) decreased significantly with the moisture content of the laminates. Specimen 11, which had a moisture content of 1.635%, only had light indentation formed at the top surface after impact attack. At the bottom surface (Figures 4-16d and 4-16e), strips of materials were found to be detached from the laminate. These were delamination caused by the impact attack. Therefore, it was concluded that impact attack imparted delamination

to CFRP unidirectional laminates and the magnitude of delamination decreased with moisture content.

The internal profile of the damaged site of the laminate was observed using scanning electron microscope. Though no visible delamination was found at the bottom surface of Specimen 11(Figure 4-16f), both delamination and matrix cracking were found in the SEM graphs of Specimen 11(Figures 4-17a and 4-17b). This proves that the impact attack induced damages in fiber reinforced composites are usually invisible at the surfaces. Since the specimens were made from unidirectional prepreg materials, fibers of the same layer had the same orientation. Therefore the plane of the cracks in the matrix was parallel to the orientation of the fibers. The impactor stroke the specimen along a direction normal to the plane of the laminate. Therefore, for Specimen 11, the principal damage modes were delamination and matrix cracking.

Figure 4-16 Photographs of the damage sites on both sides of the impact tested laminates: **a-c** are photographs of the top face of Specimens 2, 8 and 11, respectively; **d-f** are photographs of the bottom face of Specimens 2, 8 and 11, respectively($M_{f2} < M_{f8} < M_{f11}$)

However, Specimen 8, which was from the cyclically conditioned group and had lower moisture content than Specimen 11, exhibited much more severe impact induced damage (Figures 4-17c and 4-17d). Laminae in the laminate were curved or bent due to the impact attack. The overall magnitude of delamination in Figure 4-17c was apparently larger than that of Figure 4-17a. Multiple cracks were observed (Figure 4-17d), whereas in Figure 4-17b cracks in the matrix generally appeared separately as single cracks. Fiber breakage was also found (Figures 4-17c and 4-17d). The degree of impact induced damage of Specimen 8 was significantly higher than that of Specimen 11.

Figure 4-17 SEM graphs of the intersection of the CFRP unidirectional laminates at the damage sites:
a-b Specimen 11; **c-d** Specimen 8; **e-f** Specimen 2 ($M_{f2} < M_{f8} < M_{f11}$)

The extent of damage of Specimen 2 (Figure 4-17e) was even more severe than that of Specimen 8 (Figure 4-17c). Larger scale of matrix cracking and fiber breakage were found. As shown in Figure 4-16d, the scale of delamination in Specimen 2 was larger than the other two laminates. Specimen 2 experienced larger residual deflection (laminae were more severely bent) along the direction of impact attack. This explains the more severe matrix cracking and fiber breakage happened to Specimen 2.

For laminates made from unidirectional prepreg materials, the major damage modes related to impact attack included delamination, matrix cracking and fiber breakage. The SEM graphs in Figure 4-17 prove that laminates with difference moisture contents had different level of impact induced damage. The severity of delamination, matrix cracking and fiber breakage decreased with the moisture content in the CFRP laminates made from unidirectional prepreg materials, which equally implies that moisture alleviated the damage in the CFRP unidirectional laminates caused by impact attack.

4.2.2.5 Impact test results

The samples of all the three groups were tested under the same impactor weight and height, which were 2.735kg, 335mm, respectively (actual impact energy 6J). An impact event is a complicated course of contact between the impactor and the laminate. The complete evaluation of the impact resistance of a material requires the interpretation of all the information captured during the impact test, including contact force, time, energy and projectile deflection.

Three representative specimens, Specimen 2, 6 and 13, were selected from Group 1, 2 and 3, respectively, to compare the impact response of CFRP laminates of different moisture levels. The moisture contents of Specimen 2, 6 and 13 were 0.070%, 1.364% and 1.732%, respectively. Their load/time curves were shown in Figure 4-18. The response of CFRP unidirectional laminates to low-velocity impact attack as depicted in Figure 4-18 are identical to typical contact force/time curves of a low-velocity impact test (Karasek et al. 1995a; Feraboli, 2006; Feraboli and Kedward, 2004). The oscillations or load drops in Figure 4-18 are indications of the formation and propagation of damages in the laminate during impact testing. The first load drop of Specimen 2 occurred earlier than the other two specimens, implying that the under the same impact energy level, Specimen 2, which had the lowest moisture level, was significantly damaged earlier than the other two specimens. The peak load of Specimen 6 and 13 also appeared later than that of Specimen 2, proving that specimens with higher moisture contents preserved their strength for longer time. Both the peak contact force and contact force at incipient damage point of conditioned laminates were higher than the unconditioned laminate. Figure 4-19

shows the relationship between average F_i , F_p and M_f of each group. Both F_i and F_p increased monotonically with average moisture content. Therefore, the resistance of the CFRP laminates to the intruding impactor increased after absorbing moisture. In Figure 4-19, for both F_i and F_p , the coefficient of variation for each group was in the range of 1.7% to 6.0%.

Figure 4-18 Contact force/time curve of laminates from different group ($M_{f2} < M_{f6} < M_{f13}$)

Figure 4-19 Relationship between average moisture content and F_i , F_p of CFRP laminates

In Figure 4-18, it was noticed that the contact time of the three specimens was also different. The relationship between the average contact time and moisture level was summarized in Figure 4-20. In Figure 4-20, the coefficient of variation for each

group was in the range of 2.1% to 3.9%. It was found in Figure 4-20 that the contact time between the laminate and the impactor decreased with the average moisture content of each group. During an impact testing event, the velocity of the impactor was highest at the moment of striking the laminate. Subsequently, the velocity of the impactor decreased as the laminate was resisting the intruding impactor until eventually the velocity of the impactor was reduced to zero and it was rebounded from the laminate. In Figure 4-18, after the incipient damage point of Specimen 2, the contact force of Specimens 6 and 13, which represented the resistance of the laminate to the impactor, was higher than that of Specimen 2. Therefore, the velocity of the impactor decreased faster during the impact testing of Specimen 6 and 13, resulting in the shorter contact time of them. The contact time is related to the resistance of testing material in such a way that specimen with higher resistance (relatively larger contact force) has shorter contact time. It is therefore concluded from Figure 4-20 that the resistance of CFRP laminates to impact loading increased with their moisture content.

Figure 4-20 Relationship between average moisture content and contact time during impact testing of CFRP laminates

The contact force versus deflection curves of Specimens 2, 6 and 13 were plotted in Figure 4-21. The initial parts of all the three curves are approximately the same. There is no evident difference between the slopes of the linear parts of the curves, which indicates that the moisture did not affect the out-of-plane stiffness of CFRP laminates. Out-of-plane stiffness is referred to slope of the linear portion of contact force/deflection curve. Larger slope implies that the contact force increased relatively faster with the projectile deflection, therefore higher out-of-plane stiffness of the laminate is expected. As a fiber reinforced composite material, the carbon fibers in CFRP laminates carried the majority of the load exerted upon the laminate. It assumed with confidence that the current hygrothermal conditions adopted had little effect on the integrity and strength carbon fibers. Therefore, before incipient damage point, laminates with different moisture contents had approximately the same out-of-plane stiffness.

Figure 4-21 Contact force/deflection curve of laminates from different groups ($M_{f2} < M_{f6} < M_{f13}$)

The oscillations on the contact force/deflection curves in Figure 4-21 were also indicative of the formation and propagation of damages during impact testing which directly reduced the resistance of the laminate. It was found from Figure 4-21 that the first significant damage of Specimens 6 and 13 occurred at larger deflections (larger D_i). Peak loads of both Specimens 6 and 13 were observed at larger projectile deflection than that of Specimen 2 (larger D_p). The relationships between D_i , D_p and average moisture content of each group were summarized in Figure 4-22. In Figure 4-22, for D_i , D_p and D_{max} the coefficient of variation for each group was in the range of 1.3% to 3.1%. In Figure 4-22, deflections at incipient damage point and peak load point increased with moisture content of the laminates. Before incipient damage point, the testing laminate behaved in an elastic manner. Therefore, after absorbing moisture the laminate could behave elastically up to larger deflections. The impact loading applied to the specimen was a bending load in nature. The strains developed inside the structure increased with projectile deflection. Therefore, after absorbing moisture the laminate could behave elastically up to higher strain levels. That is, the elastic limit of the CFRP laminates under impact loading was increased because of the moisture absorbed. In the meantime, the increase in D_p with average moisture content as shown in Figure 4-22 indicates that the CFRP laminates could retain their resistance to the striking impactor to larger deflections.

In addition, it was found in Figure 4-22 that average D_{max} of each group decreased with moisture content. As discussed in previous paragraphs, before incipient damage point, the out-of-plane stiffness of specimens of different moisture contents were approximately the same. However, the higher D_{max} of specimens with lower moisture

contents manifested that these specimens had smaller overall contact stiffness. During an impact test, damages such as matrix cracking, fiber breakage and delamination were formed in the CFRP laminates, reducing the resistance of the testing laminate. Therefore, the smaller overall out-of-plane stiffness of laminates with lower moisture content was probably resulted from the more severe impact damage formed inside CFRP laminates during impact testing. Therefore, the decrease in D_{max} with M_f supported the conclusion that specimens with higher moisture contents had lighter impact damage formed during impact testing.

Figure 4-22 Relationship between average moisture content and D_i , D_p and D_{max} of CFRP laminates

It was noted that contact force and deflection at the corresponding point had the same varying trend with respect to moisture level (Figures 4-19 and 4-22). As shown in Figure 4-21, before the incipient damage point the laminates behaved elastically. At this stage of contact, the contact force generally increased monotonically with projectile deflection. Therefore, the increase in D_i with moisture content led to the increase in F_i . This explained why the F_i of Specimens 6 and 13 were larger than

that of Specimen 2 in Figure 4-21. The F_i and F_p values of all the 15 specimens tested were plotted against D_i and D_p , respectively, in Figure 4-23. The load corresponding to the incipient damage point (F_i) showed an evident ascending trend with D_i , while in Figure 4-23b although there was certain extent of data scatter, peak load generally increased with D_p .

Figure 4-24 shows the change in average E_d and E_{el} with average moisture content. In Figure 4-24, for E_{el} and E_d , the coefficient of variation for each group was in the range of 2.7% to 23.2%. In Figure 4-24, E_d decreased consistently with average moisture level, while E_{el} increased with average M_{final} . For specimens with higher moisture content, more of the impact energy was dissipated by the laminate through elastic deformation. Hence, less impact energy was left to initiate and propagate damage. This finding explained the alleviated impact damage of the hygrothermally conditioned laminates.

Figure 4-23 Relationship between contact force and projectile deflection: (a) F_i and D_i ; (b) F_p and D_p

Figure 4-24 Relationship between average moisture content and E_i , E_d of CFRP laminates

As reported by Karasek et al. (1995), when tested at 21°C moisture had little effect on the damage initiation energy and impact energy dissipation process of graphite/epoxy composites. The experimental study carried out on aramid–glass fiber/epoxy composites also revealed that the absorbed moisture did not affect the delamination threshold load and impact energy absorption evidently (Imielińska and Guillaumat, 2004). However, in the present investigation, absorbed moisture in CFRP unidirectional laminates significantly improved the incipient damage load and affected impact energy dissipation mechanisms.

In summary, the data collected during the impact test also proved that the impact resistance properties of both the cyclically and isothermally conditioned groups were improved after absorbing moisture. Specimens of the cyclically conditioned group were subjected to harsh and complicated hygrothermal conditions, including temperature cycling and moisture saturation. However, evident improvement in the impact response of cyclically conditioned specimens was found. This is due to the

fact that these laminates absorbed certain amount of moisture when immersed in water. Due to the moisture absorbed during hygrothermal ageing, the two conditioned groups of specimens suffered from lighter impact damage than the unconditioned dry specimens. After absorbing 1.687% by weight of moisture, F_i and E_{el} increased by 21.0% and 39.1%, respectively. Moisture improved the impact resistance of the CFRP UD-prepreg laminates and alleviated the impact induced damages.

4.2.3 Tensile test on pure epoxy resin samples

Two groups of pure epoxy tensile samples were fabricated by curing diglycidyl ether bisphenol A (DGEBA) using diethylenetriamine (DETA) as the curing agent. Prior to tensile test, one group of samples were continuously immersed in water at 80 °C for 33 days, while the other group was tested without any hygrothermal conditioning. The details about these two groups of samples are summarized in Table 4-6.

Table 4-6 Hygrothermal conditioning scheme for pure epoxy tensile samples

Group	Specimens	Hygrothermal conditioning	W_i (g)	M_f (%)
Reference Group	Dry epoxy 1~5	unconditioned	11.48875	0
Wet Group	Wet epoxy 1~5	Immersed in water at 80 °C for 33days	11.29653	3.154

No visible damage was seen at the surface of epoxy tensile coupons exposed to moisture. Figure 4-25 shows the picture of a conditioned and unconditioned epoxy tensile sample. From Figure 4-25, it was concluded that the current hygrothermal conditioning did not induce damages to the epoxy samples.

Figure 4-25 Unconditioned and conditioned epoxy samples: top-unconditioned; bottom-conditioned

Tensile test on epoxy samples was performed using an MTS 810 material test system. An extensometer with a gauge length of 25mm was attached to the sample to measure the strain in the epoxy coupon (Figure 4-26). The tensile test was conducted at room temperature with a displacement rate of 1mm/min. The results were summarized in Table 4-7.

Figure 4-26 An epoxy sample under tensile test

Table 4-7 Tensile properties of epoxy (DGEBA+DETA) samples

Properties	Unconditioned			Conditioned		
	Average	Coefficient of Variation (%)	Number of Specimens	Average	Coefficient of Variation (%)	Number of Specimens
Ultimate Tensile strength (MPa)	80.174	3.426	5	40.135	17.892	5
Ultimate Tensile strain (%)	4.608	9.142	5	1.955	24.049	5
Young's modulus (GPa)	3.165	3.880	5	2.609	5.650	5

As shown in Table 4-7, with 3.154 wt. % of moisture uptake, the tensile strength reduced by 49.94%. The Young's modulus and ultimate tensile strain reduced by 17.56% and 57.58%, respectively. The mechanical properties of epoxy resin are sensitive to moisture uptake. After absorbing moisture, the tensile strength, Young's modulus and ultimate tensile strain of pure epoxy samples decreased evidently. The same finding on epoxy resin was also reported by other researchers (Zafar et al. 2012; Nogueira et al. 2001). Typical stress/strain curves of both unconditioned and conditioned epoxy samples are plotted in Figure 4-27.

Figure 4-27 Typical stress/strain curves of dry (unconditioned) and wet (conditioned) pure epoxy samples under tensile load

As clearly shown in Figure 4-27, the slope of the two wet epoxy samples was evidently smaller than that of the two dry samples, implying the decrease in the Young's modulus after absorbing moisture. The maximum strain decreased remarkably after absorbing moisture. Reduce in Young's modulus and ultimate tensile strain contributed to the decline in the ultimate tensile strength of pure epoxy sample with moisture. The decrease in Young's modulus might be due to the softening of the epoxy resin caused by the moisture. Therefore, moisture uptake had two major influences on epoxy resin. Firstly, it softened the epoxy resin. Secondly, it reduced the ultimate tensile strain of the epoxy resin.

4.2.4 Tensile test on CFRP woven laminates

Tensile test was conducted on both unconditioned and conditioned specimens to explore the effects of hygrothermal ageing on the static properties of CFRP woven laminates. L-930HT (GT700) prepreg material, but in woven form, was used for the fabrication of tensile test specimens. The cured CFRP woven tensile samples had geometry of 252mm×26mm×1.322mm. The average weight and resin content of the cured tensile laminates was 23.35 wt. % and 12.97g, respectively. Three groups of samples were fabricated. Each group had undergone a type of hygrothermal conditioning, after which the samples were tested at room temperature to acquire their static properties. The hygrothermal conditioning scheme deployed is presented in Table 4-8.

As shown in Table 4-8, specimens of the unconditioned group were tested without any prior hygrothermal conditioning, while specimens of the conditioned group were

immersed in water at 80°C for 56 days prior to the tensile test. Specimens of the conditioned & dried group were initially immersed in water at 80°C for 56 days, after which they were dried in a vacuum oven at 45°C for 38 days until the moisture absorbed during hygrothermal ageing was completely removed. All the specimens were tested using an MTS 810 Material Testing System at the crosshead speed of 1 mm/minute. An axial extensometer was attached to the laminate during the tensile test to measure the strain in the laminate.

Table 4-8 Hygrothermal conditioning scheme of CFRP woven specimens for tensile test

Group	Number of Specimens	Hygrothermal conditioning	Moisture content after ageing (%)	Moisture content after drying (%)
Unconditioned Group	7	unconditioned	--	--
Conditioned Group	7	Immersion in water at 80 °C for 56 days	3.621	--
Conditioned & Dried Group	7	Immersion in water at 80 °C for 56 days followed by drying in a vacuum oven at 45 °C for 38 days	3.355	-0.055*

*The negative value of moisture content indicates that the weight of CFRP tensile samples after drying was smaller than their initial weight. This was due to that these samples absorbed a small amount of moisture from lab environment before the measurement of their initial weight.

The tensile test results of CFRP woven laminates are summarized in Table 4-9. The tensile stress-strain curves of samples from each group are plotted in Figure 4-28. As seen in Table 4-9, the change in ultimate tensile strain was not evident. Tensile properties are generally fiber-dominated and the fibers were the major load-bearing elements. Only after the overall strain of the sample reached the elastic limit of the fibers the laminate would break. The moisture did not affect the ductility of the fibers. Therefore, the fibers in both unconditioned and conditioned laminates failed at the same strain level, resulting in the same ultimate tensile strain for all the three groups of laminates.

However, the change in ultimate tensile strength and tensile modulus were both noticeable (Table 4-9 and Figure 4-28). After absorbing moisture, the ultimate tensile strength reduced by 15.98% while the tensile modulus reduced by 11.01% (Table 4-9). Upon the removal of the absorbed moisture through drying in the vacuum oven, the ultimate tensile strength and tensile modulus of CFRP woven composites recovered to 95.75% and 94.41% of their original value, respectively. This finding might lead to two conclusions.

Table 4-9 Tensile test results of CFRP woven laminates

Group	M_f (%)	Ultimate Tensile Strength σ_{ult} (MPa)	Ultimate Tensile Strain ϵ_{ult} (%)	Tensile Modulus E (GPa)
Reference Group	0	1232.354 (3.49)*	1.682 (4.36)	69.016 (2.20)
Conditioned Group	3.621	1035.395 (3.94)	1.696 (3.16)	61.418 (2.96)
Conditioned & Dried Group	-0.055	1179.957 (1.85)	1.783 (2.37)	65.155 (0.86)

* The value in each parenthesis is the coefficient of variation of the corresponding datum.

Firstly, moisture was the major factor that led to the decrease in both the ultimate tensile strength and tensile modulus. Moisture reduced the strength and modulus of the epoxy resin. Therefore, the magnitude of the modulus and the tensile strength of the conditioned CFRP woven laminates dropped after absorbing moisture from the surroundings.

Figure 4-28 Stress/strain diagrams of unconditioned and conditioned CFRP woven laminates

Secondly, moisture was not the only factor that caused the decrease in both the ultimate tensile strength and tensile modulus of CFRP woven laminates. Though a good recovery in both parameters was observed, the average σ_{ult} and ε_{ult} of the conditioned & dried group were lower than that of the unconditioned group. No structural defects were found in CFRP woven laminates after hygrothermal ageing. However, there might be micro-defects of low density formed during hygrothermal conditioning which were difficult to identify through FESEM observation. These micro-defects might be in the form of fiber debonding, fiber breakage and matrix cracking, all of which were possible to cause the degradation in the static properties of CFRP woven materials.

4.2.5 Mode I fracture toughness test on CFRP woven laminates

Mode I fracture toughness test was carried out on laminates made from carbon/epoxy woven prepreg material, L-930HT (GT700), according to ASTM D5528 for the purpose of investigating the effects of moisture on the Mode I fracture toughness G_{IC} of carbon fiber/epoxy composites. Two groups of samples measuring 126mm×26mm×2.65mm with an initial crack length of 50mm introduced by PTFE thin film were fabricated. Prior to fracture toughness test one group was immersed in water at 80°C for 56 days resulting in an average moisture uptake of 1.937% (wet group). The other group was not subjected to water immersion conditioning and served as the reference group. Details about the two groups of DCB samples are

summarized in Table 4-10. Compliance calibration method (ASTM D5528) was used to calculate the Mode I interlaminar fracture toughness G_{IC} as follows:

$$G_{IC} = \frac{nP\delta}{2ba} \quad (4-17)$$

where P is the load, δ is the extension, ' b ' is the width of specimen and ' a ' is the crack length. The method of finding n is illustrated in Figure 4-29. $\log (\delta_i/P_i)$ is firstly plotted against $\log (a_i)$ using all the initiation and propagation values of a Mode I fracture toughness test. A linear fit is then performed and ' n ' the slope of the straight line as shown in Figure 4-29.

Table 4-10 Hygrothermal conditioning scheme for DCB samples

Group	Specimens	Hygrothermal conditioning	W_i (g)	M_f (%)
Reference Group	R1~R5	unconditioned	13.28485	0
Wet Group	W1~W5	Immersed in water at 80 °C for 56 days	13.35029	1.937

Figure 4-29 Definition of n for Compliance Calibration Method

The effects of moisture on the initiation and propagation G_{IC} of carbon fiber/epoxy composites were illustrated in Figure 4-30. The NL G_{IC} (ASTM D5528)

was treated as the initiation G_{IC} . After absorbing moisture, the initiation G_{IC} increased by 74.40% while the propagation G_{IC} reduced by 15.92%.

Typical load vs. extension curves of both reference and wet laminates during fracture toughness test are shown in Figure 4-31. As shown in Figure 4-31, the load increased steadily with extension at the initial part of the curve of Specimen W1. However, a drop in load was observed on the curve of Specimen R1 at a smaller extension. This explains why the conditioned group had larger initiation G_{IC} . At the early stage of testing (when the load is increasing with extension), as the Mode I crack was propagating in a stable and gradual manner, the load increased monotonically with the extension for Specimen W1. However, for R1, the Mode I crack occasionally propagated suddenly resulting in an immediate drop in load. This phenomenon was generic for all the wet and dry DCB samples. Therefore, the wet group had larger initiation G_{IC} .

Figure 4-30 Comparison in G_{IC} between wet and reference group of CFRP woven-prepreg laminates

The Mode I crack in the unconditioned DCB samples generally manifested an abrupt mode of propagation, resulting in a sharp drop in the load as shown in the curve of Specimen R1 (Figure 4-31). For instance, during the fracture toughness test of R1, the crack length corresponding to point a in Figure 4-31 was 59mm. However, the crack length suddenly propagated from 59mm to 68mm resulting in the sharp drop in load from point a to point b in Figure 4-31. In fact, all the sharp load drops on the curve of R1 are indications of such abrupt crack propagation. In contrast, sharp load drops are not seen on the curve of W1. The Mode I crack in the conditioned DCB laminates propagated in a gentler manner. Therefore, the magnitude of the drop in load because of crack propagation in the wet samples was much smaller compared to the unconditioned laminate.

The difference in Mode I crack propagation mode between dry and wet DCB samples was due to the moisture absorbed in wet DCB samples. Absorbed moisture improved the chain segment mobility of epoxy molecules and softened the matrix resin. Compared to the conditioned laminates, the dry laminates was more brittle. In a dry DCB sample, Mode I crack usually propagated suddenly for a large distance resulting in an instantaneous drop in the load. In conclusion, moisture softened the epoxy resin, reduced the brittleness of DCB samples and improved their resistance to crack propagation.

Extension, compliance and load corresponding to all the initiation and propagation values are plotted against the crack length for both unconditioned and conditioned DCB samples as shown in Figure 4-32. It is found from Figure 4-32a that at the same crack length the extension of the unconditioned samples are

generally larger than that of the conditioned samples. However, the difference in compliance is not discernable as shown in Figure 4-32b. It was found that after absorbing moisture the tensile modulus of CFRP woven laminates decreased by 11.01%. The difference in stiffness between the conditioned and unconditioned CFRP woven laminates was not significant enough to bring about a distinguishable difference in compliance between the unconditioned and conditioned DCB samples. Therefore, at the same crack length due to their larger extension the load of the unconditioned DCB samples was larger than that of the conditioned sample as shown in Figure 4-32c. In conclusion, at the same crack length, the unconditioned sample had larger load and extension. Therefore, the reference group had higher propagation G_{IC} than the wet group.

Figure 4-31 Typical load/extension curves of reference and wet samples during Mode I fracture toughness test where R1 was an unconditioned laminate while W1 was a conditioned laminate

Figure 4-32 Extension, compliance and load of all the initiation and propagation values as functions of crack length during Mode I fracture toughness test of both conditioned and unconditioned CFRP woven-prepreg laminates

The Mode I fracture toughness of laminated composites is a matrix-dominated property. The modulus and strength of epoxy resin decreased after absorbing moisture, reducing the capability of the epoxy resin at the interlaminar region to withstand a peeling load. Consequently, the propagation G_{IC} decreased because of moisture uptake. In conclusion, Mode I fracture toughness test led to two conclusions. Firstly, moisture softened the matrix resin, reduced the brittleness of carbon fiber/epoxy composite materials and subsequently affected their Mode I crack propagation mode. The Mode I crack in wet DCB samples propagated steadily and slowly rather than abruptly and rapidly. In this regards, the resistance to crack propagation was improved by moisture uptake. Secondly, the strength and modulus

of the epoxy resin reduced because of moisture uptake. Consequently, the propagation G_{IC} decreased by 15.9%.

4.2.6 Mechanism of improvement

Results of the 80°C and 60°C Group led to the same finding, which revealed that the hygrothermal environments involved and duration of ageing conducted did not bring about visible damages to CFRP UD-prepreg laminates. Instead, the impact resistance of CFRP UD-prepreg laminates increased with their moisture contents. Hygrothermal ageing of this category is defined in this investigation as short-term hygrothermal conditioning, which did not cause damages but mainly resulted in moisture uptake of composite materials. Among the two constituents of laminated composites, only the matrix resin had moisture absorption behavior. It is therefore not difficult to realize that moisture improved the impact resistance of the CFRP laminates by affecting the matrix resin. Based on the experimental data acquired, the mechanism which accounted for the improved impact resistance of CFRP UD-prepreg laminates after absorbing moisture is proposed.

4.2.6.1 Softening of the epoxy resin by moisture

Compared to molecules of the cured epoxy resin, water molecules are exceptionally small in size. Therefore, water molecules could easily diffuse into the epoxy network and reside in the vacancies between epoxy molecular chains, resulting in volumetric expansion, which was evidenced by the increase in the average thickness of the laminates with moisture absorption.

The Van der Waals force between small molecules is normally of one to two orders of magnitude smaller than that of a covalent bond. Polymer molecules characterized by huge molar mass, usually have a great number of chain structural units. Therefore inter-molecular force of the polymer molecules is exceptionally high. The inter-molecular force of polymer molecules is even higher than that of a covalent bond. As illustrated in Figure 4-33, since each amine group of the hardener molecule (e.g. *mPDA*) has two active hydrogen atoms both of which can react with an epoxide group of a *DGEBA* molecule, a three-dimensional network is formed during curing in the epoxy resin, which makes the inter-molecular force of the epoxy resin even stronger. The movement of the epoxy molecular chains is inhibited by the highly interlaced or comingled molecular structure and the strong inter-molecular force, resulting in a brittle behavior of the material when mechanically loaded.

The inter-molecular force of a polymer molecule is composed of two parts, hydrogen bonding and Van der Waals force, which can further be divided into three components; dispersion force, induction force and orientation force. The interaction between water molecules and the epoxy resin weakened the inter-molecular force between them through two aspects (Figure 4-34). Firstly, the Van der Waals force is effective only over a certain distance. As water molecules diffused into the polymer network, the distance between molecular chains enlarged. Therefore, the Van der Waals force weakened. Both the orientation force and induction force depends strongly on polar groups of polymer molecules. Since water molecules (H_2O) are also polar molecules, they would further weaken orientation force and induction force by coupling with the polar groups of the polymer molecules (Figure 4-34b).

Figure 4-33 Schematic representation of formation of three-dimensional cross-links in epoxy resin

Secondly, hydrogen bonding was ready to be formed in the epoxy resin because it had amine groups and hydroxyl groups. Because of the volumetric expansion, some hydrogen bonding might be destroyed. Hydrogen bonding would also be created between water molecules and epoxy molecular chains, reducing the number of hydrogen bonding forming sites for the epoxy molecules. Therefore, the number of hydrogen bonds between epoxy molecular chains or epoxy molecules would also be reduced after absorbing moisture.

In conclusion, water molecules weakened the attractive force between different mers of one polymer molecule and/or between different polymer molecule chains by hindering Van der Waals force and disrupting hydrogen bonding of the epoxy resin. The movement of both, the various mers of an epoxy molecule and the different

molecules against each other, was therefore promoted, resulting in more ductile behavior of the epoxy resin in the conditioned CFRP laminates. The epoxy resin was therefore softened. This accounted for the lower modulus of both pure epoxy resin and laminated composite samples.

a) Hydrogen bonding and Van der Waals force of epoxy molecules before absorbing moisture

b) Disruption of hydrogen bonding and Van der Waals force of epoxy molecules after absorbing moisture

Figure 4-34 Schematic diagram of the interaction between moisture and epoxy resin

4.2.6.2 Identification of the first significant damage

Data collected during the low-velocity impact test showed that the first significant damage of the conditioned laminates (laminates filled with certain amount of moisture) occurred at larger projectile deflections, resulting in the larger contact force of conditioned laminates. The velocity of the impactor was therefore reduced to zero faster and less damage was imparted to the laminate. Essentially, it was the delay in the occurrence of the first significant damage that eventually led to the better impact resistance of CFRP UD-prepreg laminates. Therefore, it was crucial to identify what is the first significant damage and how did moisture postpone the first significant damage to larger projectile deflections.

Figure 4-35 presented the damage characteristics of two levels of impact for unidirectional prepreg laminates. Subcritical impact event refers to impact with energy values below the damage threshold. For a subcritical impact event, the first significant damage does not occur and the contact force/time curve is a smooth curve with the absence of oscillations or instant load drops, such as the curve depicted in Figure 4-35c. However, evident delamination and matrix cracking was found in the laminate after a subcritical impact attack (Figures 4-35a and 4-35b). Therefore, delamination and matrix cracking of certain magnitude did not make the laminate reduce its resistance (did not cause the decrease in contact force). It is further concluded that delamination was not the first significant damage. The major difference in damage characteristics between the subcritical and critical impact attack was that the critical impact attack involved zones of complex failure (Figures 4-35d and 4-35e). Complex failure is defined in this investigation as specific zones

in a composite layer where the lamina was evidently bent. It is typically associated with fiber debonding, fiber breakage and multiple matrix cracking (Figure 4-35e). This type of failure is capable of causing the degradation in the structural integrity of the laminate and is responsible for load oscillations or drops in contact force on the contact force/time curve in Figure 4-35f. Therefore, it was proposed that the first significant damage was the complex failure illustrated in Figures 4-35d and 4-35e.

Figure 4-35 Impact damage characteristics of unidirectional laminates subjected to different magnitude of impact damage: (a)-(b) Evident delamination and matrix cracking in a laminate after subcritical impact attack; (c) Contact force/time curve of the subcritical impact event; (d)-(e) observed fiber breakage and complex failure in a laminate after critical impact attack; (f) Contact force/time curve of the critical impact event

4.2.6.3 Delay of the first significant damage by moisture

Moisture did not increase the propagation G_{IC} values of this material. However, the initiation G_{IC} values were significantly increased because of moisture uptake.

Moisture promoted the chain segment mobility of epoxy molecules and softened the matrix resin, alleviating the brittleness of the epoxy resin. Consequently, abrupt and rapid crack propagation was prevented. This would benefit the laminate by postponing matrix cracking and delamination. Though the first significant damage was not delamination, the occurrence of a complex failure necessitated delamination and matrix cracking of sufficient scale. Therefore, the complex failure would also be postponed by the absorbed moisture. This explained why the first significant damage in conditioned laminates delayed and occurred at larger projectile deflections. Once complex failure was postponed, the strength of the laminate was maintained to larger deflections. The impactor encountered larger resisting force from the laminate, which reduced the velocity of the impactor faster. The maximum projectile deflection was therefore reduced. This explained why conditioned laminates suffered from less severe impact induced damage.

4.3 CFRP woven-prepreg laminates

Carbon/epoxy prepreg materials, L930HT(GT700) but in woven form, were used to fabricate laminates for low-velocity impact test in order to study the moisture absorption behavior of CFRP woven laminates and, more importantly, the effects of moisture on the impact properties and microstructure of CFRP woven materials. Four types of hygrothermal environments were designed for the ageing of CFRP woven laminates, which are summarized in Table 4-11. The low-velocity impact test results of both the 80°C Group and 60°C Group proved that moisture also improved the impact resistance of CFRP woven laminates. In order to avoid repeatability, only

the results of 80°C Group will be discussed in this chapter. Experimental results on 60°C Group are presented in Appendix X2.

For the 80°C Group, 12 laminates were fabricated from carbon fiber/epoxy woven prepreg materials. The average resin content of the cured CFRP woven laminates was 38.87%. The fabricated specimens were either continuously immersed in water at 80°C or exposed to a number of hygrothermal cycles. Each hygrothermal cycle consisted of 12 hour in water at 80 °C and 12 hour in the freezer at -30°C. Low-velocity impact testing was conducted at room temperature on the hygrothermally conditioned specimens. The microstructures after hygrothermal ageing and damage modes under impact were determined using a scanning electron microscope (SEM).

Table 4-11 Hygrothermal conditioning scheme for CFRP woven laminates prior to low-velocity impact test

Group	Sub-group	Hygrothermal conditioning
80°C Group	Reference (Unconditioned) Group	unconditioned
	Cyclically Conditioned Group	Exposure to certain number of hygrothermal cycles which consisted of 12 hour in water at 80 °C and 12 hour in the freezer at -30°C
	Isothermally Conditioned Group	Continuously immersed in water at 80 °C
60°C Group	Reference (Unconditioned) Group	unconditioned
	Cyclically Conditioned Group	Exposure to certain number of hygrothermal cycles which consisted of 12 hour in water at 60 °C and 12 hour in the freezer at -30°C
	Isothermally Conditioned Group	Continuously immersed in water at 60 °C

4.3.1 Hygrothermal conditioning results

The hygrothermal conditioning results are summarized in Table 4-12. The reference group represents specimens that were not subjected to any hygrothermal conditioning prior to low-velocity impact test. The weight variation of two CFRP woven laminates immersed in water at 80°C is shown in Figure 4-36. Initially, the weight of the specimen increased linearly with $t^{1/2}$. After the percentage increase in weight reached a certain point, the rate of weight increase with $t^{1/2}$ reduced significantly. Eventually, the weight of the specimens increased exceptionally slow with immersion time. The diffusion of moisture inside CFRP woven laminates at 80°C manifested as typical Fickian behavior.

Table 4-12 Hygrothermal conditioning results of CFRP woven-prepreg laminates 80°C Group

Group	Sample	W_i (g)	W_f (g)	M_f (%)	Time (h)	Thickness (mm)	Diffusivity D_z (mm ² /s)
Reference (Unconditioned) Group	Ref 1	24.45333	--	--	--	1.768	--
	Ref 2	23.91144	--	--	--	1.714	--
	Ref 3	24.31863	--	--	--	1.730	--
	Ref 4	24.30728	--	--	--	1.768	--
	Average	24.24767	--	--	--	1.745	--
Cyclically Conditioned Group	Cyc 1	24.63879	25.15477	2.09	522	1.843	--
	Cyc 2	24.23862	24.80408	1.43	522	1.838	--
	Cyc 3	24.11994	24.60285	2.00	522	1.787	--
	Cyc 4	25.14306	25.63753	1.97	522	1.895	--
	Average	24.53510	25.04981	1.87	522	1.841	--
Isothermally Conditioned Group	Iso 1	24.77896	25.44373	2.68	522	1.850	1.777×10^{-6}
	Iso 2	24.34138	24.99595	2.69	522	1.845	1.527×10^{-6}
	Iso 3	24.66145	25.30232	2.60	522	1.786	1.032×10^{-6}
	Iso 4	24.37871	25.01305	2.60	522	1.785	1.075×10^{-6}
	Average	24.54013	25.18876	2.64	522	1.817	1.353×10^{-6}

Figure 4-36 Weight change history of laminates immersed in water at 80°C

M_f in Table 4-12 was calculated as follows:

$$M_f = \frac{W_f - W_i}{W_i} \times 100\% \quad (4-18)$$

D_z was calculated as follows according to ASTM D5229:

$$D_z = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (4-19)$$

where,

$$\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} = \text{slope of moisture absorption plot in the initial linear portion of the}$$

curve.

Research work on isothermal conditioning of composite materials can be easily found in the literature. However, cyclic hygrothermal conditions, which are inevitable environments for aerospace composite structures, received relatively less attention. In this study, a hygrothermal cycle, which consisted of 12 hours in water

at 80°C and 12 hours in a dry freezer at -30°C, was designed to simulate certain in-service hygrothermal conditions. CFRP woven laminates were exposed to a number of such hygrothermal cycles and their weight was measured regularly each time after being taken out from the water bath or the freezer. Little variation in weight was observed when specimens were aged in the freezer, indicating that moisture resided inside CFRP laminates lost their transport capability at -30°C. The actual state of moisture inside composite materials is still not fully understood and substantial disagreement needs to be solved. Zhou and Lucas (1999) proposed that water molecules bind with epoxy resins through hydrogen bonding, while Woo and Piggott (1987) found that the moisture did not appear to be bound to polar groups in the resin although water inside did not behave as free water. Clustering of water molecules was found based on experimental results. However, whether absorbed moisture could form clusters that were large enough to allow the formation of ice crystals is not completely answered (Moy and Karasz, 1980). In our study, it was found that the absorbed moisture did not migrate out from the composite materials at -30°C.

4.3.2 Microstructure after hygrothermal conditioning

After the hygrothermal conditioning, the microstructure of the laminates was characterized by observing their cross-sections using a JOEL 5600LV scanning electron microscope (SEM). Prior to SEM observations, laminates were sectioned by a diamond saw and later polished by 800, 1200, 2400 grit SiC paper and 0.3µm micro-polish alumina powder. Typical microstructure of laminates from different hygrothermal groups is shown in Figure 4-37.

Figure 4-37 Microstructures of CFRP woven laminates exposed to different hygrothermal environments

The two constituents of a composite laminate, fiber and matrix, have coefficient of thermal expansion (CTE) of different magnitudes. The epoxy resin has a CTE greater than that of carbon fiber; as a consequence the laminate cannot expand or contract freely under changing temperatures, inducing thermal stresses at the fiber-matrix interface and interlaminar region. The diffusivity of moisture in the carbon fiber is negligible compared with the epoxy resin. Stresses are also introduced at the fiber-matrix interface and interlaminar region when the expansion of the moisture-saturated epoxy resin is constrained by the fibers. These moisture and temperature

induced stresses may cause the degradation of the microstructure of the laminate, such as micro-cracks (Garnich et al. 2011) and fiber debonding.

Specimens of the isothermally conditioned group were put in 80°C water for 522 hours and their average moisture content reached 2.64%. However, no surface micro-cracks were found and their microstructure was analogous to that of the unconditioned samples (Figure 4-37c) without delamination and fiber-matrix interface failure. Specimens of the cyclically conditioned group experienced both temperature cycling and possible volumetric expansion associated with water-to-ice transition. However, microstructure degradation was not found in the SEM picture of this group of specimen. In both Figures 4-37b and 4-37c, no cracks at the fiber-matrix interface and the interlaminar region were found, indicating good environmental durability of the composite materials investigated. In summary, current hygrothermal conditioning and time span of environmental ageing did not have detrimental effects on the microstructure of the CFRP laminates.

4.3.3 Damages to woven laminates under impact

As concluded in previous section, the hygrothermal conditioning carried out in the current investigation did not bring about any visible structural defects. The major difference between specimens of different groups was that they had different moisture contents. The isothermally conditioned group had the highest moisture content while the reference group had the lowest. After the hygrothermal conditioning, specimens with different moisture saturation levels were tested under the same impact energy level.

An impact loading normal to a clamped laminated is a bending load in nature. The largest stress and strain usually appear near the top and bottom surface of the composite and the general damage modes include matrix cracking, delamination, and fiber breakage. In Figure 4-38, when tested under the same impact energy level, Ref 1 had evident indentation while no visible indentation was found at the top surface (surface that had direct contact with the impactor) of Iso 2. This apparently means that specimen with higher moisture contents had lighter impact-induced damage. Severe fiber and tow splitting was observed at the bottom surface of Ref 1, while no splitting was found at the bottom surface of Iso 2. Only minor delamination and matrix cracking was found at the bottom surface of Iso 2. The photographs of the three specimens with different moisture contents proved that the extent of impact damage decreased with moisture content.

Careful observation on the damage site of the bottom surface of these three laminates revealed that delamination and fiber breakage are the major modes of damage for CFRP woven laminates under impact. As the degree of impact damage increased, the scale of delamination and the volume of fiber breakage also increased.

In order to examine the damage modes inside the laminate, the cross-section of the laminate near the damage site was observed under SEM; the micro-graphs of the laminates from each group are presented in Figures 4-39 and 4-40.

From Figure 4-39a to Figure 4-39d, it was found that the specimen with highest moisture content, Iso 2, had minimum impact damage. There was no evident damage near the top surface of the specimen (Figure 4-39a). Minor matrix cracking and

delamination near the bottom surface was observed (Figure 4-39b). Thus the major damage mode for Iso 2 was delamination.

Figure 4-38 Photographs of impact tested specimens from different groups, M_f (Ref 1) $< M_f$ (Cyc 1) $< M_f$ (Iso 2): (a) top surface of Ref 1; (b) bottom surface of Ref 1; (c) top surface of Cyc 1; (d) bottom surface of Cyc 1; (e) top surface of Iso 2; (f) bottom surface of Iso 2

More severe delamination and fiber breakage was observed in Figure 4-39c. The epoxy resin in this composite material is a type of brittle polymer. Therefore, large-scale matrix cracking was expected when severe delamination occurred (Figure 4-39c). Compared with Iso 2, Cyc 1 experienced more severe delamination (Figure 4-39c), large-scale matrix cracking (Figure 4-40c) and evident fiber breakage (Figure

4-40d). However, catastrophic failure was found in Ref 1 (Figure 4-39d), which was not hygrothermally conditioned and had the lowest moisture content. The damage modes of Ref 1 included large-scale delamination (Figures 4-39d and 4-40a) and severe splitting (Figure 4-40b). Among all the three laminates, Ref 1 experienced the most severe delamination (Figure 4-39d) and fiber breakage (Figure 4-40b). In summary, moisture significantly affected the damage characteristics of the laminates during impact testing. The degree of impact damage decreased rapidly with moisture content, which equally indicates that absorbed moisture alleviated the damage characteristics of CFRP woven laminates.

Figure 4-39 SEM graphs of the cross sections of impact tested specimens with different moisture levels, M_f (Ref 1) $< M_f$ (Cyc 1) $< M_f$ (Iso 2): (a)-(b) Iso 2 with minimum level of impact damage; (c) Cyc 1 with more severe delamination and fiber breakage; (d) Ref 1 with catastrophic failure

Figure 4-40 Comparison of the damage features of Ref 1 and Cyc 1, $M_f(\text{Ref } 1) < M_f(\text{Cyc } 1)$: (a) Ref 1 with large-scale catastrophic delamination; (b) Complete fiber splitting in Ref 1 after impact; (c) Matrix cracking in Cyc 1; (d) fiber breakage in Cyc 1 after impact

4.3.4 Impact Testing Results

After conditioning, the impact properties of CFRP woven laminates were measured by an instrumented low-velocity impact tester, Instron Dynatup 8250 drop tower impact tester. The impactor height and weight applied during impact testing were 2.735kg and 600mm, respectively.

Load versus time, load versus deflection and energy versus time curves of three specimens selected from each group are plotted in Figures 4-41 to 4-43. The relationship between the moisture contents of these three specimens was $M_f(\text{Ref } 1)$

$\langle M_f(\text{Cyc } 1) < M_f(\text{Iso } 1)$. In Figure 4-41, the load versus time curve of Iso 1 is more symmetrical than that of the other two specimens. The contact force dropped suddenly for Ref 1 and Cyc 1, while the instant sharp load drop of Ref 1 occurred earlier in time than that of Cyc 1. The oscillations and sharp load drops on the load/time and load/deflection curves are indications of the initiation and propagation of damages, such as matrix cracking, fiber breakage, delamination, etc. Once certain damage occurred, the stiffness of the structure would decrease and become more compliant. Iso 1, which had highest moisture content, experienced lowest level of impact damage. Therefore, no sharp load drop was observed on the load/time curve of Ref 1.

Figure 4-41 Typical load versus time curves of woven laminates under low-velocity impact, $M_f(\text{Ref } 1) < M_f(\text{Cyc } 1) < M_f(\text{Iso } 1)$

The area under load versus deflection curve represented the portion of impact energy that was stored in the laminate, therefore was a measure of the degree of impact damage. As shown in Figure 4-42, it is evident that the area under load versus deflection curve decreased as the moisture content inside the material increased,

which was consistent with the conclusion that the extent of impact damage decreased with the moisture content. No sharp load drop occurred for Iso 1, while the sharp load drop of Cyc 1 occurred at larger projectile deflection when compared with Ref 1. A sharp load drop on the load/time and/or load/deflection curve should be attributed to a significant damage created in the laminate. Damage modes that could contribute such an evident drop in contact force to the laminate might be severe delamination, fiber breakage or the combination of both. This leads to the important finding that moisture could prevent or postpone the occurrence of impact damage in CFRP woven laminate.

Figure 4-42 Typical load versus deflection curves of CFRP woven laminates under low-velocity impact, $M_f(\text{Ref } 1) < M_f(\text{Cyc } 1) < M_f(\text{Iso } 1)$

The slope of the initial linear part on the load/deflection curve generally reflects the magnitude of the out-of-plane contact stiffness of the laminate. In Figure 4-42, the curves of all the three samples coincide with each other at the initial linear part. Therefore, before impact laminates with different moisture contents had

approximately the same out-of-plane stiffness. Moisture did not affect the out-of-plane stiffness of CFRP woven laminates. This could be explained by the fact that the fibers in the laminate carried the majority of the applied load and moisture did not affect the mechanical properties of the carbon fiber.

In Figure 4-43, there is no evident difference between the initial parts of the energy/time curve of each specimen. However, after point a (Figure 4-43), the impact energy dissipation rate of Ref 1 became lower than the other two laminates. As shown in Figure 4-41, there was no sharp load drop on the curve of Iso 1, while the instant sharp load drop of Ref 1 occurred earlier in time than that of Cyc 1. Compared to the other two laminates, Ref 1 suffered from severe impact damage at an earlier time. Therefore, the contact stiffness of Ref 1 suffered from significant decrease earlier than that of the other two specimens, which consequently reduced the energy absorption ability of the laminate. Moreover, specimen with higher moisture content had lower E_d and higher E_{el} , which proves that specimens with more moisture consumed more of the impact energy through elastic deformation and the energy accounting for damage generation reduced.

The impact testing results of the three groups of specimens are plotted in Figures 4-44 to 4-47. In Figure 4-44a, D_i of both cyclically conditioned and isothermally conditioned groups was higher than that of the unconditioned reference group. This indicates that for conditioned laminates, the incipient damage or first significant damage occurred at larger deflections (higher strain levels accordingly) on an average scale. Thus, moisture absorbed during conditioning played a positive role in the CFRP woven laminates by improving their ability to sustain higher deflections

without significant damage. Projectile deflection at peak load point increased monotonically with average moisture content, proving that CFRP laminates with higher moisture content could retain their resistance to the impactor up to larger deflections. The increase in D_i and D_p proves that the elastic response of the laminate under impact improved after absorbing moisture.

Figure 4-43 Typical energy versus time curves of CFRP woven laminates under low-velocity impact, $M_f(\text{Ref } 1) < M_f(\text{Cyc } 1) < M_f(\text{Iso } 1)$

In Figure 4-44a, D_{max} decreased with average M_f . This should be attributed to the difference in the overall contact stiffness of the laminates with different moistures. As proved in Figure 4-42, before impact testing the laminates had approximately the same contact stiffness. However, specimens with higher moisture content suffered from lower impact damage and hence had less decrease in contact stiffness, which consequently resulted in the higher overall contact stiffness of conditioned laminates. Therefore, the intruding impactor was stopped faster and traveled shorter distance (smaller projectile deflection accordingly).

In Figure 4-44b, the average peak load of the conditioned specimens increased with average moisture content. As shown in Figure 4-42, when a sharp drop in load occurred, the contact force no longer continued to increase. This explained why Iso 1 had relatively larger F_p than the other two specimens. Cyc 1 experienced the sharp load drop at a larger deflection, resulting in a larger F_p than that of Ref 1. Therefore, after absorbing moisture, the sharp load drop was either prevented or postponed to larger deflections, resulting in the increasing trend of average F_p with moisture content. The average F_i also exhibited a monotonic increasing trend with moisture content. Despite some scatter in the test data, overall, the values of F_p and F_i showed a rising trend. The increase in F_i was due to the higher D_i of the conditioned CFRP laminates. Before incipient damage point, the contact force generally increased with projectile deflection (Figure 4-42). Therefore, Higher D_i would bring about higher F_i . The F_i values of the CFRP woven laminates tested were plotted against their respective D_i in Figure 4-45. The test results within the shown band prove that in general F_i is directly proportional to D_i .

Figure 4-44 Relationship between average moisture content and projectile deflection, contact force of CFRP woven laminates during impact test: (a) D_i , D_p and D_{max} ; (b) F_i and F_p

Figure 4-45 Relationship between F_i and D_i of CFRP woven laminates

In Figure 4-46, the average elastic energy E_{el} of each group of specimens increased evidently with the average moisture content, while E_d showed an opposite trend. For specimens of the isothermal group, E_{el} increased by nearly 2 times, while E_d decreased by 27.7%. After absorbing moisture, the portion of the kinetic energy of the impactor dissipated by CFRP woven laminates through elastic deformation increased, and the rest of the impact energy which accounted for the damage induced to the laminate decreased. This is consistent with the conclusion that moisture alleviated the extent of impact damage in CFRP woven laminates. The increase in E_{el} further supported the conclusion that the elastic response of CFRP woven laminates under impact improved after absorbing moisture. It was also noted that E_{d2} decreased with M_f . For unconditioned laminates, after the peak load point the impactor still had certain speed which was relatively higher when compared with the case of conditioned laminates. Therefore, E_{d2} of the unconditioned group was larger than the other two groups. This also explained the fact that D_{max} of the reference group was larger of the two conditioned groups.

Figure 4-46 Relationship between average moisture content and E_{el} , E_d and E_{d2}

For the drop weight impact testing of composite materials, contact time between the impactor and the laminate is also a parameter that generally reflects the behavior of the laminate under an impact load. Figure 4-47 shows the variation of contact time with respect to the average moisture content of each group, which clearly shows that specimens with higher moisture content had shorter contact time. The impactor stroke the laminate with approximately the same speed (same impact energy). If the laminate had relatively higher overall stiffness (lower compliance), the speed of the impactor would be reduced to zero faster and shorter contact time would be expected. In this study, it is assumed that initially laminates of different moisture contents had approximately the same stiffness (Figure 4-42). However, laminates with less moisture content experienced more severe impact damage, which reduced their contact stiffness consequently. Therefore, specimens with less moisture content had longer average contact time.

Figure 4-47 Relationship between average moisture content and contact time

Thus, the experimental results showed that the moisture absorbed by CFRP woven laminates during hygrothermal conditioning alleviated the degree of impact induced damage. Another important finding from the data collected during the impact test was that moisture delay the occurrence of impact damage. Laminates with higher moisture contents could deform to larger projectile deflections without significant damage. The moisture also altered the energy dissipation mechanism of CFRP woven laminate. The kinetic energy of the impactor consumed by elastic deformation increased with moisture content while less impact energy was left for damage generation resulting in the alleviated damage state in the laminate. Although the fibers in the laminate carried the majority of the load, it was moisture that improved the impact resistance of CFRP woven laminate. The overall conclusion is the same as that of CFRP UD-prepreg laminates.

4.3.5 Mechanism behind improvement

In Figure 4-39, the damage characteristics of three laminates with different moisture levels were depicted. In the meantime, Figure 4-39 also presents three extents of damage of CFRP woven laminates under impact. When the laminate

experienced only moderate impact damage such as Iso 2 (Figure 4-39a), the major damage modes included light delamination and moderate matrix cracking. This type of damage is schematically depicted in Figure 4-48b. If the impactor strikes the laminate with higher velocity, more severe impact damage is expected. More severe delamination and large-scale matrix cracking and fiber breakage will occur (Figure 4-39c). As the impact energy increased, catastrophic delamination and severe fiber splitting will be caused. This process is depicted in Figure 4-48c. The impact damage evolution of CFRP woven laminates shown in Figure 4-48 proves that the first damage might be delamination, matrix cracking or the combination of both and the catastrophic failure of the laminate usually occurred after severe delamination was initiated. For laminated structures, once large-scale delamination and matrix cracking were initiated, fiber breakage was ready to occur. Consequently, the laminate lost its structural integrity and hence the mechanical properties along through-the-thickness direction.

Moisture softened the epoxy resin within this prepreg material by weakening Van der Waals forces and by reducing the number of hydrogen bonds. The mobility of the various mers (or the chain segments) of the epoxy molecules was therefore promoted. Consequently, the ductility of the epoxy resin improved and the laminate became less brittle. The abrupt and rapid crack propagation mode was therefore avoided. This benefits the laminate by effectively preventing or postponing the occurrence of interlaminar failure and matrix cracking. Therefore, after absorbing moisture the first significant failure occurred at larger projectile deflections (higher D_i). The rapid decrease in load which was attributed to impact damage was also

delayed (Figures 4-41 and 4-42). This explains the important finding that Iso 1 which had the highest moisture content did not experience such sharp load drop while Cyc 1 experienced a sharp load drop at a larger projectile deflection compared with Ref 1. Moisture softened the epoxy resin and alleviated the brittleness of the laminates, which in turn delayed the initiation of matrix cracking and delamination in the laminate and maintained the structural integrity of CFRP woven laminates. The elastic response of the laminate was therefore improved, which explains the higher E_{el} exhibited by conditioned laminates.

Figure 4-48 Schematic representation of the evolution of impact damage in CFRP woven laminate

In summary, it was proposed that absorbed moisture promoted mobility of the chain segment of the epoxy molecules and increased the ductility of the epoxy resin. The epoxy matrix with higher ductility benefited the laminate by effectively preventing or postponing the occurrence of delamination and matrix cracking. The elastic response of the laminate was therefore improved. The portion of the kinetic energy of the impactor dissipated by the laminate through elastic deformation was increased by nearly 2 times after absorbing 2.64% wt. of moisture. This explains the alleviated impact damage in the conditioned CFRP woven-prepreg laminates.

4.4 Overall conclusions: short-term hygrothermal ageing

The durability of CFRP UD-prepreg, woven-prepreg laminates and pure epoxy resin affected by short-term hygrothermal conditioning was evaluated in details in this chapter. Emphasis was placed on the role played by moisture in epoxy resin and the laminated (normal and staggered as well as woven) composites, and its influence on the various mechanical properties of both, the pure epoxy samples and the carbon fiber reinforced epoxy composites. Important findings and conclusions include:

(1) The differences in both the moisture absorption rate (D_z) and impact resistance between the normal and staggered lay-up laminates were not significant from a statistical point of view. The effect of automated tape lay-up process on the impact resistance of CFRP UD-prepreg laminates was not significant.

(2) For both, the CFRP UD-prepreg and woven-prepreg laminates, their moisture content or weight vs. $\sqrt{time/h}$ curves revealed that the transport of moisture in the CFRP composites followed Fickian behavior. At -30°C, the absorbed moisture lost its capability of migrating out from the laminate.

(3) For both, the CFRP UD-prepreg and woven-prepreg laminates, neither isothermal water immersion ageing at 60°C or 80°C until moisture saturation nor repeated hot-to-cold and wet-to-dry hygrothermal cycling caused any evident structural defects. No cracks at the fiber-matrix interface and the interlaminar region were found.

(4) Moisture softened the epoxy resin by promoting the mobility of the various mers of an epoxy molecule and the different epoxy molecules against each other, resulting in the more ductile behavior of the epoxy resin and thereby reducing the brittleness of CFRP laminates.

(5) Tensile modulus, tensile strength and ultimate tensile strain of pure epoxy resin decreased after absorbing moisture.

(6) Tensile strength and modulus of CFRP composites decreased after absorbing moisture, while the tensile strain remained approximately the same. Good recovery in both the tensile strength and modulus were achieved upon the removal of the absorbed moisture.

(7) Mode I fracture toughness test provided a key insight into the effects of moisture on the crack propagation mode of CFRP composite materials. Though the propagation G_{IC} reduced by 15.9%, the abrupt and rapid crack propagation did not

take place after absorbing moisture, resulting in an increase in the initiation G_{IC} by 74.4%.

(8) Moisture had the same effects on the behavior of CFRP UD-prepreg and woven-prepreg laminates under low-velocity impact. Moisture softened the epoxy resin and reduced the brittleness of the CFRP laminates, which subsequently delayed impact damage and preserved their strength. Laminates with higher moisture contents had larger contact force under impact and suffered from alleviated impact damage.

(9) The short-term conditioning did not bring about discernable defects to both pure epoxy and CFRP laminated composites. However, moisture was the major factor which was responsible for the change in the mechanical properties of the pure epoxy and the CFRP composites exposed to short-term hygrothermal ageing.

Chapter 5 Long-term ageing on CFRP

laminates

Short-term hygrothermal conditioning on CFRP laminates showed that moisture played a positive role in improving the impact resistance of both woven- and UD-prepreg CFRP laminates. However, it was reported elsewhere (as stated in Chapter 2) that various mechanical properties of composites degrade after exposure to hygrothermal conditions. Therefore, in order to identify the onset of such properties degradation, long-term conditioning on CFRP laminates was planned and conducted.

5.1 Specimen fabrication

There were four groups of specimens fabricated for the long-term conditioning study. Carbon fiber reinforced epoxy unidirectional prepreg materials, L-930HT (GT700), were used for the fabrication of the specimens. The stacking sequence was [45/90/-45/0]_s. The laminates were cured in the autoclave. The average resin content of the cured laminates was 30.51 wt. %.

5.2 Hygrothermal conditioning scheme

These fabricated specimens were then immersed in water at 80°C for different durations. A general water bath was used for water immersion conditioning. The temperature stability of the water bath is ± 0.3 °C. The long-term hygrothermal conditioning scheme is shown in Table 5-1. In Table 5-1, each datum is the average value of 5 specimens.

The values of M_f in Table 5-1 were calculated as follows:

$$M_f = \frac{W_f - W_i}{W_i} \times 100\% \quad (5-1)$$

Table 5-1 Summary of long-term hygrothermal conditioning on CFRP UD-prepreg laminates

Group	Number of specimens	Hygrothermal conditioning	W_i (g)	W_f^* (g)	M_f (%)
Group 1	5	unconditioned	21.61057	21.62628	0.073
Group 2	5	immersed in water at 80°C for 2 months	21.59210	22.27177	3.149
Group 3	5	immersed in water at 80°C for 6 months followed by drying in a vacuum oven at 45°C for 2 months	21.79381	21.80332	0.044
Group 4	5	immersed in water at 80°C for 9 months followed by drying in a vacuum oven at 45°C for 3 months	21.57490	21.58049	0.026

* W_f was the average final weight of each group before impact test. For Group 2, W_f was the average weight after hygrothermal ageing. For Groups 3 and 4, W_f was the average weight after drying.

In Table 5-1, Group 1 was treated as the control group. Specimens of Group 1 were fabricated to obtain the impact properties of unconditioned CFRP UD-prepreg laminates. As shown in Table 5-1, the average final moisture content of Group 1 is 0.073%. After curing, cured laminates were stored in a dry cabinet (at 23°C and 22% relative humidity) before impact testing or hygrothermal conditioning in order to prevent specimens from absorbing moisture at the lab conditions (at 25°C and 50% relative humidity). However, the specimens still adsorbed substantial amount of moisture when stored in the dry cabinet. Therefore, prior to conditioning or impact testing, the specimens were dried in a vacuum oven at 45°C. However, there was still certain amount of moisture residing inside specimens after being dried in the vacuum oven for 24hours. According to the conclusion made by Zhou (Zhou and Lucas, 1999), temperature in excess of the glass transition temperature was required to remove the residual water. In the current work, such a high drying temperature

was not used in order to prevent the effect of high temperature on the properties of laminates.

The average absorption and desorption curves of each group are shown in Figure 5-1, while the weight variation history of each sample of Group 4 during both absorption and desorption process is shown in Figure 5-2. As shown in Figure 5-1, the moisture absorption curves of Groups 3 and 4 can be divided into three stages according to the slope of the moisture vs. $\sqrt{\text{time}/h}$ curve. Stage I and Stage II are common for diffusion governed by Fick's law. Initially, moisture content increased linearly with $\sqrt{\text{time}/h}$ (Stage I), after which the rate of diffusion decreased evidently (Stage II). At this stage, the weight of the CFRP specimen increased relatively slowly with immersion time and moisture saturation was considered to have been achieved. However, in this study it was found that if the hygrothermal conditioning continued, Stage III would take place. The moisture diffusion rate at Stage III was larger than that of Stage II but lower than that during Stage I.

Figure 5-1 Moisture absorption and desorption curves of CFRP unidirectional laminates

During the course of experiments, at the end of Stage II (around 1500hours) tiny blisters began to appear at the surface of the laminates, implying that damages were

formed inside the laminates. It is proposed that damages formed during hygrothermal ageing affected the moisture absorption pattern for the CFRP laminates and contributed to the occurrence of Stage III. Typical surfaces of unconditioned and conditioned laminates are shown in Figure 5-3, which shows that evident blisters formed at the surface of a conditioned sample which was immersed in water for 6 months.

Figure 5-2 Weight change history of specimens of Group 4 during both the absorption and desorption process

Figure 5-3 Comparison between surfaces of unconditioned and conditioned CFRP unidirectional laminates: a) smooth surface of an unconditioned sample; b) wrinkles formed at the surface of a conditioned sample immersed in water at 80°C for 6 months

The conditioned sample was sectioned using a diamond saw to observe its internal microstructure. After polishing it using 1200-grit, 2400-grit SiC sand papers and a polishing cloth which was sprayed with 0.3 μ m micro-polish aluminum powder, the conditioned sample was observed under FESEM. As seen in the FESEM images in Figure 5-4, it is found that the blisters shown in Figure 5-3b are essentially large-scale delamination. In conclusion, long-term hygrothermal ageing would cause severe delamination or blisters in CFRP laminates made from unidirectional prepreg materials. At Stage II the moisture absorption of CFRP unidirectional laminates already reached the saturation level. However, the cracks produced by delamination provided extra free spaces for moisture absorption. Therefore, the laminates continued to absorb moisture. This explains why Stage III occurred in CFRP unidirectional laminates exposed to long-term hygrothermal ageing.

Figure 5-4 Comparison between cross-section of unconditioned and conditioned CFRP unidirectional laminates: a) unconditioned sample with no delamination; b) cross-section of a conditioned sample immersed in water at 80°C for 6 months

The hygrothermal ageing of Group 2 was terminated at the end of Stage II as shown in Figure 5-1. Later, low-velocity impact test with an impact energy level of 9J was conducted on Group 2. The impact response of Group 2 was compared with

that of Group 1. It was found that the impact response was improved by the moisture absorbed during the hygrothermal ageing. Though a few tiny blisters were sparsely distributed at the surface of several samples of Group 2, the moisture played a major role in affecting the impact behavior of CFRP UD-prepreg laminates. The overall finding was the same as that of the short-term conditioning study on CFRP UD-prepreg laminates. Therefore, to avoid repeatability the impact test results of Group 2 were present in Appendix X3.

5.3 Characteristics of hygrothermal ageing induced damages

Besides the large-scale delamination at the interlaminar region, no evident damages were found in individual ply of a long-term hygrothermally aged CFRP laminate. As shown in Figure 5-5b, fiber debonding and matrix cracking were not identified via FESEM in the interior of each ply. Long-term water immersion conditioning for 9 months did not cause damages such as fiber debonding and matrix cracking inside each ply. In conclusion, during long-term isothermal water-immersion conditioning, the observable structural flaws were mainly initiated at the interlaminar region rather than inside individual ply.

After carefully observing the aged laminate under FESEM, it was found that the initiation and propagation of delamination in the CFRP laminates made from unidirectional prepreg materials had two features. The first feature was that the delamination caused by moisture uptake occurred mainly at the interlaminar region between plies of different fiber orientations. As seen in Figure 5-6, while

delamination was found at the interfaces of plies of different fiber orientations, no delamination was observed between the two 0° plies.

Figure 5-5 SEM images of the cross-section of unconditioned and conditioned CFRP unidirectional laminates: a) unconditioned sample; b) conditioned sample immersed in water at 80°C for 9 months. Fiber debonding and matrix cracking was not identified in the micrograph of conditioned sample

Figure 5-6 FESEM image of the cross-section of a conditioned sample immersed in water at 80°C for 6 months showing that delamination occurred between layers of different fiber orientation

The second feature refers to the general propagation pattern of delamination at the interlaminar region. Figure 5-7 shows the delamination tips in a conditioned sample. Both matrix cracking and fiber debonding were found at the delamination tips. It was concluded from Figure 5-7 that the propagation of delamination usually involves matrix cracking and fiber debonding at the interlaminar region. When the delamination propagated along the interface between two adjacent layers, the crack might propagate either in the matrix or cross the fiber/matrix interface as

schematically shown in Figure 5-8. Therefore, both matrix cracking and fiber debonding were likely to occur at the interlaminar region as the delamination was propagating.

Figure 5-7 FESEM image of the cross-section of a conditioned sample immersed in water at 80°C for 6 months showing that delamination propagated through matrix cracking and fiber debonding along the interlaminar region

Figure 5-8 Schematic representation of the propagation of delamination which involves matrix cracking and fiber debonding

The mechanism of the formation of delamination caused by moisture uptake in CFRP unidirectional laminates is schematically illustrated in Figure 5-9. Among the two constituents of laminated composites, namely the carbon fiber and epoxy resin, only the epoxy resin had moisture absorption behavior, which subsequently caused the swelling of individual ply. Due to the constraint of the carbon fiber, the principal

direction of ply swelling was perpendicular to the orientation of the fiber as shown in Figures 5-9a and 5-9b. In the current investigation, the laminates were made from unidirectional prepreg materials and the stacking sequence was $[45^\circ/90^\circ/-45^\circ/0^\circ]_2$. Therefore, the principal swelling directions of plies of different angles would be different, resulting in an interlaminar shear stress at the interlaminar region as shown in Figure 5-9c. Consequently, the ply was forced out from the lay-up under the combined action of ply swelling resulted from the moisture uptake and the interlaminar shear stress.

Figure 5-9 Schematic representation of the formation of delamination resulted from ply swelling because of moisture uptake and interlaminar shear stress

5.4 Post-immersion impact testing result

After hygrothermal ageing, the moisture absorbed by CFRP UD-prepreg laminates of Groups 3 and 4 was completely removed through drying in a vacuum oven. Low-velocity impact test was then conducted to study the impact response of laminates with hygrothermal ageing resulted damages. The impactor weight and height was 2.735kg, 335mm, respectively, resulting in an impact energy level of 9J.

The impact response of Groups 1, 3 and 4 are to be compared to understand the difference between the impact properties of the conditioned and unconditioned laminates. Typical curves including load/time, load/deflection and energy/time curves from different hygrothermal groups are plotted to aid in the comparison between the impact response of the unconditioned laminates and laminates with damages. The variation of contact force with contact time for samples from different groups was shown in Figure 5-10. For the current impact energy level (9J), the impact events of all the three samples belonged to supercritical impact. The peak load of the unconditioned sample was larger than the other two samples which were subjected to water immersion conditioning.

While the load vs. time curve shows the category of the impact event, the load vs. deflection curve provides a full range of information about the impact resistance properties of composite materials. Figure 5-11 shows the typical contact force vs. projectile deflection curves of samples subjected to different duration of water immersion conditioning. It was found that before the peak load point the load of the unconditioned sample increased faster with projectile deflection than the two

conditioned laminates. Before the peak load point, at the same projectile deflection the unconditioned sample had larger load (higher resistance correspondingly). Though D_p of the unconditioned sample was smaller than the two conditioned samples, F_p of the unconditioned sample was larger than that of the conditioned samples. This apparently proved that the capacity of CFRP laminates to bear a load applied perpendicularly to the plane of the sample degraded after hygrothermal conditioning.

Figure 5-10 Typical load-time curves of CFRP laminates from different hygrothermal groups

The average peak load (F_p) of different groups is shown in Figure 5-12, while the average deflection to peak load (D_p) of each group is shown in Figure 5-13. The average peak load of the unconditioned group was higher than the other two conditioned groups, while the average deflection to peak load of the two conditioned

groups was larger than the unconditioned group. This directly indicates that the unconditioned sample had larger out-of-plane stiffness.

Figure 5-11 Typical contact force-deflection curves of CFRP laminates from different hygrothermal groups

Figure 5-12 Average *peak contact force* of different groups of samples

Figure 5-13 Average D_p of different groups of samples

The maximum deflection of the unconditioned laminate was also smaller than the other two samples as shown in Figure 5-11. The average maximum deflection of each group is shown in Figure 5-14, which proves that the average D_{max} of the unconditioned group was smaller compared to that of the two conditioned groups. For an impact event without perforation, the velocity of the impactor reached its maximum value at the moment when it reached the surface of the laminate (Figure 5-15). Once the impactor contacted with the sample under testing, its velocity decreased gradually to zero which corresponded to the point where the projectile deflection was maximum. The rate of decrease in the velocity of the impactor depended on the magnitude of the contact force. As shown in Figure 5-15, due to the larger contact force of the unconditioned sample, the velocity of the impactor decreased to zero within a shorter contact time compared to the conditioned samples. Therefore, D_{max} of the unconditioned sample was smaller than that of the conditioned

samples. For a supercritical impact event, smaller D_{max} also indicated that less damage was caused to the laminate by impact.

Figure 5-14 Average maximum deflection (D_{max}) of different groups of samples

Figure 5-15 Velocity of the impactor during impact test showing that during the impact test of the unconditioned sample the velocity of the impactor was reduced to zero within a shorter contact time compared to the two conditioned samples

During a low-velocity impact test, when the velocity of the impactor was reduced to zero, both the projectile deflection and impact energy reached their maximum values. That is, E_{total} , D_{max} and zero impactor velocity occurred essentially at the same point of contact time. Figure 5-16 shows the average contact time to E_{total} of each group. The average time to E_{total} of the unconditioned groups was smaller than the two conditioned groups. This is due to that the velocity of the impactor was reduced to zero within a shorter contact time during the low-velocity impact test of the unconditioned laminate (Figure 5-15).

Figure 5-16 Average time to E_{total} (contact time required to reduce the velocity of the impactor to zero) of different groups of samples

The energy-time curves of samples from different hygrothermal groups are plotted in Figure 5-17. The energy-time curve can be divided into two parts. At the first part, the energy value keeps increasing until it reaches its maximum value, which is normally defined as E_{total} . This part corresponds to the attacking stage of an impact event. During the attacking stage, the impactor was falling down and

penetrating the laminate. At the same time its velocity decreased from its maximum value to zero. Therefore, the kinetic energy of the impactor was absorbed by the laminate under testing. If the resistance of the testing structure was higher, the velocity of the impactor would be reduced to zero earlier such as the case described in Figure 5-15. Consequently, the kinetic energy of the impactor would be absorbed faster by the testing structure. As shown in Figure 5-17, at the first part of the energy vs. time curves, the energy value of the unconditioned sample was always higher than that of the conditioned samples when the contact time was the same. This was due to that the unconditioned sample had larger contact force as shown in Figures 5-10 and 5-11.

Figure 5-17 Typical energy-time curves of CFRP laminates from different hygrothermal groups

The second part of the energy vs. contact time curve corresponds to the rebounding stage of the impact event, during which the impactor rebounds back from

the testing laminate and part of the impact energy absorbed by the laminate is returned back to the impactor. This part of energy is defined as elastic impact energy E_{el} . As shown in Figure 5-17, after hygrothermal conditioning E_{el} decreased while E_d increased. The average E_{el} and E_d of each group were shown in Figure 5-18, which proves that the unconditioned group had larger average E_{el} and smaller average E_d . This equally means that more impact energy was returned to the impactor during the rebounding stage. At the end of the low-velocity impact test, the impactor left the laminate with certain speed. As seen in Figure 5-15, the final velocity (V_{final}) of the unconditioned laminate was higher than that of the two conditioned samples. Therefore, the impactor had higher kinetic energy when it rebounded from the unconditioned laminate as compared to the two conditioned samples. This explained why the average E_{el} of the unconditioned group was larger than that of the two conditioned groups.

Figure 5-18 Average E_{el} and E_d of different groups of samples

In the meantime, the higher final velocity of the impactor for the impact test of the unconditioned sample should be attributed to the larger contact force of the unconditioned sample at the rebounding stage. As shown in Figure 5-11, during the rebounding stage, at the same magnitude of projectile deflection the contact force of the unconditioned sample was apparently larger than that of the two conditioned sample. There was a larger contact force which was “pushing” the impactor away from the laminate. Hence the final velocity of the impactor was higher during the low-velocity of impact test of the unconditioned sample. In conclusion, it was the larger contact force of the unconditioned sample that was responsible for the larger E_{el} of the unconditioned sample. After the long-term isothermal water immersion conditioning, the impact resistance of CFRP laminates made from unidirectional laminates degraded, resulting in the smaller contact force under impact.

5.5 Mechanism of reduced impact resistance

Based on the analysis of the low-velocity impact test results, it was found that the contact force during impact test decreased for samples exposed to long-term hygrothermal conditioning. Though the deflection to the peak load point was smaller, the peak contact force of the unconditioned sample was larger than that of the conditioned laminates, implying the decrease in the out-of-plane stiffness of the CFRP UD-prepreg laminates after long-term hygrothermal conditioning. In conclusion, the impact resistance, which was related to the magnitude of the contact force during impact test, degraded after the hygrothermal ageing.

Tensile tests on CFRP woven laminates showed that after being immersed in water at 80°C for 2 months, the ultimate tensile strength and tensile modulus of CFRP woven laminates decreased by 15.98% and 11.01%, respectively. Upon removing the moisture absorbed during hygrothermal ageing, a good recovery in both the tensile strength and tensile modulus was observed. However, the average σ_{ult} and ε_{ult} of the conditioned & dried groups were still lower than that of the unconditioned group. This might be resulted from the micro-defects formed during hygrothermal conditioning. For the samples exposed to long-term conditioning (6 months), severe delamination was formed and the overall extent of structural degradation was much more severe. Therefore, a higher percentage of loss in static properties would probably occur.

An impact load was essentially a bending load applied normal to the CFRP laminate. For a structure which was clamped by two aluminum plates at the edges, the contact force was a function of projectile deflection and the out-of-plane stiffness of the laminate. The out-of-plane stiffness was, however, function of the tensile strength and tensile modulus of the laminate. Due to the damages formed during long-term hygrothermal ageing, the static properties of the CFRP laminates were expected to degrade by a certain extent, consequently making the decrease in the out-of-plane stiffness possible. This explains why the contact force or the impact resistance was observed to decrease after long-term hygrothermal ageing.

5.6 Conclusions: long-term hygrothermal ageing

The important findings of the long-term hygrothermal conditioning studies (immersion in water at 80°C for prolonged duration) conducted on laminates made from carbon fiber/epoxy unidirectional prepreg materials include:

- (1) The principal hygrothermal conditioning induced damage observable under FESEM was delamination. In a quasi-isotropic laminate, the ply was forced out under the combined action of ply swelling resulted from moisture uptake and interlaminar shear stress, causing delamination between plies of different fiber orientations.
- (2) A three-stage moisture absorption behavior of CFRP UD-prepreg laminates exposed to long-term conditioning was identified. Delamination or blisters began to take place at the end of Stage II of the moisture absorption process. These delamination or blisters provided extra free spaces for moisture absorption. Consequently, even after the saturation level was reached, the laminates continued to absorb more moisture, resulting in the Stage III moisture uptake state.
- (3) The impact resistance of CFRP unidirectional laminates degraded after the long-term hygrothermal ageing. The out-of-plane stiffness and contact force during impact test was reduced for samples exposed to long-term hygrothermal conditioning. The hygrothermal conditioning induced damages caused the decrease in the strength and modulus of the laminates. Consequently, the impact resistance of CFRP UD-prepreg laminates also declined.

Chapter 6 GFRP laminates with CSP particles

6.1 Introduction

Effects of hygrothermal ageing and moisture on the mechanical properties of glass fiber reinforced epoxy composites were studied. The GFRP composites were immersed in water at elevated temperatures for different durations. Low-velocity impact test and tensile test were then conducted on the hygrothermally aged GFRP laminates. Core-shell polymer particles have been proved to be effective additives to improve the impact resistance of composite materials (Ali and Joshi, 2012, 2013). CSP particles filled GFRP laminates were fabricated to explore the effects of CSP particles on the moisture uptake behavior and environmental durability of GFRP composite materials.

Exposure to hygrothermal environments mainly brought about two influences, namely, structural degradation and moisture uptake. Both of these might have different effects on specific properties of composite materials. In order to distinguish between the effects of moisture and structural degradation on the performance of GFRP laminates, two groups of hygrothermally aged GFRP laminates were dried in a vacuum oven until the moisture absorbed during hygrothermal ageing was completely removed.

6.2 Hygrothermal conditioning scheme

Two groups of GFRP laminates without CSP particles were fabricated, each consisting of 5 samples. The geometry of cured GFRP laminates without particles

was 100mm × 100mm × 1.429mm. Five groups of CSP particle reinforced GFRP laminates were fabricated, each consisting of 5 samples. The geometry of CSP particle filled laminates was 100mm × 100mm × 1.650mm. The resin content of the cured GFRP laminates for low-velocity impact tests was 17.01% by weight (30.00% by volume).

The IDs of specimens of each group are shown in Table 6-1. In Table 6-1, Groups GI and GII consisted of GFRP laminates without particles, while Groups G(0.3)I-V were composed of CSP particle reinforced GFRP laminates. The ‘0.3’ in the IDs of the five groups indicates that 0.3 grams of CSP particles were added to each interply interface of the 8-ply GFRP laminates. Specimens with ‘0.3’ in their IDs are CSP particles reinforced laminates.

Table 6-1 The IDs of specimens of each group

Group	Hygrothermal conditioning	Specimen ID
GI	unconditioned	G1, G2, G3, G4, G5
GI	immersed in water at 80°C for 1860.33 hours	G6, G7, G8, G9, G10
G(0.3)I	unconditioned	G(0.3)1, G(0.3)2, G(0.3)3, G(0.3)4, G(0.3)5
G(0.3)II	immersed in water at 80°C for 1860.33 hours	G(0.3)6, G(0.3)7, G(0.3)8, G(0.3)9, G(0.3)10
G(0.3)III	immersed in water at 80°C for 2651.67 hours	G(0.3)11, G(0.3)12, G(0.3)13, G(0.3)14, G(0.3)15
G(0.3)IV	immersed in water at 80°C for 2651.67 hours followed by drying in a vacuum oven at 45°C for 986.33 hours	G(0.3)16, G(0.3)17, G(0.3)18, G(0.3)19, G(0.3)20
G(0.3)V	immersed in water at 80°C for 3953.67 hours followed by drying in a vacuum oven at 45°C for 2130 hours	G(0.3)21, G(0.3)22, G(0.3)23, G(0.3)24, G(0.3)25

As seen in Table 6-1, the GFRP laminates with and without CSP particles were exposed to different types of hygrothermal ageing prior to the low-velocity impact testing. The hygrothermal conditioning results for both types of GFRP laminates are summarized in Table 6-2.

Table 6-2 Summary of hygrothermal conditioning of GFRP laminates with and without CSP particles

Group	Hygrothermal conditioning	W_i (g)	W_f^* (g)	M_f (%)	D_z (mm ² /s)
GI	unconditioned	29.06793	29.06793	0	-
GII	immersed in water at 80°C for 1860.33 hours	29.08571	29.38729	1.037	6.295×10^{-7}
G(0.3)I	unconditioned	31.27495	31.27495	0	-
G(0.3)II	immersed in water at 80°C for 1860.33 hours	31.23404	31.70717	1.515	3.932×10^{-7}
G(0.3)III	immersed in water at 80°C for 2651.67 hours	31.07158	31.63097	1.800	3.866×10^{-7}
G(0.3)IV	immersed in water at 80°C for 2651.67 hours followed by drying in a vacuum oven at 45°C for 986.33 hours	31.32671	31.30544	-0.068	3.913×10^{-7}
G(0.3)V	immersed in water at 80°C for 3953.67 hours followed by drying in a vacuum oven at 45°C for 2130 hours	31.24966	31.17111	-0.251	4.511×10^{-7}

* Except G (0.3) V, W_f was the average final weight of each group before impact test. For GI and G (0.3) I, W_f was the average weight after curing. For GII, G (0.3) II and G (0.3) III, W_f was the average weight after hygrothermal ageing. For G(0.3)IV and G(0.3)V, W_f was the average weight after drying in the vacuum oven.

Specimens of Groups GI and G(0.3)I were not exposed to any type of hygrothermal ageing prior to the low-velocity impact test. The other five groups were immersed in water for different durations. The weight change, moisture absorption and desorption characteristics of GFRP laminates with and without particles are shown in Figure 6-1. As shown in Figure 6-1a, the weight of the specimens increased linearly with $\sqrt{t}$ at the early stage of immersion. Later, the rate of weight gain because of moisture uptake decreased gradually. The diffusion of moisture in GFRP composite materials also followed Fick's law. The average moisture contents of each group as function of $\sqrt{t}$ during absorption and desorption are presented in Figure 6-1b. The total amount of immersion time was the same for Groups GII and G(0.3)II. However, it is seen in Figure 6-1b that the moisture level of Group G(0.3)II was higher than that of Group GII. Due to the addition of CSP

particles, the total amount of moisture absorbed by GFRP laminates increased by 46.10%.

(a) Weight gain as function of $\sqrt{t}$ for specimens of the G (0.3) II Group

(b) Average moisture contents of each group as function of $\sqrt{t}$ during absorption and desorption

Figure 6-1 Moisture absorption behavior of GFRP laminates with and without CSP particles exposed to water at 80°C

Specimens of Group G(0.3)III were immersed for a longer duration than that of Group G(0.3)II, resulting in a higher moisture level as compared with Group G(0.3)II. Group G(0.3)IV had been immersed in water for the same duration as Group G(0.3)III. However, specimens of Group G(0.3) IV were dried in a vacuum oven until the complete removal of the moisture absorbed during the hygrothermal

ageing. As shown in Table 6-2, the average weight of Group G(0.3) IV after drying was smaller than its average initial weight. The reason was that the samples absorbed a small amount of moisture from the surroundings (23°C and RH 23%) before the measurement of their initial weight.

Group G(0.3)V was immersed in water for the longest duration. After the hygrothermal ageing, the specimens of this group were dried for 2130 hours (89 days) and complete moisture desorption curve was obtained. The moisture content in the laminates decreased linearly with $\sqrt{t}$ at the early stage of drying. Later, the rate of moisture desorption decreased gradually. At the last stage of desorption, the weight of the samples remained nearly unchanged. The weight of the samples decreased by 650.18mg on average within the first 986 hours of drying. For the last 1144 hours, only 28.39mg of decrease in weight was observed. In addition, specimens of Group G(0.3)V were not test under low-velocity impact after drying.

6.3 Microstructural studies

The microstructures of the cured GFRP laminates and hygrothermally aged GFRP laminates were observed using either SEM or FESEM. Important findings are discussed in this section.

6.3.1 Core-shell polymer particles in cured GFRP laminates

An intact core-shell polymer particle is shown in Figure 6-2b. Exactly 0.3 grams of CSP particles were dispersed at each ply interface during lamination. The melting

temperature of PMMA, which served as the shell of the CSP particles, is 160°C. Since the curing temperature for the GFRP laminates (122°C) was lower than the melting temperature of PMMA, CSP particles maintained their original shape after curing (Figure 6-2b). The cured GFRP laminates were sectioned and later observed using SEM. A good adhesion was noticed between the CSP particles and epoxy resin (Figures 6-2b and 6-2c). It was therefore concluded that the CSP particles added during lamination into the ply interface were eventually got fully coated by the epoxy matrix resin during the curing and were trapped within the interlaminar region.

Figure 6-2 SEM images of CSP particles in cured GFRP laminates showing the good adhesion between the CSP particles and the epoxy resin

6.3.2 Microstructure after hygrothermal ageing

The cross sections of the hygrothermally conditioned GFRP laminates were observed using FESEM to identify possible hygrothermal ageing induced damages. Figure 6-3 shows typical FESEM images of the unconditioned and conditioned GFRP laminates with CSP particles. Evident damages are seen in the FESEM images of the conditioned GFRP laminate which was immersed in water at 80°C for 2651.67 hours.

Figure 6-3 FESEM images of unconditioned and conditioned GFRP laminates with CSP particles showing that structural defects formed during hygrothermal ageing

After carefully observing these defects, it was found that they were not necessarily initiated at the interlaminar region. As shown in Figures 6-3 and 6-4, no damages are seen at the interlaminar region where CSP particles were located. Therefore, the inclusion of CSP particles did not pose discernable damages to GFRP laminates during hygrothermal ageing. Instead, these damages were generally initiated between glass fiber bundles of different orientations as shown in Figure 6-4. These fiber bundles might belong to either the same layer or two adjacent layers. The matrix resin would swell as a result of moisture uptake. Due to the constraint of

the glass fibers, the epoxy resin would swell along a direction normal to the fiber orientation. Therefore, the principal direction of swelling was different for fiber bundles with different orientations, leading to a stress field at regions where fiber bundles of different orientations coexisted. Therefore, damages were formed at these regions. This type of damage was similar to delamination although they did not necessarily occur at the interlaminar region.

Figure 6-4 Characteristics of the structural defects formed during hygrothermal ageing for the CSP particles reinforced GFRP laminate

Except the delamination illustrated in Figures 6-3 and 6-4, no other forms of damages were identified in the microstructure of the hygrothermally conditioned GFRP laminates. As illustrated in Figure 6-5, no evident fiber debonding and matrix cracking were observed at the other areas of the cross sections of the conditioned GFRP laminate with particles. In summary, the major structural defects caused by hygrothermal ageing or moisture absorption were delamination at regions where fiber bundles of different orientations coexisted.

Figure 6-5 FESEM images of the unconditioned and conditioned GFRP laminates with CSP particles

6.4 Tensile test on GFRP laminates

In order to investigate the effects of hygrothermal ageing on the tensile properties of GFRP laminates, three groups of GFRP tensile samples were cured from the same type of GFRP prepreg materials. Cured GFRP tensile samples had geometry of 252mm×26mm×1.627mm and average weight of 19.92g. The resin content of the cured GFRP laminates for tensile test was 26.80 wt. %. The hygrothermal conditioning scheme for GFRP tensile samples was summarized in Table 6-3. Specimens of the unconditioned group were not exposed to any type of hygrothermal ageing prior to the tensile test. Specimens of the conditioned group were immersed in water at 80°C for 38 days, obtaining a total moisture content of 0.938 wt. %. Another group (conditioned & dried group) was exposed to the same type of hygrothermal ageing. However, prior to the tensile test specimens of this group were dried in a vacuum oven until the complete removal of the moisture absorbed during hygrothermal ageing. As shown in Table 6-3, the moisture content after drying for

the conditioned & dried group was -0.186 wt. %. The negative value of the moisture content indicates that the weight of GFRP tensile samples after drying was smaller than their initial weight. This was due to that these samples absorbed a small amount of moisture from lab environment (23°C and RH around 50%) before the measurement of their initial weight.

Table 6-3 Hygrothermal conditioning scheme of GFRP specimens for tensile test

Group	Number of Specimens	Hygrothermal conditioning	Moisture content after ageing (%)	Moisture content after drying (%)
Unconditioned Group	5	unconditioned	--	--
Conditioned Group	5	Immersed in water at 80 °C for 38 days	0.938	--
Conditioned & Dried Group	5	Immersed in water at 80 °C for 38 days followed by drying in a vacuum oven at 45 °C for 32 days	1.019	-0.186

After hygrothermal ageing or drying the GFRP tensile samples were tested using an MTS 810 Material Testing System at a crosshead speed of 1 mm/minute. An axial extensometer was attached to the laminate during the tensile test to measure the strain in the laminate. The tensile properties of each group of samples are shown in Table 6-4. Typical stress vs. strain curves of laminates from different groups are plotted in Figure 6-6. A moderate decrease in the Young's modulus was observed after hygrothermal ageing. The absorbed moisture softened the epoxy resin, leading to the decrease in the Young's modulus of the laminates. Upon the removal of the absorbed moisture, the Young's modulus of the GFRP laminates was completely recovered.

While the change in the Young's modulus after hygrothermal ageing was only moderate, the degradation in the strength and tensile elongation were both pronounced. As shown in Figure 6-6, the conditioned sample had a much smaller

ultimate tensile strain, resulting in a much lower ultimate tensile strength. After drying, both the tensile strength and elongation increased by small percentages (less than in 5%). However, the tensile strength and elongation of the conditioned & dried group were still significantly lower than that of the unconditioned group. As shown in Table 6-3, the moisture absorbed by specimens of the conditioned & dried group during hygrothermal ageing was completely removed via drying in the vacuum oven. Therefore, permanent damages must have been caused by the combined attack of moisture and elevated temperature, which subsequently led to the degradation in the tensile strength of GFRP composite materials.

Table 6-4 Tensile properties of GFRP laminates of different groups

Properties	Unconditioned		Conditioned		Conditioned & Dried	
	Average	Coefficient of Variation (%)	Average	Coefficient of Variation (%)	Average	Coefficient of Variation (%)
Ultimate Tensile strength (MPa)	357.751	6.929	255.700	2.278	267.071	3.795
Ultimate Tensile strain (%)	1.561	8.235	1.138	0.207	1.156	6.294
Young's modulus (GPa)	25.425	2.344	24.226	1.277	25.679	1.488

An important conclusion is therefore drawn based on the experimental data. After hygrothermal ageing, the tensile properties of GFRP laminates degraded significantly. The two degradation mechanisms, moisture uptake and damage formation, had different influences on the tensile properties of GFRP composite materials. The softening of the epoxy resin because of the absorbed moisture accounted for the decrease in Young's modulus after hygrothermal ageing. However, moisture only had a minor influence on the tensile elongation and tensile strength of

this material. Permanent damages, though not identified using FESEM, were formed in the GFRP laminates during hygrothermal ageing, which subsequently led to the degradation in the tensile strength and elongation of GFRP laminates. For carbon fiber reinforced polymer composites, which had the same type of matrix resin as the GFRP laminates, the tensile elongation did not decrease after hygrothermal ageing. Though the E-glass fibers did not absorb moisture, as the major load-bearing constituent, the strength of the E-glass fiber might decrease by certain extent after hygrothermal ageing leading to the decrease in the tensile strength and elongation of composites with glass fiber reinforcements.

Figure 6-6 Tensile stress vs. strain curves of GFRP laminates from different groups showing the reduced tensile elongation after hygrothermal ageing

Degradation in the tensile strength of glass fiber reinforced composites after exposure to aqueous environments was frequently reported (Kim et al. 2008; Tokaji et al. 1998; Ellyin and Maser, 2004; Carra and Carvelli, 2014). It is commonly known that glass fibers do not absorb moisture from the surrounding and have good

chemical resistance. However, the strength of the glass fibers was frequently reported to degrade upon exposure to various types of hygrothermal ageing (Guzman and Brøndsted, 2014; Merah et al. 2010; Vauthier et al. 1998; Chateauminois et al. 1993; Tokaji et al. 1998), which further led to the decrease in the tensile strength of GFRP composites. The strength degradation of the glass fibers under aggressive environments depends on the presence of stress (either externally applied or residual), characteristics of the aqueous environment (acidic, alkaline, neutral, etc.), exposure time, compositions of the glass fibers and their surface flaws (Schutte, 1994; Tomozawa, 1996).

The degradation mechanisms for the glass fiber include dissolution of the glass fiber (Tomozawa, 1996; Schutte, 1994), stress corrosion cracking (Schutte, 1994; Jones et al. 1983), weakening of the glass fiber/matrix resin interface (Kim et al. 2008; Ellyin and Rohrbacher, 2000; Chateauminois et al. 1993), leaching out or weakening of the sizing (Ellyin and Maser, 2004; Ishida and Koenig, 1980), etc.

Considering the duration of the hygrothermal ageing conducted on GFRP tensile samples (38 days) in the current work and the intact glass fibers seen in FESEM images of the conditioned GFRP laminates (Figure 6-5), it is assumed that dissolution of the glass fibers as well as their stress corrosion cracking did not occur due to the hygrothermal ageing performed. However, weakening of the glass fiber/epoxy interface because of water immersion conditioning would have probably been incurred. This is corroborated by finding greater separation of the epoxy resin from the glass fibers during the mechanical tests as was seen in the SEM images of hygrothermally aged GFRP samples (Ellyin and Maser, 2004; Kim et al. 2008;

Tokaji et al. 1998). The decrease in the interfacial bond strength because of the weakening of the glass fiber/epoxy interface would hinder the effective transfer of load between the epoxy resin and the reinforcing glass fibers. As a result, performance of the glass fibers would be negatively affected.

The weakening of the glass fiber/epoxy interface can be separated from the wearying of the sizing on the glass fibers during the water immersion conditioning. This is another possible mechanism which might cause the reduction in the strength of the glass fibers. The chemical compositions of the sizing on the E-glass fibers are not indicated by the manufacturer of this particular prepreg material used in the current study. It is commonly known that the sizing may include coupling agents and film formers, etc. The coupling agents are used to bond the resin matrix (organic) to the surface of the glass fibers (inorganic), while film formers protect the glass fibers. The sizing would influence the mechanical properties and moisture resistance of the glass fibers. Moisture that had reached the fiber/matrix interface very likely would cause the weakening of the sizing through mechanisms such as hydrolysis (Schutte, 1994; Ellyin and Maser, 2004; Ishida and Koenig, 1980).

In summary, it is proposed that permanent damages were formed in the GFRP laminates during hygrothermal ageing, which subsequently led to the degradation in the tensile strength of those laminates. The strength or performance of the glass fibers might have been negatively affected due to the moisture and elevated temperature, which possibly caused (i) weakening of the fiber/epoxy interface, and (ii) wearying of the sizing on the glass fibers.

6.5 Impact resistance of GFRP laminates

Except Group G(0.3)V, laminates of different groups were tested after hygrothermal ageing or drying to investigate the effects of moisture and hygrothermal ageing on the impact resistance of GFRP laminates. All the GFRP laminates with and without CSP particles were tested at room temperature using an instrumented impact testing machine, Instron Dynatup 8250 drop tower impact tester. The weight and height of the impactor were 2.735kg and 380mm, respectively (impact energy 10J).

6.5.1 Improved impact resistance after adding CSP particles

During the fabrication of GFRP laminates filled with CSP particles, 0.3 grams of CSP particles were added to each interface. GFRP laminates with and without CSP particles were tested by the same energy level of impact. Figure 6-7 shows the contact force history of these two types of laminates during low-velocity impact testing. The peak load of both G(0.3)3 and G(0.3)4 were higher than that of G3 and G5, indicating the larger resistance of GFRP laminates reinforced by CSP particles.

The load vs. deflection curves of the two types of laminates are plotted in Figure 6-8. The difference in the slope of the initial loading part of the four curves in Figure 6-8 is not significant. However, the peak load of GFRP laminates filled with CSP particles occurred at larger deflection. The impact test results of these two groups of samples are summarized in Table 6-5.

Figure 6-7 Load vs. time curves of GFRP laminates with and without CSP particles before ageing

Table 6-5 Comparison between the impact resistance of the reference and CSP particles reinforced GFRP laminates before ageing

Group	M_f	F_i (kN)	F_p (kN)	D_i (mm)	D_p (mm)	D_{max} (mm)	Contact time (ms)
GI	0	1.665 (16.47)*	2.455 (2.93)	5.076 (10.14)	6.562 (4.25)	8.241 (2.61)	10.560 (14.33)
G(0.3)I	0	2.566 (9.16)	2.830 (3.16)	6.312 (5.80)	6.860 (5.18)	7.726 (1.77)	9.564 (2.10)

* The number in the parenthesis is the coefficient of variation (%) of the corresponding parameter.

Figure 6-8 Load vs. deflection curves of GFRP laminates with and without CSP particles before ageing

With the addition of CSP particles, incipient damage force and peak load increased. The CSP particles effectively improved the impact resistance of GFRP laminates. Consequently, the velocity of the impactor was reduced to zero faster. Therefore, D_{max} and *Contact time* of Group G(0.3)I were both smaller than that of Group GI. The same finding was reported by Ali and Joshi (2013).

6.5.2 Degradation in impact resistance of GFRP laminates

Specimens of Group GII were immersed in water at 80°C for 1860.33 hours, absorbing 1.037 wt. % of moisture on average. The impact resistance of the hygrothermally aged GFRP laminates (Group GII) is compared with that of Group GI to evaluate the effects of hygrothermal ageing on the response of GFRP composites to low-velocity impact. Typical load/time and load/deflection curves of the unconditioned and conditioned GFRP laminates are shown in Figures 6-9 and 6-10.

As seen in Figure 6-9, the peak load of GFRP laminates during impact decreased significantly after hygrothermal ageing. In contrast, for both CFRP woven-prepreg and UD-prepreg laminates, the peak load increased because of moisture uptake. The GFRP and CFRP composite laminates had the same type of matrix resin (DGEBA). However, hygrothermal ageing had entirely different effects on the impact resistance of these two types of composite materials.

Load-deflection curves in Figure 6-10 also show that the contact force of GFRP laminates decreased after hygrothermal ageing. Two lines parallel to the initial linear parts of the load vs. deflection curves are drawn in Figure 6-10. It is evidently shown

that the slope of the line for the unconditioned laminate is larger than that of the conditioned laminate, implying that the unconditioned laminate had larger out-of-plane stiffness. After absorbing moisture, the Young's modulus of the GFRP laminates decreased. Therefore, the conditioned laminates had smaller contact stiffness.

Figure 6-9 Comparison between the load vs. time curves of the unconditioned and conditioned GFRP laminates.

Figure 6-10 Comparison between the load vs. deflection curves of the unconditioned and conditioned GFRP laminates.

The average values of the various characteristic impact parameters for both groups are shown in Table 6-6. The peak load, F_p , decreased by 33.44% after hygrothermal ageing. For GFRP laminates, after absorbing moisture, the impact resistance degraded significantly. Therefore, the impactor travelled for longer time and projectile deflection before it was completely stopped. The maximum projectile deflection increased by 42.39% after hygrothermal conditioning.

Table 6-6 Comparison between the impact resistance of unconditioned and conditioned GFRP laminates

Group	M_f (%)	F_i (kN)	F_p (kN)	E_i (J)	E_p (J)	D_i (mm)	D_p (mm)	D_{max} (mm)
GI	0	1.665 (16.47)*	2.455 (2.93)	3.123 (23.10)	6.137 (5.23)	5.076 (10.14)	6.562 (4.25)	8.241 (2.61)
GII	1.037	1.177 (20.85)	1.634 (6.53)	2.140 (29.03)	3.894 (10.60)	4.309 (13.52)	5.605 (2.86)	11.734 (6.96)

* The number in the parenthesis is the coefficient of variation (%) of the corresponding parameter.

It is also noted that both D_i and D_p of GFRP laminates decreased after absorbing moisture. For the conditioned GFRP laminates, the incipient damage occurred at smaller projectile deflection, while the increase in contact force with deflection also ceased at a smaller deflection (smaller D_p). Tensile test on GFRP laminates proved that the ultimate tensile strain of GFRP laminates decreased after hygrothermal ageing. Therefore, the conditioned GFRP laminates experienced significant damages at smaller projectile deflections.

E_i and E_p are the impact energy absorbed up to the incipient damage point and peak load point, respectively. The unconditioned GFRP laminates had larger values of F_i and F_p . In the meantime, F_i and F_p took place at larger projectile deflections for

the unconditioned laminates. Therefore, both E_i and E_p of Group GI were higher than that of Group GII.

In summary, due to the degradation in the tensile strength of GFRP composite materials the impact resistance of GFRP laminates reduced after hygrothermal ageing. The absorbed moisture reduced the out-of-plane stiffness of GFRP laminates. The conditioned laminates had smaller contact force (smaller F_i and F_p) and experienced larger D_{max} .

6.5.3 Impact resistance of GFRP laminates with CSP particles

The test on GFRP laminates showed that the impact resistance of GFRP laminates degraded after hygrothermal ageing. Longer duration of hygrothermal ageing was conducted on GFRP laminates with CSP particles to investigate the impact resistance of CSP particle reinforced GFRP laminates as function of immersion time. Typical load vs. time and load vs. deflection curves for CSP particle reinforced laminates from different groups are shown in Figures 6-11 and 6-12. As shown in Figure 6-11, the peak load of GFRP laminates with CSP particles also decreased with the immersion time.

The decreasing trend of the peak contact force with immersion time is also seen in Figure 6-12. Moreover, the slope of the initial linear part of the load vs. deflection curve for GFRP laminates with CSP particles also decreased after hygrothermal ageing, implying the smaller out-of-plane stiffness of the conditioned GFRP laminates. The maximum deflection of G(0.3)9 and G(0.3)10 were larger than that

of G(0.3)3 and G(0.3)4. This was due to that the contact force of the conditioned laminates was smaller than that of the unconditioned laminates. Consequently, longer contact time and larger projectile deflection were needed to completely arrest the impactor. In contrast to G(0.3)9 and G(0.3)10, the projectile deflection of G(0.3)12 and G(0.3)15 increased continuously at the last stage of impact. Since, G(0.3)12 and G(0.3)15 were penetrated, the impactor did not rebound from the laminate and the value of the projectile deflection continued to increase.

Figure 6-11 Comparison between the load/time curves of CSP particles reinforced GFRP laminates exposed to different durations of hygrothermal ageing

Figure 6-12 Comparison between the load/deflection curves of CSP particles reinforced GFRP laminates with different moisture contents

The average values of the various characteristic impact parameters for the three groups of CSP particle reinforced GFRP laminates are shown in Table 6-7. Hygrothermal ageing had the same effects on the impact resistance of GFRP laminates with and without CSP particles. As the exposure time increased, F_i and F_p decreased evidently, indicating that the impact resistance of CSP particle reinforced GFRP laminates decreased after hygrothermal ageing. Each group consisted of 5 samples. For the unconditioned group, Group G(0.3)I, none of the five samples were penetrated. However, for Group G(0.3)III, which was immersed for the longest duration and had the highest moisture content among the three groups in Table 6-7, all the five samples were penetrated. Number of samples penetrated increased with the exposure time. In summary, the impact properties of CSP particle reinforced GFRP laminates also degraded after hygrothermal ageing.

Table 6-7 Comparison between the impact resistances of CSP particles reinforced GFRP laminates with different exposure times

Group	M_f (%)	F_i (kN)	F_p (kN)	E_i (J)	E_p (J)	D_i (mm)	D_p (mm)	Number of samples penetrated
G(0.3)I	0	2.566 (9.16)*	2.830 (3.16)	5.887 (15.15)	7.327 (8.78)	6.312 (5.80)	6.860 (5.18)	0
G(0.3)II	1.515	1.411 (9.87)	1.670 (10.20)	2.760 (13.13)	4.137 (8.11)	4.821 (5.88)	5.730 (2.02)	2
G(0.3)III	1.800	1.236 (15.91)	1.451 (11.03)	2.378 (21.60)	3.599 (17.36)	4.486 (8.88)	5.399 (5.71)	5

* The number in the parenthesis is the coefficient of variation (%) of the corresponding parameter.

6.5.4 Recovery of impact resistance after drying

Laminates of Group G(0.3)IV were immersed in water for the same duration as that of Group G(0.3)III. Later, they were dried in the vacuum oven at 45°C until the complete removal of the moisture absorbed during hygrothermal ageing. Their

impact properties were compared with that of Groups G(0.3)I and G(0.3)III to distinguish the effects of moisture from that of the structural degradation caused by hygrothermal ageing. Load/time and load/deflection curves of two samples from Group G(0.3)IV are plotted in Figures 6-13 and 6-14. The peak contact force of Specimens G(0.3)16 and G(0.3)18 were larger than that of Specimens G(0.3)12 and G(0.3)15, which were from Group G(0.3)III, showing a recovery in the impact resistance of CSP particle reinforced GFRP laminates upon the removal of the absorbed moisture. However, The peak contact force of G(0.3)16 and G(0.3)18 were still lower than that of G(0.3)3 and G(0.3)4, which were from the unconditioned group.

The initial linear part of the curves for Specimens G(0.3)16 and G(0.3)18 coincides with the curves for Specimens G(0.3)3 and G(0.3)4. The difference in the out-of-plane stiffness between the unconditioned and conditioned laminates became less significant after the removal of the absorbed moisture. Therefore, a recovery in the out-of-plane stiffness was also achieved after drying. This could be explained by the recovery in the Young's modulus after drying. As shown in Figure 6-14, the maximum projectile deflections of G(0.3)16 and G(0.3)18 were still larger than that of G(0.3)3 and G(0.3)4. However, they were not penetrated by the impactor. In contrast, All the five samples of Group G(0.3)III were penetrated. Therefore, the impact resistance partially recovered after drying. Complete recovery in the impact properties was not achieved.

Figure 6-13 The load/times curves of vacuum oven-dried CSP particles reinforced GFRP laminates in comparison with that of undried and unconditioned samples

The average values of the characteristic impact parameters for the conditioned & dried group, Group G(0.3)IV, are presented in Table 6-8. For all the 6 parameters considered, the values of Group G(0.3)IV were higher than that of Group G(0.3)III, but lower than that of the unconditioned group, Group G(0.3)I. For instance, the peak contact force decreased by 48.73% after 2651.67 hours of hygrothermal exposure. After drying, the average peak contact force of the conditioned & dried group was 35.09% lower than that of the unconditioned group.

Figure 6-14 Load/deflection curves of vacuum oven-dried CSP particles reinforced GFRP laminates in comparison with that of undried and unconditioned samples

Table 6-8 Recovery of the impact resistance of the CSP particles reinforced GFRP laminates upon the removal of moisture

Group	Hygrothermal ageing	M_f (%)	F_i (kN)	F_p (kN)	E_i (J)	E_p (J)	D_i (mm)	D_p (mm)	Number of samples penetrated
G(0.3)I	unconditioned	0	2.566 (9.16)*	2.830 (3.16)	5.887 (15.15)	7.327 (8.78)	6.312 (5.80)	6.860 (5.18)	0
G(0.3)III	immersed in water for 2651.67 hours	1.800	1.236 (15.91)	1.451 (11.03)	2.378 (21.60)	3.599 (17.36)	4.486 (8.88)	5.399 (5.71)	5
G(0.3)IV	immersed in water for 2651.67 hours and then completely dried	- 0.068	1.580 (17.66)	1.837 (9.81)	3.059 (27.61)	4.263 (15.40)	4.778 (10.33)	5.520 (6.10)	2

* The number in the parenthesis is the coefficient of variation (%) of the corresponding parameter.

The absorbed moisture improved the impact resistance of CFRP laminates. However, it had different influence on the impact resistance of GFRP laminates. Upon the removal of the absorbed moisture, the impact properties of the CSP particle reinforced GFRP laminates improved, implying that moisture had negative effects on the impact resistance of these laminates. The moisture absorbed during hygrothermal conditioning was completely removed for the samples of Group G(0.3)IV. However, they were still weaker than the unconditioned samples. This was due to the structural degradation caused by hygrothermal ageing. These damages might include delamination, matrix cracking and the degradation of glass fibers.

6.5.5 Durability of CSP particles

Before ageing, CSP particles improved the impact resistance of GFRP laminates. Samples of Groups GII and G(0.3)II were immersed in water for the same duration. Detailed comparison was conducted to evaluate the effect of CSP particles on the durability of GFRP laminates under hygrothermal environments. Typical load/time

and load/deflection curves for samples from Groups GII and G(0.3)II are plotted simultaneously in Figures 6-15 and 6-16, respectively. No discernable difference is seen in both Figures 6-15 and 6-16 between the curves for GFRP laminates with and without CSP particles, implying that the reference and CSP particles reinforced GFRP laminates had approximately the same impact response.

Figure 6-15 Load vs. time curves of GFRP laminates with and without CSP particles after ageing

Figure 6-16 Load vs. deflection curves of GFRP laminates with and without CSP particles after ageing

The average values of the various characteristic impact parameters for both groups were summarized in Table 6-9. Table 6-9 also supported the conclusion that there was no significant difference between the impact response of the reference and CSP particle reinforced GFRP laminates after ageing.

Table 6-9 Comparison between the impact resistance of the reference and CSP particles reinforced GFRP laminates after ageing

Group	Hygrothermal ageing	M_f (%)	F_i (kN)	F_p (kN)	E_i (J)	E_p (J)	D_i (mm)	D_p (mm)
GII	immersed in water at 80°C for 1860.33 hours	1.037	1.177 (20.85)*	1.634 (6.53)	2.140 (29.03)	3.894 (10.60)	4.309 (13.52)	5.605 (2.86)
G(0.3)II	immersed in water at 80°C for 1860.33 hours	1.515	1.411 (9.87)	1.670 (10.20)	2.760 (13.13)	4.137 (8.11)	4.821 (5.88)	5.730 (2.02)

* The number in the parenthesis is the coefficient of variation (%) of the corresponding parameter.

Before hygrothermal ageing, the CSP particle reinforced GFRP laminates exhibited better impact resistance than laminates without CSP particles. However, after exposure to the same hygrothermal environment for the same duration, the advantage brought about by the CSP particles diminished. As shown in Figure 6-1b and Table 6-9, the average moisture content of Group G(0.3)II was higher than that of Group GII. The higher moisture content in the CSP particle reinforced GFRP laminates should be attributed to the CSP particles residing at the ply interfaces, which were essentially polymers and also had moisture uptake behavior. The CSP particles in the unconditioned laminates improved their impact resistance. However, under the hygrothermal conditions the CSP particles absorbed moisture and might possibly experience structural degradation. Both of these would reduce the capability of the CSP particles as impact resistance modifiers. Therefore, after hygrothermal ageing GFRP laminates with and without CSP particles had approximately the same impact response.

6.6 Impact damage observation

The damage sites of the GFRP laminates after impact test were examined. It is noted that the damage characteristics of the GFRP laminates under impact loading were different from that of the CFRP laminates. Large-scale delamination was found at the bottom surface of a CFRP laminate after impact test (Figure 4-13). Due to the particular weave pattern of 7781 glass fiber fabric, the propagation of large-scale delamination in the GFRP laminates was prevented (Figure 6-17). Therefore, no large-scale delamination is found at the bottom surface of GFRP laminates. As shown in Figure 6-17, the impact damage was confined at the contact spot on the laminate.

Photographs of both the front and bottom surface of laminates subjected to different durations of hygrothermal ageing are shown in Figure 6-18. Fiber breakage is seen on both the front and bottom surface of the laminate after impact. Glass fiber is the major load-bearing constituent. Therefore, under low-velocity impact fiber breakage was the major damage mode for laminates made from GFRP prepreg materials. Data collected during low-velocity impact testing had indicated that the impact resistance of the CSP particle reinforced GFRP laminates degraded after hygrothermal ageing. When tested by the same impact energy level, the unconditioned laminate, Specimen G(0.3)4, experienced the lightest impact damage, while Specimen G(0.3)12, which had been immersed in water for the longest duration, was penetrated (Figures 6-18c and 6-18f). Apparently, the water immersion ageing aggravated the impact damage in GFRP composite materials.

Figure 6-17 Backlight images of a CSP particle reinforced GFRP laminate after impact showing that the impact damage mainly occurred at the contact spot

Figure 6-18 Photographs of the damage sites of CSP particles reinforced GFRP laminates with different moisture contents

6.7 Effects of moisture on the impact resistance

As concluded in Chapter 4, moisture postponed delamination and delayed the occurrence of the first significant damage in CFRP laminates under impact. Consequently, the impact resistance of composites made from CFRP prepreg materials improved after absorbing moisture. However, the damage mode of GFRP laminates under low-velocity impact was different. The softening of the epoxy resin due to moisture absorption did not alleviate the impact damage in GFRP laminates but rather reduced their modulus. Consequently, moisture reduced the contact stiffness of GFRP laminates under low-velocity impact.

The CSP particles at the ply interfaces also absorbed moisture and lost their capability of improving the impact resistance of GFRP laminates. In summary, moisture did not alleviate the impact damage in GFRP laminates. Instead, moisture reduced their out-of-plane stiffness and caused the degradation of CSP particles. This explains why the impact resistance of the CSP particle reinforced GFRP laminates partially recovered after drying.

6.8 Conclusions

In this chapter, results of experimental work carried out on laminates made from fiberglass fabric reinforced epoxy prepreg materials were presented. Key findings are as follows:

- (1) The diffusion of moisture in GFRP composite materials also exhibited a Fickian feature.

(2) Under the curing conditions for GFRP laminates, core-shell polymer particles did not melt but rather formed a good adhesion with the epoxy resin and resided at the interface.

(3) Evident damages are seen in the FESEM images of the conditioned GFRP laminate which was immersed in water at 80°C for 2651.67 hours. These damages were mainly formed at regions where fiber bundles of different orientations coexisted.

(4) After being immersed in water at 80°C for 38 days, the tensile strength and tensile elongation decreased significantly. Upon the removal of the absorbed moisture, only a small percentage (less than 5%) of recovery in the tensile strength was obtained. The strength of the E-glass fibers was negatively affected by hygrothermal ageing, possibly due to the weakening of the fiber/matrix interface and the sizing on the glass fibers, leading to the degradation in the tensile properties of GFRP composite materials.

(5) The impact resistance of GFRP laminates with and without CSP particles decreased with the durations of hygrothermal ageing. For the CSP particle reinforced laminates, moderate recovery in the impact resistance was obtained after drying. Because of the structural degradation occurred during hygrothermal ageing, the complete recovery in the impact resistance was not achieved.

(6) CSP particles improved the impact response of GFRP laminates. However, CSP particles lost their capability as impact resistance modifiers after exposure to water immersion conditioning.

(7) The extent of impact induced damage increased with durations of hygrothermal ageing. These damages occurred only at the site of contact and no large-scale delamination was observed. The major damage mode for GFRP laminates under impact was fiber breakage.

(8) Moisture negatively affected the impact resistance of the CSP particle reinforced GFRP laminates by reducing the contact stiffness of these laminates and causing the degradation of the CSP particles.

Chapter 7 Durability of GLARE 4A laminates

7.1 Introduction

The objective of the current study is to explore the durability of GLARE 4A laminates to harsh environment (water immersion ageing at 80°C). GLARE 4A laminates (Figure 7-1), which had the geometry of 200mm×12mm×2.317mm and the average weight of 12.93821g, were immersed in water at 80°C for 120 days. The durability of GLARE 4A laminates to hygrothermal environment was evaluated in two aspects. The structures of the samples were observed at both macro and micro levels to identify possible structural defects formed under the combined attack of moisture and elevated temperature. Tensile tests and tension-tension fatigue tests were conducted on hygrothermally aged GLARE 4A laminates to explore mechanical properties of this material after exposure to hygrothermal surrounding.

Figure 7-1 Cross-section of a GLARE 4A laminate

The weight of the laminates was monitored during water immersion ageing to determine the moisture uptake behavior of GLARE material. A Field emission scanning electron microscope (FESEM) was used to observe the microstructure of hygrothermally conditioned GLARE 4A laminates. OLYMPUS SZX7 zoom stereo microscope was used to observe the surface as well as the damage sites of the sample after mechanical test. The static properties of both dry and conditioned, GLARE 4A laminates were tested using an MTS 810 Material Testing System at a crosshead speed of 1 mm/min. Tension-tension fatigue test was performed on the same testing machine. The load (stress) was the test control parameter during the course of the constant-amplitude fatigue test. Three fatigue stress levels ($= \frac{\text{Peak fatigue stress}}{\text{Average ultimate tensile strength}}$) were chosen for both the unconditioned and conditioned GLARE 4A laminates. The fatigue ratio R ($= \frac{\text{Valley load}}{\text{Peak load}}$) selected was 0.1, insuring a tension-tension cyclic load during the fatigue test.

7.2 Hygrothermal conditioning scheme

The dimensions of the GLARE 4A laminates were 200mm×12mm×2.317mm. Moisture could not be transported through the thickness direction (the z direction as depicted in Figure 7-2) of the GLARE laminate since the two surface layers are of an aluminum alloy. Glass fiber/epoxy composite layers could only absorb moisture from the edges which were exposed to water. The majority of the moisture was absorbed through the sides as seen in Figure 7-2.

The weight of GLARE 4A laminates was measured periodically during conditioning. Once the saturation state was reached, the water immersion ageing was

stopped. The total time of immersion was 120 days and the final moisture content obtained was 0.41% by weight on average. The moisture absorption profile of GLARE laminates is shown in Figure 7-3. The moisture content in the laminates increased linearly with $\sqrt{t}$ initially. Later, the rate of moisture diffusion appeared to be stabilized. Moisture only diffused into the glass fiber/epoxy composite layers. Therefore, the diffusion of moisture in GLARE laminates could also be categorized as Fickian behavior. The calculated diffusivity was $2.817 \times 10^{-7} \text{ mm}^2/\text{s}$.

Figure 7-2 Schematic representation of the principal direction of moisture diffusion showing that the majority of absorbed moisture diffused along the x direction (namely width direction)

Figure 7-3 Moisture uptake characteristics of GLARE 4A laminates when immersed in water at 80°C

7.3 Structural characterization

Polymeric matrix composites are known to form structural defects when continuously exposed to hygrothermal environments. Difference between the two constituents of PMCs in physical properties such as coefficient of thermal expansion and moisture absorption behavior are usually the sources of structural degradation under hygrothermal environments. This phenomenon turns to be more complex in the case of GLARE laminates, which involve layers made of aluminum alloy. Stresses resulted from hygrothermal environments are generally maximum at the fiber/matrix interface and boundaries between two composite layers of different fiber orientations. Therefore, structural defects usually initiate at these two areas. These two types of interfaces as well as the area between the composite layer and the aluminum layer in the conditioned samples were particularly observed using FESEM.

Figure 7-4 shows typical images of the cross sections of both unconditioned and conditioned GLARE 4A laminates. During the observations made using FESEM, it was found that there was no evident difference between the microstructures of the unconditioned and conditioned GLARE 4A laminates. No visible cracks were found near the fiber/matrix interface and the interlaminar region (Figure 7-4b).

Special attention was paid to the interface between the composite layer and the aluminum layer. As shown in Figure 7-5, the interlaminar region between the aluminum layer and the composite layer remained intact after hygrothermal ageing for 4 months. The GLARE 4A laminates had exhibited good environmental durability in this investigation.

Figure 7-4 FESEM images of the glass fiber/epoxy composite layers of GLARE 4A laminates: a) unconditioned laminate; b) conditioned laminate

Figure 7-5 FESEM images of the interfacial region between the aluminum layer and the glass-fiber composite layer: a) unconditioned; b) conditioned

Although structural defects such as matrix cracking and delamination were not found inside the GLARE 4A laminate, corrosion was observed at the two outer aluminum layers. The GLARE 4A laminates were immersed in water at 80°C during the course of hygrothermal ageing. Pitting corrosion of different sizes was observed at several of the conditioned samples. Since the edge of the aluminum layer was free of protective material, most pitting corrosions were initiated at the edges of the outer

aluminum layer as seen in Figure 7-6. At the same time, a few pitting corrosion sites were found at the surface of the outer aluminum layer rather than near the edge (Figure 7-7). This was possibly due to the local rupture of the protective painting layer prior to the initiation of pitting corrosion.

Figure 7-6 Comparison between optical micrographs of unconditioned and conditioned GLARE laminates showing the occurrence of pitting corrosion at the edge of the outer aluminum layer after hygrothermal ageing: a) surface of an unconditioned sample; b) surface of a conditioned sample

Figure 7-7 Comparison between the surface of unconditioned and conditioned GLARE laminates showing a pitting corrosion formed at the surface of the outer aluminum layer of a conditioned GLARE laminate: a) surface of an unconditioned sample; b) surface of a conditioned sample

7.4 Static properties

Hygrothermally aged GLARE 4A laminates were immediately tested under tension after taking out from the water bath and their static properties were compared with that of the unconditioned samples. The static properties of the unconditioned and conditioned GLARE 4A laminates are summarized in Table 7-1.

Table 7-1 Static properties of GLARE 4A laminates (Unconditioned and Conditioned Group)

Properties	Unconditioned			Conditioned		
	Average	Coefficient of Variation (%)	No. of Specimens	Average	Coefficient of Variation (%)	No. of Specimens
Ultimate Tensile strength (MPa)	860.912	2.774	4	470.445	4.207	5
Ultimate Tensile strain (%)	4.053	4.047	4	1.880	6.587	5
Young's modulus (GPa)	53.656	1.779	4	50.864	3.417	5

The 5 conditioned GLARE 4A laminates subjected to tensile tests had absorbed only 52mg of moisture on average, which equaled to 0.41 wt. % of their original weight. However, as shown in Table 7-1, the ultimate tensile strength decreased by 45.36%. The decrease in Young's modulus was only moderate, approximately by 5.20% of the average Young's modulus of the unconditioned GLARE 4A laminates. However, the ultimate tensile strain declined by 53.62%. Typical stress vs. strain curves of the conditioned and unconditioned samples are presented in Figure 7-8. It was clearly seen in Figure 7-8 that the initial linear part of the curves for the unconditioned and conditioned samples coincided very well with each other, which also indicates that the difference in the elastic modulus between the unconditioned and conditioned GLARE laminate was not significant. However, the conditioned

sample broke at a much smaller strain, resulting in the lower tensile strength of the conditioned sample.

Several factors that might be responsible for the reduced static properties of GLARE 4A laminates included (i) pitting corrosion at the aluminum layers, (ii) 0.41 wt. % of moisture absorbed, (iii) degradation of epoxy resin because of hygrothermal ageing and (iv) decrease in the strength of the glass fibers because of hygrothermal ageing. Among the five conditioned GLARE 4A specimens tested under tension, only one specimen failed at the vicinity of the pitting corrosion site. As seen in Figure 7-9, the rupture of the outer aluminum layer might have started from the pitting corrosion site highlighted by a red circle. However, the ultimate tensile strength of this sample was not lower than the average tensile strength of all the five samples tested. Therefore, pitting corrosion was not the major factor that caused the degradation in the tensile strength of GLARE 4A.

Figure 7-8 Typical tensile stress/strain curves of GLARE 4A laminates before and after hygrothermal ageing showing that the ultimate tensile strain and tensile strength reduced markedly after hygrothermal ageing

In order to check whether the degradation in the mechanical properties had resulted from the absorbed moisture or not, two hygrothermally aged GLARE 4A laminates were dried in a vacuum oven at 45°C and their tensile properties were presented in Table 7-2. The tensile stress-strain curve of a conditioned & dried sample was added to Figure 7-8. After removing the moisture absorbed, the Young's modulus recovered to 98.8% of that of the unconditioned GLARE 4A laminates, indicating that the absorbed moisture was responsible for the decrease in the Young's modulus of the conditioned GLARE laminates. However, the recovery in both the ultimate tensile strain and ultimate tensile strength was limited. Therefore, moisture was not the major factor that caused the degradation in the tensile strain and strength of GLARE 4A laminates.

Figure 7-9 A conditioned GLARE 4A laminate with a tensile failure across a pitting corrosion

Table 7-2 Static properties of GLARE 4A laminates (Conditioned and Dried Group)

Sample	Hygrothermal ageing	Moisture content after ageing (%)	Drying time (day)	Moisture content after drying (%)	Ultimate Tensile strength (MPa)	Ultimate Tensile strain (%)	Young's modulus (GPa)
GLARE 35	In water at 80°C for 2 months	0.300	44	0.005	518.612	2.105	52.909
GLARE 47	In water at 80°C for 4 months	0.395	58	-0.003*	484.486	1.884	53.117
Average	--	--	--	0.001	501.549	1.995	53.013

* There might be a small amount of moisture in GLARE 47 before it was immersed into water. Therefore, the weight of GLARE 47 after drying was smaller than its initial weight.

Degradation of the epoxy resin because of moisture uptake should not have been the major factor that caused the decrease in the tensile elongation and strength of conditioned GLARE 4A laminate. In continuous fiber-reinforced composite materials, the fibers are the major load-bearing constituent. Only after the strain in the laminate reached the ultimate tensile strain of the reinforcing fibers, the laminate would break. This assumption was supported by the tensile test results of the CFRP woven laminates, which showed that the ultimate tensile strain of all the three groups (conditioned, unconditioned, conditioned and dried) was very close to each other. Therefore, it may be said that hygrothermal ageing caused the reduction in the ultimate tensile strain and strength of the S2 glass fibers in the GLARE 4A laminates. In addition, investigation on the GFRP samples (7781 E-glass fabric) revealed that after hygrothermal conditioning the tensile strength of the E-glass fiber was negatively affected.

The free swelling of the matrix resin because of moisture intake would be restrained by the glass fibers which did not have moisture absorption behavior.

Residual stresses would therefore be caused at the interface, leading to the degradation of the interface. Moisture would reach the interface between the glass fiber and the epoxy resin, making the degradation of the sizing on the glass fibers possible. Both the degradation of the sizing and the weakening of the interface would influence the mechanical properties of the glass fibers. Therefore, the strength of the glass fiber might decline after hygrothermal ageing, leading to the reduction in the strength of the composite layers of the GLARE laminates.

Therefore, one of the important findings in this thesis is that while the carbon fibers are relatively immune to the detrimental effects of elevated temperature and moisture, the glass fibers are more vulnerable to hygrothermal attack. The tensile strength of the glass fiber decreased under the combined attack of elevated temperature and moisture. Consequently, the tensile elongation and strength of the glass fiber/epoxy composite layers degraded significantly after hygrothermal ageing.

Figure 7-10 shows the failure characteristics of a conditioned GLARE 4A laminate after the tensile test. As seen in Figure 7-10, all the three glass fiber/epoxy composite layers broke while the four aluminum layers still remained intact. The ultimate tensile strain of the glass fiber/epoxy composite layer decreased substantially after hygrothermal ageing. The composite layers failed at a tensile strain of 1.880% on average. However, the aluminum layer could withstand tensile strain larger than 1.880%. Therefore, the composite layers failed earlier than the aluminum layers when tested under tension. This explains the phenomenon described in Figure 7-10.

Figure 7-10 Optical micrograph of the damage portion of a conditioned GLARE 4A laminate after tensile test showing that the glass fiber/epoxy layers were broken while the aluminums layers remained intact

7.5 S-N curves

The S-N curves of both the unconditioned and conditioned groups were plotted in Figure 7-11. At the same fatigue stress level ($= \frac{\text{Peak fatigue stress}}{\text{Average ultimate tensile strength}}$), the conditioned GLARE 4A laminates had longer fatigue life (Figure 7-11a). However, this phenomenon could not lead to the conclusion that the fatigue life of the conditioned GLARE 4A laminates was longer than that of the unconditioned samples. As concluded above, the conditioned samples had smaller ultimate tensile strength. At the same fatigue stress level, the peak fatigue stress of the unconditioned group was higher than that of the conditioned group. For instance, when the fatigue stress level was 0.59, the peak fatigue stress of the unconditioned and conditioned group was 507MPa and 277MPa, respectively.

The fatigue of GLARE 4A laminates included the fatigue of the aluminum layers and the cross-ply composite layers. As shown in Figure 7-8, at the same strain value, the stress in the unconditioned and conditioned GLARE 4A laminates was fairly close to each other. It is reasonable enough to conclude from Figure 7-8 that the strain value in the aluminum layers in both, the unconditioned and conditioned GLARE 4A laminates would be approximately the same as long as a normal stress of the same magnitude was applied on them. At the same fatigue stress level, the peak fatigue stress of the conditioned GLARE 4A laminate was lower than that of the unconditioned GLARE 4A laminates. Therefore, the peak strain in the aluminum layers of a conditioned GLARE 4A laminate was also lower than that of an unconditioned GLARE 4A sample. When the fatigue stress level was the same, the aluminum layers in the conditioned GLARE 4A laminates were actually subjected to lower stresses and strains. This explains why the fatigue life of the conditioned samples was longer than that of the unconditioned samples when cycled at the same fatigue stress level ($\frac{\text{Peak fatigue stress}}{\text{Average ultimate tensile strength}}$).

Figure 7-11 The S-N curves of the unconditioned and conditioned GLARE 4A laminates: a) fatigue stress level vs. Log (N); b) maximum fatigue stress vs. Log (N). The average moisture content in conditioned samples was 0.41 wt. %

As shown in Figure 7-11b, at the same maximum fatigue stress, the fatigue life of the unconditioned samples was significantly longer than that of the conditioned samples. This was due to that the tensile strength of GLARE 4A laminates reduced substantially after hygrothermal ageing. It was therefore concluded that the fatigue life of the GLARE 4A laminates also decreased after hygrothermal ageing.

7.6 Stiffness curves

It was reported that the damage accumulation and subsequent loss in stiffness of composite materials under fatigue load showed three stages (Daniel and Charewicz, 1986; Naik, 2003). The overall extent of damage increased rapidly at the first stage accompanied by a rapid decrease in the residual stiffness of the material as shown in Figures 2-14 and 2-15. Consequently, the extension corresponding to the peak load would increase rapidly for a constant-amplitude fatigue test in which the load was the test control parameter.

The trend of maximum extension (extension corresponding to the peak force during tension-tension fatigue test) verses fatigue cycle at the first 500 fatigue cycles for both unconditioned and conditioned sample is shown in Figure 7-12a. Numbers in the legend represent the fatigue stress levels. For instance, Unconditioned 59% represented an unconditioned sample which was subjected to a fatigue stress level of 59% during the fatigue test. A rapid increase in the maximum extension within the first 50 cycles of the fatigue test was observed. However, it is noted that the peak load also increased drastically within the first 50 fatigue cycles as seen in Figure 7-12b. The relationship between the maximum extension and peak load at the early

stage of fatigue test is plotted in Figure 7-12c. It is found that the maximum extension increases linearly with the peak load. This can be explained by the stress-strain curves shown in Figure 7-8, which shows that after the yielding point the strain had a linear relationship with stress.

(a) Change of the maximum extension at the early stage of fatigue test. (b) Change of the peak load at the early stage of fatigue test.

(c) The relationship between the maximum extension and peak load at the early stage of fatigue test.

Figure 7-12 Change of the peak load and maximum extension at the early stage of fatigue test of GLARE 4A laminates showing that there was no rapid damage accumulation during the early stage of fatigue test

During a specific fatigue test, a certain number of cycles were usually needed for the peak force to increase to the desired value. At this stage, the maximum extension

would also increase with the peak load. Hence it is concluded that the rapid increase in the maximum extension at the early stage of fatigue life depicted in Figure 12a was actually caused by the increase in the peak load rather than by damage accumulation. This equally indicates that no rapid damage accumulation occurred at the early stage of fatigue test for GLARE 4A laminates. These findings also led to the important conclusion that the fatigue behavior of GLARE 4A laminates is different from conventional composite materials.

The fatigue test in the current investigation was a constant-amplitude fatigue test. Figure 7-13 shows the peak force vs. normalized fatigue cycle ($= \frac{\text{Instant fatigue cycle}}{\text{Total number of fatigue cycle}}$) curves of both groups. As shown in Figure 7-13, for all the fatigue stress levels the values of the peak load of both the unconditioned and conditioned GLARE 4A laminates during tension-tension fatigue tests remained constant to a certain degree.

Figure 7-13 Variation in the magnitude of the peak load with fatigue cycles during the tension-tension fatigue tests

In contrast, the maximum extension increased evidently during the course of fatigue tests as seen in Figure 7-14. The maximum extension/fatigue cycle and maximum extension/normalized fatigue cycle curves have evident three stages for several samples. At the first and the third stages, the maximum extension increased relatively slower as the number of fatigue cycles was increasing. However, at Stage II the maximum extension increased much faster as the sample was continually tested under fatigue loading. This was due to that the aluminum layers usually failed before the entire GLARE 4A laminate eventually failed during the tension-tension fatigue tests. For instance, at around 11500 cycles, small cracks began to appear at the outer aluminum layers for the unconditioned GLARE 4A laminates when tested at a fatigue stress level of 42%. As shown in Figure 7-15, during the fatigue test of GLARE 4A laminates, the aluminum layers generally failed earlier than the composite layers leaving the composite layers taking the fatigue load alone. Therefore, at this stage the extension corresponding to the peak force increased rapidly (a larger extension of the laminate was needed for the peak load to reach the desired value).

As shown in Figure 7-14, for laminates from the same hygrothermal group, such as the unconditioned group, the aluminum layers failed within smaller number of fatigue cycles at higher fatigue stress levels. Therefore, as the fatigue stress levels increased, Stage II occurred within smaller number of fatigue cycles.

After absorbing moisture, the composite layers significantly lost their tensile strength. However, the influence of moisture on the strength of the aluminum layers was relatively negligible. At the same fatigue stress level, the rapid increase in the

maximum extension (Stage II) is seen at the larger number of fatigue cycles for the conditioned samples (Figure 7-14a). This was due to that at the same fatigue stress level the peak load of the conditioned group was much smaller than that of the unconditioned group.

Figure 7-14 Variation in the maximum extension during the fatigue tests showing that for both the unconditioned and conditioned GLARE laminates the maximum extension increased significantly while for some samples the change in extension with fatigue cycles evidently manifested three stages

Figure 7-15 Photograph of a GLARE 4A laminate under tension-tension fatigue test showing that the two outer aluminum layers failed making the composite layers solely bearing the load

The mechanical properties of the GLARE 4A laminate degraded as it was continually subjected to fatigue cycles. Therefore, the maximum extension increased as the number of fatigue cycles increased. This equally indicated that the stiffness of the sample decreased as the fatigue test was continuing.

In this investigation, the ratio of the peak load to the maximum extension was defined as the stiffness ($= \frac{\text{Peak load}}{\text{Maximum extension}}$) of the GLARE 4A laminates for the convenience of observing the decrease in the stiffness of the GLARE 4A laminates during fatigue tests. The degradation in stiffness of the GLARE 4A laminates during fatigue tests was seen in Figure 7-16, where the normalized stiffness ($= \frac{\text{Instant stiffness}}{\text{Maximum stiffness}}$) was defined as the ratio of the instant stiffness to the maximum stiffness. As seen in Figure 7-16b, the normalized stiffness vs. normalized fatigue cycle curves manifested three distinct stages. This is apparently due to that the

increase in maximum extension could be divided into three stages (Figure 7-14). Therefore, the stiffness of the GLARE 4A laminates decreased gradually during fatigue test. Once the aluminum layers began to fail, the stiffness of the sample declined rapidly (Stage II).

Figure 7-16 Degradation in the stiffness of the GLARE laminates during tension-tension fatigue tests showing that the degradation in the stiffness of the GLARE 4A laminates during fatigue tests was featured by a three-stage phenomenon

7.7 Fatigue damage characteristics

As shown in Figure 7-16, the change in the stiffness of the GLARE 4A laminate with fatigue cycles followed three stages. This was actually associated with the unique damage evolution in the GLARE 4A laminates during fatigue. During Stage I, the specimen was usually intact without any evident damages that could be seen externally (Figure 7-17a). However, there would be damages initiated internally in the glass/epoxy and aluminum layers, and/or at the GFRP-aluminum interface during Stage I, which caused the gradual decrease in stiffness of the GLARE 4A laminates.

Stage II began when a crack was observed at the outer aluminum layers. Once a crack was formed in the aluminum layer, there would be shear stresses acting on the aluminum layer to make it deform in accordance with the composite layer. Therefore, once a crack was formed delamination would be initiated by the shear stress between the aluminum layer and the composite layer. Delamination further propagated into larger scale delamination. More cracks were ready to form and more delamination would be initiated at the vicinity of the cracks (Figure 7-17b). This process repeated and occurred not only in the outer aluminum layers, but in all the four aluminum layers. This directly caused the loss in the load bearing capability of the aluminum layers, making the load solely taken by the composite layers. Consequently, the stiffness of the laminate decreased rapidly (Figure 7-16) while the maximum extension increased correspondingly (Figure 7-14).

At Stage III, damages such as delamination and fiber breakage took place in the glass/epoxy composite layers as the cyclic load was applied to the laminate until the specimen failed catastrophically and in a sudden manner (Figure 7-17c).

(a) Photograph of a GLARE 4A laminate at Stage I.

(b) Photograph of a GLARE 4A laminate at Stage II.

(c) Photograph of a GLARE 4A laminate after failure.

Figure 7-17 Photographs of GLARE 4A laminates at different stages during fatigue test

However, whether such three-stage feature would take place during a specific fatigue test depends on the fatigue stress level and the strength of the laminate. For instance, the curve for conditioned 66% in Figure 7-16 did not have Stage III. This was due to that the composite layers could not take the fatigue load after the aluminum layers failed.

Both the conditioned and unconditioned GLARE 4A laminates had the three-stage damage accumulation feature and hygrothermal conditioning did not affect their general damage evolution under fatigue. However, it was found that the first crack at the outer aluminum layer occurred near cavities which were formed during hygrothermal conditioning for some conditioned samples (Figure 7-18). Therefore, defects formed during hygrothermal conditioning provided sites where cracks were easier to be initiated. However, the effects of pitting corrosion on the tensile strength and fatigue life of GLARE 4A laminates were merely limited.

Figure 7-18 Fatigue crack at the outer aluminum layer which crossed a pitting corrosion formed during hygrothermal ageing

7.8 Conclusions

Both static and tension-tension fatigue tests were conducted on hygrothermally aged GLARE 4A laminates. Effects of hygrothermal ageing on the structural

integrity and mechanical properties of GLARE 4A laminates were explored in details. The key findings include:

(1) The outer aluminum layers shielded the composite layers from moisture uptake. However, the moisture could diffuse into the GLARE 4A laminates through the edges in a Fickian manner. The principle direction of moisture diffusion was from the sides.

(2) On the microscopic level, no fiber/matrix resin debonding and matrix cracking was observed during FESEM observation. Pitting corrosion was found at the outer aluminum layers due to the rupture or absence of the protective painting layer at the corresponding zones.

(3) Static properties were significantly affected by hygrothermal conditioning. Decrease in the tensile modulus was moderate. Upon the removal of the absorbed moisture, Young's modulus recovered to 98.8% of its original value. However, the decrease in the tensile strain and tensile strength was remarkable. Upon removal of the absorbed moisture, only a minor recovery in the tensile strain and tensile strength was observed. It is proposed that the strength of the S2 glass fiber in the GLARE 4A laminates might reduce because of hygrothermal ageing, which consequently resulted in the decrease in the tensile strain and tensile strength of the GLARE 4A laminates.

(4) Due to the degradation in the tensile strength, a pronounced decrease in the fatigue life of GLARE 4A laminates was observed. Under the same peak force, the fatigue life of the conditioned GLARE 4A laminates was considerably shorter than that of the unconditioned specimens.

(5) No rapid damage accumulation within the early fatigue cycles was observed. The damage accumulation of GLARE 4A laminates was different from conventional fiber-reinforced composites. In contrast, a distinct three-stage stiffness degradation behavior was identified for both the unconditioned and conditioned GLARE 4A laminates. During the fatigue test, the aluminum layers generally failed earlier than the composite layers, making the composite layers solely bearing the load.

Chapter 8 Overall conclusions

8.1 Major contributions

This thesis investigated the effects of short- and long-term hygrothermal exposure at elevated temperatures and/or hot-to-cold cyclic conditions on CFRP, GFRP (with and without CSP particles at inter-ply interfaces) and GLARE composites. Tension-tension fatigue and low-velocity impact properties were studied. The materials studied and the major mechanical testing conducted are illustrated in Figure 8-1.

The major contributions of this Ph.D. thesis include:

- (1) No visible damage was found using SEM in both the CFRP UD-prepreg and woven-prepreg laminates after short-term (48 days) hygrothermal ageing. Instead, the impact resistance of CFRP composite laminates was found improved because of the moisture absorbed during their hygrothermal ageing. It was found for the first time that moisture significantly alleviated impact induced damage in both the CFRP UD-prepreg and woven-prepreg laminates.
- (2) Exposure to long-term (183days) hygrothermal ageing caused delamination in the CFRP UD-prepreg laminates. Due to the damages formed during the hygrothermal ageing, the strength of the CFRP laminates decreased, which eventually led to the reduction in the impact resistance of the CFRP laminates.
- (3) The tensile strength and tensile elongation of the E-glass fabric reinforced epoxy laminates declined significantly after exposure to water at 80°C for 38 days. It was proposed that the strength of the E-glass fiber was negatively affected by

hygrothermal ageing, leading to the reduction in the tensile strength of the GFRP laminates. Moisture did not alleviate the impact induced damage in GFRP laminates but rather reduced their modulus and subsequently caused the decrease in their contact stiffness during low-velocity impact. Due to the reduction in the strength and the negative effects of the absorbed moisture, impact resistance of both the reference and CSP particle reinforced GFRP laminates dropped after hygrothermal ageing.

(4) Addition of CSP particles generally improved the impact properties of the GFRP laminates. However, the CSP particles were prone to the detrimental effects of hygrothermal environments. Consequently, the beneficial effects of the CSP particles on the impact damage resistance of GFRP laminates diminished after hygrothermal ageing.

(5) Tensile tests on hygrothermally aged GLARE 4A laminates were conducted. It is proposed that the strength of the S2 glass fiber in the GLARE 4A laminates was negatively affected by the water immersion conditioning, leading to the degradation in the tensile strength and tensile elongation of the GLARE 4A laminates. Consequently, the fatigue life of GLARE 4A laminates decreased drastically after hygrothermal ageing.

(6) Pitting corrosion was found at the outer aluminum layers of GLARE due to rupture or absence of any protective coating. The pitting corrosion provided sites for easy crack initiation. However, the experimental data proved that pitting corrosion was not the major factor that contributed to the degradation in the tensile strength of GLARE laminates.

Figure 8-1 Materials studied and major mechanical testing conducted in this study

8.2 Investigation on CFRP composite materials

Hygrothermal ageing mainly affected the mechanical properties of CFRP composite materials through two mechanisms, namely, degradation of the microstructure and moisture uptake. In this study, two categories of hygrothermal

conditioning were defined for CFRP composite materials, namely, short-term and long-term hygrothermal conditioning (Figure 8-2).

During hygrothermal ageing, structural defects, such as degradation of the fiber/matrix interface and delamination would take place. These damages would cause the reduction in the mechanical properties of the CFRP composite materials. When exposed to water immersion ageing for a limited duration (within Stage II in Figure 8-2), visible structural damages in CFRP composite materials were not yet formed. Instead, moisture uptake in CFRP laminates occurred and the impact resistance of CFRP laminates improved because of the absorbed moisture. Hygrothermal ageing with duration falling within Stage II (Figure 8-2) is defined as the short-term hygrothermal conditioning.

Figure 8-2 Three-stage moisture absorption behavior of CFRP UD-prepreg laminates exposed to long-term conditioning

Moisture had the same effect on the impact response of CFRP UD-prepreg and woven-prepreg laminates. Moisture softened the epoxy resin by promoting the

mobility of the various mers of an epoxy molecule and the different molecules against each other, resulting in the more ductile behavior of the epoxy resin and reducing the brittleness of laminates with an epoxy matrix. This benefited the laminate by effectively preventing or postponing the occurrence of interlaminar failure and matrix cracking. Therefore, after absorbing moisture the first significant failure occurred at larger projectile deflections and the strength of the laminate was preserved up to larger projectile deflections. The impact resistance of the laminate was therefore improved and the impact induced damage was alleviated.

As the hygrothermal ageing continued, individual plies of a UD-prepreg laminate faced the combined action of (i) ply swelling that was resulted from the moisture uptake and (ii) the interlaminar shear stresses, resulting in initiation of delamination between the plies of different fiber orientations. Hygrothermal ageing of this category is defined in this thesis as the long-term hygrothermal conditioning. Delamination or wrinkles began to take place at the end of Stage II of the moisture uptake curve (Figure 8-2). Delamination or wrinkles that were resulted from hygrothermal ageing provided extra free spaces for moisture absorption. Consequently, after the saturation level (Stage II) was reached the laminates still continued to absorb moisture, resulting in Stage III moisture uptake state (Figure 8-2). As the damages accumulated, hygrothermal conditioning induced damages caused the decrease in the strength and modulus of the laminates. Consequently, the out-of-plane stiffness and contact force during the impact test decreased. The impact resistance of the CFRP UD-prepreg laminates exposed to long-term hygrothermal conditioning therefore reduced.

All CFRP laminates in general exhibited good environmental durability. After the short-term hygrothermal exposure, their tensile strength and modulus decreased slightly, while their impact resistance improved due to the moisture absorbed. However, under the long-term hygrothermal exposure, structural defects such as delaminations occurred. This would eventually degrade the quality and mechanical performance of these composites. Therefore, measures must be taken to prevent any CFRP composite structures from long-term exposure to humid environments at elevated temperatures.

8.3 Investigation on GFRP composite materials

An in-depth study on the durability of GFRP laminates with and without CSP particles under hygrothermal conditions was conducted. After being immersed in water at 80°C for 38 days, the tensile elongation and tensile strength of the GFRP laminates decreased significantly. It was proposed that the strength of the E-glass fibers was negatively affected by the hygrothermal ageing, leading to the degradation in the tensile properties of GFRP composite materials. Moreover, the softening of the epoxy resin due to moisture absorption did not alleviate the impact damage in GFRP laminates but rather reduced their modulus and strength. Consequently, moisture had detrimental effects on the impact resistance of GFRP laminates. Due to the reduction in the strength and the negative effects of the absorbed moisture, the impact resistance of both the reference and CSP particle reinforced GFRP laminates degraded after hygrothermal ageing.

It was observed using FESEM that CSP particles resided at the ply interfaces. During curing, a good adhesion between the CSP particles and the epoxy resin was achieved. The CSP particles improved the impact response of the GFRP laminates. However, CSP particles absorbed moisture during hygrothermal ageing and experienced property degradation. The beneficial effects of CSP particles as impact resistance modifiers diminished after hygrothermal ageing.

It is observed in this study that the CFRP composites have better environmental durability than GFRP composites. In contrast to the CFRP laminates, the GFRP laminates experienced much higher percentage of loss in their tensile strength after hygrothermal exposure. Their impact resistance also degraded after the hygrothermal conditioning. These phenomena should not be ignored when selecting GFRP composites for real applications. This also implies that special measures must be taken to prevent GFRP composite structures from direct exposure to humid environments.

8.4 Investigation on GLARE laminates

Effects of hygrothermal ageing (immersion in water at 80°C for four months) on the structural integrity and mechanical properties of GLARE 4A laminates were explored in details. On the microscopic level, no fiber debonding, matrix cracking and delamination was observed during the FESEM observation. Pitting corrosion was found at the outer aluminum layers due to the rupture or absence of the protective painting layer. Pitting corrosion provided sites where cracks in the aluminum layers were easier to be initiated. However, experimental data proved that

pitting corrosion was not the major factor that contributed to the degradation in the tensile strength of GLARE laminates.

It was proposed that the S2-glass fibers in GLARE 4A laminates experienced a decrease in their strength after the exposure to hygrothermal ageing, leading to the decrease in the ultimate tensile strain and strength of GLARE 4A laminates. Due to the degradation in the tensile strength, a pronounced decrease in the fatigue life of GLARE 4A laminates was observed. This also implies that hygrothermal exposure or moisture uptake is a concern in terms of the structural integrity of S2-glass fiber reinforced GLARE laminates. Although the glass fiber/epoxy composite layer in a GLARE laminate is protected by the two outer aluminum layers, the moisture could seep in and attack the laminate through the edges. Therefore, the free edges of a GLARE structure should be properly sealed and protected from moisture absorption.

The damage accumulation of GLARE 4A laminates under cyclic load was different from conventional fiber-reinforced composites. No rapid damage accumulation within the early fatigue cycles was observed. In contrast, a distinct three-stage stiffness degradation behavior was identified for both the unconditioned and conditioned GLARE 4A laminates. During the fatigue test, aluminum layers generally failed earlier than the glass epoxy composite layers, making the composite layers solely bearing the load. Consequently, the unique stiffness degradation feature of GLARE laminates was observed.

Chapter 9 Recommendations for future work

Although we have carried out extensive experimental work on the durability of three types of materials, namely, CFRP, GFRP and GLARE laminates, the following studies are important and should be performed in the future:

- (1) Investigation on the effects of moisture and hygrothermal ageing on the strength of the fiber/matrix interface through single-fiber pullout test.
- (2) Investigation on the effects of long-term exposure to sub-zero temperature on the microstructure of CFRP composite materials.
- (3) Investigation on the effects of hygrothermal ageing on the durability of individual glass fibers.
- (4) Investigation on the strength of the core-shell polymer particles as function of immersion time or moisture content.
- (5) Investigation on the effects of exposure to salt medium on the microstructure and mechanical properties of laminated composites.
- (6) Development of new resins that have better hygrothermal environment durability and impact resistance.

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APPENDIXES

Appendix X1: Hypothesis testing - two independent sampling data sets

Normal and staggered lay-up laminates had the same stacking sequence and were cured under the same conditions. Within each group, normal and staggered lay-up laminates were subjected to the same duration of hygrothermal conditioning. The major concern is to investigate the effects of such manufacturing technique (automated tape lay-up) on the moisture uptake behavior and mechanical properties of laminated composites.

During the course of experiments, W_{dry} and D_Z of each laminate were collected. During the low-velocity impact testing, F_i , F_p , E_{el} , DI and E_{d2} of each laminate including both the normal and staggered lay-up laminates were obtained. The difference in the moisture uptake behavior and impact resistance between the normal and staggered lay-up laminates is to be determined based on the analysis on the experimental data collected. Statistical method is adopted for such comparison turning this into a statistical problem.

Suppose that certain parameter (e.g., W_{dry} and F_p) of the normal laminates is a population labeled Y_1 with mean value μ_1 and standard deviation σ_1 , while the same parameter of the staggered lay-up laminates is a population labeled Y_2 with mean value μ_2 and standard deviation σ_2 . Population Y_1 and Y_2 are two independent populations. A sample of size n_1 is drawn from population Y_1 ; its average value is

$\bar{Y}_1$ and sample variance is s_1^2 . Another sample of size n_2 is drawn from population Y_2 ; its average value is $\bar{Y}_2$ and sample variance is s_2^2 .

A hypothesis, which is defined as the null hypothesis (H_0), is proposed, which states that the two populations, namely Y_1 and Y_2 , have the same mean value (i.e., $\mu_1 = \mu_2$). The t statistic is adopted for the testing of this null hypothesis:

$$t = \frac{\bar{Y}_1 - \bar{Y}_2}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad (X1-1)$$

and,

$$S_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \quad (X1-2)$$

Under the null hypothesis, Equation X1-1 follows the t distribution.

If $|t| > t_{\alpha/2}(n_1 + n_2 - 2)$, then the null hypothesis should be rejected and one can claim with a confidence coefficient of $(1 - \alpha)$ that the two populations have different mean values (i.e., $\mu_1 \neq \mu_2$) and that the two samples are taken from two populations that have different mean values.

If $|t| < t_{\alpha/2}(n_1 + n_2 - 2)$, then the null hypothesis should be accepted and the two populations have the same mean value (i.e., $\mu_1 = \mu_2$).

Essentially, if $\mu_1 \neq \mu_2$, then this manufacturing technique will affect certain properties of the laminates and if $\mu_1 = \mu_2$, then this manufacturing technique will not affect certain properties of the laminates, which equally means that the normal and staggered lay-up laminates have the same mean value for certain parameter, such as

W_{dry} and F_p . Therefore, Equation X1-1 can be used to check the effects of automated tape lay-up process on the various properties of CFRP laminates.

Appendix X2: CFRP woven-prepreg laminates 60°C Group

Under this group, there were six specimens, which were divided into three sub-groups. Specimens 1 and 2 (reference group) were tested without any hygrothermal ageing, Specimens 5 and 6 (isothermally conditioned group) were continuously immersed in water at 60°C, while Specimens 3 and 4 (cyclically conditioned group) were subjected to a number of hygrothermal cycles, which was composed of 12 hours in water at 60°C and 12 hours in freezer at -30°C.

X2.1 Moisture absorption behavior

Figure X2-1 shows the weight change history of Specimens 5 and 6 resulted from water uptake. As shown in Figure X2-1, the moisture absorption behavior of both Specimens 5 and 6 followed Fick's law.

Figure X2-1 Weight change history of laminates immersed in water at 60°C

After curing, Specimens 1 and 2 were stored in a dry cabinet, in which the relative humidity was maintained around 23%. However, CFRP woven laminates still absorbed certain amount of moisture. Therefore, they were dried in a vacuum oven at 50°C for 24 hours before impact test. After drying, there was still certain amount of moisture residing in the laminate as shown in Table X2-1.

Table X2-1 Details of CFRP woven laminates of 60°C Group

Group	Sample	W_i (g)	W_f (g)	M_f (%)	Time (day)	Thickness* (mm)	D_z (mm ² /s)
Reference Group	1	23.65823	23.66311	0.021	0	1.702	--
	2	24.82352	24.82434	0.003	0	1.824	--
	Average	24.24088	24.24373	0.012	0	1.763	--
Cyclically Conditioned Group	3	23.72244	24.07662	1.493	78	1.757	--
	4	24.30789	24.65503	1.428	78	1.772	--
	Average	24.01517	24.36583	1.461	78	1.765	--
Isothermally Conditioned Group	5	24.86276	25.35145	1.966	77	1.835	2.864×10^{-7}
	6	24.75392	25.24123	1.969	77	1.838	2.992×10^{-7}
	Average	24.80834	25.29634	1.967	77	1.837	2.928×10^{-7}

*Thickness- thickness of specimens measured before impact testing.

The weights of Specimens 3 and 4 (cyclic group) were measured regularly each time after being taken out from the water bath or the freezer. Little variation in weight was observed when specimens were aged in the freezer, indicating that moisture resided inside CFRP laminates lost their mobility at -30°C.

X2.2 Impact Testing Results

Representative load versus time, load versus deflection and energy versus time curves of each group are plotted in Figures X2-2 to X2-4. The relationships between the moisture contents of the three laminates selected were $M_{f1} < M_{f3} < M_{f5}$. In Figure X2-2, the curve of Specimen 5, which had the highest moisture level, is more

symmetrical than the curves of the other two specimens. Generally, a sharp drop on the load versus time curve of an impact test indicates that a damage which is significant enough to affect or reduce the ability of the material to resist the dropping impactor tip is initiated and progressing. In both the curves of Specimens 1 and 3, a sharp drop is observed. When tested under approximately the same impact energy, Specimen 5, which had the highest moisture content, experienced lightest impact induced damage. The sharp load drop of Specimen 1 appeared earlier in time than that of Specimen 3. It was also found that the incipient damage load and peak load of conditioned Specimens 3 and 5 were higher than that of the unconditioned one, Specimen 1.

Figure X2-2 Typical load versus time curves of woven laminates 60°C Group ($M_{f1} < M_{f3} < M_{f5}$)

In Figure X2-3, Specimen 3 experienced the sharp load drop at larger deflection than Specimen 1, while no sharp load drop was observed for Specimen 5. Specimens with higher moisture content could retain their impact resistance to higher

deflections. Both the area under the load-deflection curve and the final residual deflection decreased with the moisture content, implying that the degree of impact damage decreased with moisture content.

Figure X2-3 Typical load versus deflection curves of woven laminates 60°C Group ($M_{f1} < M_{f3} < M_{f5}$)

In Figure X2-4, specimen 5 has the highest E_{el} and lowest E_d . It was noted that the E_d of Specimen 3 was higher than that of Specimen 1, which had lower moisture content than Specimen 3. The reason was that the actual impact energy exerted on Specimen 3 was higher than that of Specimen 1. Compared to Specimen 1, Specimen 3 had higher elastic energy E_{el} . It is concluded that as the moisture content increased, laminates could dissipate more impact energy through elastic deformation (higher E_{el} , correspondingly).

The relationship between average moisture content and average values of characteristic impact parameters was plotted in Figures X2-5, X2-6 and X2-8. As shown in Figure X2-5(a), both the average incipient damage load F_i and peak contact

force F_p increased with average moisture content of each sub-group with F_p increased monotonically with moisture content.

In Figure X2-5(b), apparently, both D_i and D_p had the same trends as F_i and F_p in Figure X2-5(a), respectively. The relationship between D_i and F_i as well as D_p and F_p for all the samples of 60°C Group are shown in Figure X2-7. From Figure X2-7, it is convincing that during an impact event the contact force was related to its corresponding deflection in such a way that generally a higher deflection corresponded to a higher incipient damage load or peak load, though there are some exceptions in Figure X2-7.

Figure X2-4 Typical energy versus time curves of woven laminates 60°C Group ($M_{f1} < M_{f3} < M_{f5}$)

The average D_i and D_p of the conditioned specimens were both higher than that of the unconditioned group. The increase in D_i implies that the first significant damage occurred at larger deflection for specimens exposed to water immersion, while the increase in D_p proved that laminates with higher moisture content could retain their resistance to the impactor to higher projectile deflections. Before the

incipient damage point, the test specimen generally behaved in an elastic manner and the magnitude of the strain level of the laminate is determined by the projectile deflection. Under impact loading, which was a bending load in nature, the strain in the laminate increased with projectile deflection. Therefore, for laminates with higher moisture content, incipient damage occurred at higher strain level. The increase in D_i with moisture content served to prove that the absorbed moisture extended the elastic limit of the CFRP laminates under impact loading. Moisture inside woven laminates improved the elastic deformation ability of the material under impact so that the incipient damage occurred at larger projectile deflection (higher D_i) when attacked by the impactor, which in turn increased the incipient damage load of CFRP woven laminates.

Figure X2-5 Relationship between average moisture content and deflection, contact force of woven laminates 60°C Group: a) F_i , F_p ; b) D_i , D_p and D_{max}

In Figure X2-6, average E_{el} increased with moisture, which further supports the conclusion that after absorbing moisture the elastic deformation ability of the material under impact was improved so that specimens could tolerate higher elastic strain without failure and more of the impact energy was absorbed by the material through elastic deformation. In addition, it was noticed in Figure X2-6 that the average E_d of cyclic group was higher than that of the unconditioned group. The reason was that higher impact energy was exerted on the cyclic group. Even though the same impactor height and weight were used, the average total impact energy of the unconditioned group was about 0.4J lower than that of the other two groups. The fact that E_{d2} decreased with moisture content also served to prove that less damage was induced to hygrothermally conditioned specimens.

Figure X2-6 Relationship between average moisture content and E_i , E_d and E_{d2} of woven laminates 60°C Group

For the drop weight impact testing of composite materials, contact time between the impactor and the laminate is also a parameter that generally reflects the behavior of the laminate under an impact attack. Figure X2-8 shows the variation of contact

time with respect to the average moisture content of each group, which clearly shows that specimens with higher moisture content had shorter contact time. The impactor stroke the laminate with approximately the same speed (same impact energy). If the laminate had relatively higher overall stiffness (lower compliance), the speed of the impactor would be reduced to zero faster and shorter contact time would be expected. In this study, it is assumed that initially laminates of different moisture contents had approximately the same stiffness (same material). However, laminates with less moisture content experienced more severe impact damage, which reduced their contact stiffness consequently. Therefore, specimens with less moisture content had longer average contact time.

Figure X2-7 Relationship between deflection and their respective contact force of woven laminates 60°C Group: (a) deflection and contact force at incipient damage point; (b) deflection and contact force at peak load point

Figure X2-8 Relationship between average moisture content and contact time of woven laminates
60°C Group

Appendix X3: Impact responses of samples of Group 2

The impact test result of Group 2 of the long-term conditioning study is presented in this section. The samples were fabricated from unidirectional carbon/epoxy prepreg materials, L-930HT (GT700). Samples of Group 2 were immersed into water at 80°C for 2 months, attaining an average moisture content of 3.149%. The low-velocity impact test (impact energy 9J) result of Group 2 was summarized in Table X3-1 and compared with that of Group 1, which was an unconditioned group. Typical load-deflection curves of specimens of Group 1 and Group 2 are plotted in Figure X3-1.

Table X3-1 Comparison between the low-velocity impact response of samples of Group 1 and Group

2

Group	M_f (%)	F_i (kN)	F_p (kN)	D_i (mm)	D_p (mm)	D_{max} (mm)	Time to E_{total} (ms)
Group 1	0.073	2.576 (2.72) *	2.976 (3.38)	3.905 (1.45)	4.287 (1.89)	6.010 (0.38)	3.893 (0.20)
Group 2	3.149	3.383 (9.23)	3.589 (8.10)	4.410 (4.20)	4.582 (3.29)	5.780 (1.15)	3.742 (1.04)

* All the numbers in the parentheses are the coefficient of variation of the corresponding parameters.

Figure X3-1 Typical load-deflection curves of specimens of Group 1 and Group 2 (Specimens 1 and 7 belongs to Group 1, Specimens 2 and 14 belongs to Group 2)

From Figure X3-1, it can be seen that moisture did not affect the out-of-plane stiffness of CFRP UD laminates. Instead, F_i and F_p of Group 2 were both larger than that of Group 1, indicating the improved impact resistance of CFRP UD laminates after absorbing moisture. Consequently, the velocity of the impactor was reduced to zero faster, resulting in the smaller D_{max} and *time to* E_{total} as shown in Table X3-1. Therefore, the overall conclusion is the same as that of the short-term conditioning study conducted on both CFRP UD and woven laminates.