Interfacial properties in the CFRP and CFRP-Ti composites under hygrothermal conditions

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**NANYANG
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**INTERFACIAL PROPERTIES IN THE CFRP AND
CFRP-TI COMPOSITES UNDER HYGROTHERMAL
CONDITIONS**

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2016

Interfacial Properties in the CFRP and CFRP-Ti Composites under Hygrothermal Conditions

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Abstract

Carbon fiber-reinforced plastic (CFRP) based composite riser integrated with titanium liner (namely CFRP-Ti composite riser) is a promising choice for deep-water oil exploration and production to replace conventional metal risers due to its various advantages including lightweight, high specific strength and stiffness, and outstanding corrosion resistance, etc. In achieving optimal performance of this hybrid composite system, interfaces in the composite system play a critical role, which include fiber-matrix interface, interlaminar interface, and metal-composite interface (MCI). Therefore, good tuning of these interfaces determines overall performance of the hybrid composite system. To improve the interfacial properties of the CFRP-Ti composites, two different strategies have been adopted in this work: i) modification of the interfaces in CFRPs and ii) tuning of the MCI via surface treatment of titanium alloy.

Multiwalled carbon nanotubes (MWCNTs) are incorporated into silane coating and applied onto carbon fiber surface to enhance the interfacial bonding in CFRPs. The results of microbond tests show that the interfacial shear strength (IFSS) of prepared multi-scale phase reinforced composite (MPRC) can be significantly increased in comparison with that of common composite. It is observed that densification of CNTs forest within the interphase between carbon fiber and matrix during forming of nano-composite coating can lead to a high volume fraction of CNTs within the interphase and augment effects of interface-interlocking, which makes the coating-modification method a more efficient way than traditional matrix-tuning method for improving interfacial bonding. Long-term interfacial performance of the prepared hybrid composite in

environments under fresh water and sea water has been studied based on single fiber microbond tests. IFSS of the MPRC is found to decrease with immersion time, just like common composite. However, carbon nanotube-modified silane coating well maintains its improvement effect on interfacial performance during a 120-day immersion test in both de-ionized water and simulated seawater. Interlaminar properties of CFRPs are also characterized and results show that glass transition temperature (T_g), interlaminar shear strength (ILSS), mode I and mode II interlaminar fracture toughness of laminates decrease under hygrothermal environment. However, silane treatment can improve the interlaminar fracture toughness of laminates, and incorporation of MWCNTs can further enhance these interlaminar properties even under hygrothermal environment.

Surface of titanium alloy is anodized using mixture of NaOH, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ and EDTA as electrolyte. Anodization treatment can create nano-structured metal surfaces to substantially increase bonding area along interface. And the generated oxide layer has potential to react with epoxy by forming organo-metallic complex, facilitating wetting of titanium alloy surface by epoxy resin. Mechanical testing results show that this eco-friendly surface treatment on titanium alloy is quite effective to improve interlaminar fracture toughness of CFRP-Ti composites, as well as compressive properties of CFRP-Ti composite risers. Furthermore, according to the experimental study in hygrothermal environment, the surface treatments introduced in this work are found to maintain their improvement effects on hygrothermal resistance of the CFRP-Ti composites and result in considerably enhanced interlaminar properties.

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List of Abbreviations

CFRP	carbon fiber-reinforced plastic
CFRP-Ti	composite riser integrated with titanium liner
MCI	metal-composite interface
MWCNTs	multiwalled carbon nanotubes
IFSS	interfacial shear strength
MPRC	multi-scale phase reinforced composite
T _g	glass transition temperature
ILSS	interlaminar shear strength
FMLs	fiber metal laminates
DCB	double cantilever beam
ENF	end-notch flexure
SBS	short beam shear
OM	optical microscope
SEM	scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
EDX-S	energy-dispersive X-ray spectroscopy
BSE	back scattered-electron
DMA	dynamic mechanical analysis

SCB	single cantilever beam
WTDCB	width tapered double cantilever beam
ELS	end loaded split
SLB	single-leg bending
SLFPB	single leg four point bend
CLS	cracked-lap shear

Chapter 1 Introduction

1.1 Background

Nowadays carbon fiber-reinforced plastics (CFRPs) have been maturely developed as a type of engineering materials for high performance applications due to their high specific mechanical properties. Fiber-metal laminates (FMLs), which combine excellent specific strength, stiffness, and fatigue properties of composites with superior machinability and toughness of metals [1, 2], are also being widely used. As interest in deep-water reserves grew exponentially, composite materials are introduced for offshore applications in recent years because of their superior performance. Carbon fiber-reinforced plastics based composite riser integrated with titanium liner (namely CFRP-Ti composite riser) becomes a promising choice for deep-water oil exploration and production to replace metal risers. However, the mechanical and other properties of CFRP-Ti composites have not yet been studied to quite an extent.

The interface, which is defined as the non-homogenous region between different materials, has profound influence on the performance of CFRP-Ti composites. A satisfactory bonding property is very important in developing hybrid composites to ensure load transfer and provide delamination resistance [3]. As a result, designing composites should be based on good understanding of the level of composites interfacial adhesion [4]. Interfaces in CFRP-Ti composite systems consist of fiber-matrix interface, inter-laminar interface, and metal-composite interface, which are illustrated in Fig 1.1. Properties of these interfaces can be characterised through different methods, such as

microbond test, double cantilever beam test, end notched flexure test, single cantilever beam test and compressive test of risers.

To improve the interfacial properties of CFRP-Ti composites, two different aspects can be taken into consideration: modification of CFRPs and surface treatment on titanium. For the modification of CFRPs, approaches can be also be categorized into two major types: i) surface treatment of carbon fibers, including fiber sizing and coating [5], electrochemical oxidation [6], liquid-phase chemical oxidation [7], high energy beam irradiation plasma treatment [8], etc.; ii) modification of polymer matrix, i.e. the reinforcement of interphase is achieved by tuning the properties of matrix materials with deliberately chosen fillers, such as fullerene [9, 10], silica nano-particles [11] and carbon nanotubes [12-17]. As to the surface treatment on titanium, a lot of surface treatment methods have also been developed, such as abrasion and grit blasting [18, 19], etching [20, 21], coupling agent [22], anodization [23-26], and so on. Among all of these different treating methods, anodization yields good bonding strength, and it is able to modify structure and elements of the oxide layer easily [27].

Figure 1.1 The interfaces in CFRP-Ti composite systems and characterization methods.

What's more, composites structures still face another qualification challenge when it is used for offshore area. Interfacial properties of the hybrid composites usually experience severer deterioration in a humid environment than in dry air due to the attack of moisture [28, 29]. They will be subjected to high relative humidities, temperatures, and chlorine ion concentrations over long periods of times [30]. So, to design an appropriate hybrid composite system with good environmental resistance is of importance.

Considering the limitation and problems existing, the present study aims to develop a set of new methods to improve the interfacial bonding properties of CFRP-Ti composites in marine environment. The method should take advantages of cost saving and easy to perform when being compared with previous treating methods. A series of experiments, which starts from single fiber to CFRP laminates to FMLs to final CFRP-Ti composite risers, are developed to characterize the interfacial properties. A rich set of data including load-displacement curves, experimental data points, fractured surface pictures and chemical characterization are presented. The effects of moisture on the interfacial properties of CFRP-Ti composites have also been investigated. High temperature was used to accelerate moisture diffusion rates and obtain the effect of water on final performance within shorter time.

1.2 Objective

Since only a small amount of papers has touched the mechanical behaviour of CFRP-Ti composites under hygrothermal conditions in a comprehensive way, the primary objective of this research is to explore scalable approaches to effectively tune interfacial properties in the hybrid CFRP-Ti composite riser and to provide benchmark

data to refine the design and prediction of filament wound riser. To achieve this target, the detailed breakdown objectives are:

- a) to set up devices which can perform different mechanical tests, for example single fiber microbond test;
- b) to explore novel treatment methods which can improve fiber/matrix interfacial properties and interlaminar properties of CFRPs;
- c) to explore optimized treatments on titanium to increase bonding strength between CFRPs and titanium alloy;
- d) to fabricate different CFRPs, FMLs and CFRP-Ti risers based on the achieved treatment methods and study their interfacial performances;
- e) to analyse the effect of hygrothermal environment on the interfacial properties of different treated hybrid composites.

1.3 Scope of work

The current research is focusing on the development of new surface treatment methods for CFRP-Ti composites used in marine environment. It mainly includes four steps from the very beginning single fiber surface treatment to the last environmental resistance under hygrothermal conditions. The details of these four consecutive steps are shown below.

- a) Surface treatment of carbon fibers and characterization using micro and macro-test methods.

A novel method to deliver multiwalled carbon nanotubes (MWCNTs) into interphase was developed, which has following advantages: i) Much less CNTs are required; (ii) the incorporation procedure is easy to perform compared to dispersion of CNTs in epoxy resin; and (iii) the coating can be directly applied onto the as-received fibers. These

merits provide the coating-modification method great potential to scale up from research laboratory to industrial manufacturing.

- b) Characterization of carbon fiber surface treatment effects on hygrothermal resistance.

CFRPs have been immersed in hygrothermal environment up to four months. Long-term effects of moisture on the properties of CFRPs were evaluated through single fiber microbond, double cantilever beam (DCB), end-notch flexure (ENF) and short beam shear (SBS) tests.

- c) Characterization of surface treated CFRP-Ti hybrid composites under long-term hygrothermal conditions

Titanium was well anodized and carbon fibers were treated using MWCNTs modified silane coating to improve the long-term interfacial properties against humidity of FMLs. Hygrothermal effects on different treated hybrid FMLs were compared, and interlaminar fracture toughness was measured using single cantilever beam (SCB) tests.

- d) Surface treatment effects on the compressive properties of CFRP-Ti risers

Last but not least, CFRP-Ti risers were manufactured using filament winding method. Titanium pipes were surface treated using previous methods. The surface treatment effects on lateral and axial compressive strength and pipe stiffness were characterized. The experimental results were compared with finite element analysis results.

1.4 Approach

The main focus of this study is on the interfacial properties of CFRP-Ti composites in hygrothermal environment. Since the interfaces in system are fiber-matrix

interface, inter-laminar interface and metal-composite interface, details of approaches adopted in present study are as follows:

a) Surface treatment on carbon fibers

A method to deliver multiwalled carbon nanotubes into interphase was developed. The MWCNTs are first dispersed in silane coupling agent, and then the solution is applied to as-received carbon fiber wrapped with commercial sizing in order to form a nano-composite coating. Interfacial shear strength (IFSS) between carbon fiber and epoxy matrix is evaluated using microbond testing technique. A comparison of reinforcing efficiency of MWCNTs is performed between our method and conventional CNT-based modification of matrix. As to interlaminar properties, mode I and mode II interlaminar fracture toughness and interlaminar shear strength of CFRPs are evaluated using DCB, ENF and SBS tests, respectively. Reinforcement mechanisms are analysed according to the characterization of surface morphology and chemical composition by different analytic techniques such as optical microscopy (OM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX-S), back scattered-electron (BSE) and dynamic mechanical analysis (DMA), etc.

b) Surface treatment on titanium alloy

A well optimized anodization method is used, and electrolyte consisting of NaOH, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ and EDTA is chosen to treat Ti6Al4V and proved to achieve good bonding properties with epoxy. Interlaminar fracture toughness is measured using SCB tests. Stiffness, lateral and axial compressive strength of CFRP-Ti composite risers are also characterized. Fractured topography and chemical composition of specimens are

examined using SEM, XPS, EDX-S and BSE imaging to determine the failure modes and effect of surface treatments.

c) Hygrothermal treatment on hybrid composites

Then different treated CFRPs and FMLs have been immersed in de-ionized water and simulated seawater for up to four months. Long-term effects of moisture on interfacial properties of the CFRPs and FMLs are evaluated through different mechanical tests. Mechanisms of property degradation are explored based on the SEM, XPS, EDX-S and BSE characterization of the fracture surfaces.

1.5 Report outline

This report is outlined as follows:

Chapter 1 gives a brief introduction to the background of the proposed research, and highlights the objective and scope of the project.

Chapter 2 presents the literature review related to the topic of the research, which mainly includes backgrounds of CFRP-Ti composites, surface treatments of carbon fiber, modification of polymer matrix, surface treatments of titanium, hygrothermal effects on the interfacial properties and different mechanical test methods to characterize hybrid composites.

Chapter 3 describes the experimental procedures and characterization methods. It includes the materials used in the project, preparation of specimens, detailed experiment procedure and product characterizations methods.

Chapter 4 presents results and discussion for long-term interfacial shear strength between surface treated carbon fiber and epoxy matrix under moisture condition. Effects of carbon

fiber surface treatment, modification of epoxy matrix using MWCNTs and influences of different parameters are discussed. IFSS of different single fiber composite systems and effects moisture environment are characterized by different methods.

Chapter 5 describes results and discussion for long-term interlaminar properties of surface-treated CFRPs under hygrothermal conditions. Surface treatments and hygrothermal environment effects are carefully investigated. Interlaminar properties of CFRPs are characterized by different methods.

Chapter 6 discusses the long-term interfacial performance of surface treated CFRP-Ti hybrid composites under hygrothermal conditions. The effects of carbon fiber surface treatment and titanium anodization treatment are presented. Hygrothermal influence and interlaminar properties of FMLs are characterized by different methods.

Chapter 7 presents results and discussion of surface treatment effects on compressive properties of CFRP-Ti risers. Two directional compressive strength and stiffness of different surface treated CFRP-Ti risers are investigated by experiments and simulation.

Chapter 8 concludes this report with the highlights of future works.

Chapter 2 Advances in Interfacial Properties of Hybrid CFRP-metal Composites

2.1 Development of CFRP-metal composites

Due to excellent chemical and mechanical properties such as high specific strength, stiffness, fatigue resistance and thermal and electrical conductivity, carbon fibers attracted much attention as reinforcing material [31]. When carbon fibers are used in polymers, advanced polymer composites are created with all of the advantages relative to conventional metallic materials. As a result, carbon fiber-reinforced plastics are widely used in automobile and aircraft industries [32, 33]. If the composites are used together with metals, the hybrid material combines the excellent specific strength, stiffness, and fatigue properties of composites with the superior machinability and toughness of metals. At present, the hybrid composites are used in many different areas, such as flowlines, accumulator vessels and flexible risers [34, 35]. CFRPs based composite risers integrated with metal liners have attracted a great amount of interest from the offshore oil industries in recent decades to maximize the impact of the weight saving for deep-water oil exploration and production [36-39]. The primary function of metal liner is to prevent leakage from the annulus. The liner material is also required to resist corrosion and abrasion. Typical used metal liner materials are steel and titanium. Structural composite is the major load bearing element. Since significant weight reduction is achieved through using composites, the composite riser with the high specific stiffness would experience much lower axial tension and bending moment than its equivalent steel riser. Although the composites require higher manufacturing costs than traditional metal, the overall system

requirements and operational costs are much lower especially when design is holistically executed at a full system level. The cost effectiveness of composites has been investigated in numerous studies, and the findings unanimously point out decreasing platform size and mooring pretension leads to cost saving as well as weight reduction [40-42].

2.2 Interfacial issues in hybrid CFRP-metal composites

However, composite structures for offshore still face a qualification challenge, which is to design good interfacial properties to achieve the best performance of this hybrid composite system. This is because the interfaces are usually the weakest part in the composite system and experience severer deterioration in humid environment than in dry air [28, 29]. As a result, when designing CFRP-Ti pipes, the adhesion properties of fiber-matrix interface, inter-laminar interface and metal-composite interface (as shown in Fig.1.1) are of great importance, and their performance in hygrothermal environment should also be given attention.

For CFRPs, The main disadvantage of composite materials is their tendency to delaminate. Delamination or interlaminar separation is the most predominant and life-limiting failure mechanism in composite structures [43]. The quality of the fiber/matrix interface will influence the initiation and propagation of the delamination cracks. The significant role of delamination in the fracture of composites is reflected in a number of papers [44-46]. In these investigations, delamination or interlaminar fracture toughness properties of different fiber reinforced composites were investigated.

For metal-composite interface, it should provide a secure connection between the composite body and metal couplings at the terminations of a riser joint. The primary requirement for the MCI design is to effectively transfer loads from the connection to the composite tube. Under combined axial and pressure loads, the preferred failure is more likely to occur at this site rather than the tube body [47]. Therefore, it is recommended that the MCI should be carefully designed.

When being used in marine application, the hybrid composite material will be subjected to high relative humidities, temperatures, and chlorine ion concentrations over long periods of times. These conditions limit the use of the hybrid composites, which leads to a deterioration of the interfacial properties and ultimately result in the failure of the structure [48].

2.3 Interfacial shear strength (IFSS) between single carbon fiber and epoxy matrix

2.3.1 Testing methods

2.3.1.1 Fiber push-out test

The push-out test utilizes a micro-hardness indenter with various tip shapes and sizes to apply a compressive force to push against a fiber end into the metallographically polished surface of a matrix block. In the original version of the test (Fig. 2.1a), a selected fiber is loaded using spherical indenters in steps of increasing force, and the interface bonding is monitored microscopically between steps, until debonding is observed [49]. In the second approach shown in Fig. 2.1b, a force is applied continuously using a Vickers micro-hardness indenter to compress the fiber into the specimen

Figure 2.1 Schematic drawings of indentation (or fiber push-out) techniques: using (a) a spherical indenter [49]; (b) a Vickers micro-hardness indenter [50]; (c) on a thin slice [51].

surface [50]. When specimens are thin in thickness direction, a technique as shown in Fig. 2.1c is often used [51] to distinguish debonding force and friction during the whole process.

The most important advantage of this push-out method is that it is possible to test real composites simply. The major drawbacks are the physical significance and how to interpret the results. Besides that, it is difficult to distinguish failure if specimen is not transparent. Fibers may also be crushed by sharp indenter [52] and matrix may be cracked at interface [53].

2.3.1.2 Fiber fragmentation test

Fiber fragmentation test shows great similarity with real conditions, which makes it the most popular method. However, there is still confusion about the mechanics of the method.

Kelly and Tyson [54] devised the method in 1965 when they investigated tungsten fibers and copper matrix. Fig. 2.2 shows Birefringence patterns of the fiber fragmentation process for a single fiber composite at different strain increments. The requirement of the

method is that the failure strain of matrix material should be much greater than that of fiber. When load is applied onto the composites, fiber will break into several pieces when it reaches its tensile strength. This phenomenon will last until all of the segments of the fiber are too short to be broken.

When matrix is transparent, it is easy to measure the fiber fragmentation length by using an optical microscope. The spatial distribution of stresses around fibers can be measured by using photoelastic technique. If matrix is opaque, acoustic emission technique could be used. Some researchers such as Netravali [55], Vautey [56] and Manor [57] developed another method to monitor the fiber breakage in non-transparent matrix. The matrix can be dissolved in chemical solvent or burned off, and specimens can be polished to expose the broken fragments.

Figure 2.2 Birefringence patterns of the fiber fragmentation process for a single fiber composite at different strain increments [58].

Kelly and Tyson [54] proposed that the average shear strength at interface τ_a can be estimated from a simple force balance equation supposed that the interface shear strength is constant:

$$\tau_a = \frac{a\sigma_f^*}{(2L)_c} \quad (2.2)$$

where σ_f^* is the tensile strength of fiber, a is the fiber diameter and $(2L)_c$ is the critical transfer length.

The drawbacks of the method are also obvious and inevitable at the same time. The calculated τ_a is not accurate interface property and affect by other factors such as matrix shear yield strength. Bacom and Jensen [59] discussed the τ_a is more decided by the matrix yield strength instead of shear strength. Besides that, the properties of fiber may also affect the measurements of the interfacial shear strength of micro-composites. For example, the pre-stress existed in fiber as a result of sample preparation also causes experimental error.

2.3.1.3 Single fiber pull-out test

For single fiber pull-out test, a single fiber is pulled out of a fixed matrix block. During the process, the displacement and load of the tension are recorded to calculate the interface bond strength. A conventional way to calculate interfacial shear strength is shown in following equation

$$\tau_b = \frac{d\sigma}{4l} \quad (2.3)$$

where the τ_b is the interfacial shear strength, d is the diameter of the fiber, σ is the maximum debond stress and the l is the embedded length of the fiber. The embedded length of fiber can't be too long to guarantee the success of the test, especially when interface bond is strong and the diameter of the fiber is small. Hoecker et al. [60] concluded that the microdroplet pull-off test is the most sensitive technique in resolving interfacial effects.

Another method called microbond test is a variation of the pull out test to alleviate some difficulties of the conventional method [61-63]. The procedure of microbond test is to deposit a small drop of matrix onto fiber in the form of one microdroplet (Fig. 2.3). Fiber diameter and microdroplet dimensions were required for the analysis of microbond tests.

There are many factors that can influence the accuracy of the test such as droplet size, shape of loading jigs, the meniscus formed at the end of fiber. This is a partial reason why researchers get different results using same materials and testing method. However, there are many advantages of this kind of testing method. The variation of experimental results could be reduced because the curvature at boundary between fiber and matrix is smooth, and stress concentration is reduced to certain extent. In addition, the microbond technique has potential to be used for any combination of fiber and polymer matrices.

Figure 2.3 Schematic illustrating the microbond technique.

2.3.2 Effects of carbon fiber surface treatment on IFSS

2.3.2.1 Solution dip coating and roll coating method

It is common that carbon fibers are sized or coated with some kinds of polymer in industry application for the ease of application and simplicity of principle [64-69]. The process of sizing is to insert a polymer layer between carbon fiber and polymer matrix. By doing so, interfacial properties of composites can be improved and carbon fibers can also be protected. The quality of sizing has great influence on the final interfacial properties of composites [70].

Until now, almost all kinds of polymers can be applied as long as the solvent is appropriate. The thickness of the coating is mainly decided by two parameters: the concentration of solution and the drawing speed. To obtain uniform thickness is very difficult for the method, and good impregnation of fibers is also very important. The solvent should be chosen carefully to make sure polymer can be dissolved, and the viscosity should be low so that good coating can be achieved [71]. After proper coating,

the structure integrity of the CFRPs can be improved, and load can be transferred from matrix to the fibers by good adhesion. The working mechanism of sizing can be divided into two aspects: the first one is that sizing layer can increase the surface roughness of fiber surfaces and then improve the mechanical interlocking with matrix; another function is that sizing can form certain kinds of chemical bonds with both fibers and matrix. In this way, a stronger connection between carbon fiber and matrix is established.

A new method emerged very recently, in which nano-fillers are incorporated into sizing materials to form enhanced interphase between fibers and polymer matrix. It was found that the sizing doped with various nano-fillers, such as carbon nanotubes [72], inorganic nanoparticles [31, 73] and graphene [4], contributes positively to the interfacial bonding of carbon fiber or glass fiber reinforced composites. Godara et al. [72] dispersed CNTs into the sizing for glass fibers and achieved 92% increase in interfacial shear strength. Kamae and Drzal [74] found that the introduction of CNTs into sizing for carbon fiber resulted in further improvement in interfacial shear strength compared with pure epoxy sizing. The work of Yang et al. [31, 73] showed that epoxy emulsion sizing doped with nano-SiO₂ particles for carbon fiber can yielded improvements in both interfacial shear strength and interlaminar shear strength. The ILSS increased from 77.8 MPa to 88.7 MPa. Zhang et al. [4] introduced graphene oxide sheets into the sizing for carbon fiber and also observed more significant increase in interfacial shear strength (39%) and interlaminar shear strength (16%) compared with commercial sizing modified CFRPs.

Another similar process is called roll coating. In the roll coating process, solvents should be chosen as slow evaporated, and the thickness of coating is partially decided by

the concentration of the solution. Another influencing factor is the distance between feeding roller and applicator roller. By using the roll coating method, coating can be applied onto fibers uniformly, which is its obvious advantage over other techniques.

2.3.2.2 Electrochemical oxidation method

Because of the easy control and allowing continuous processing of carbon fibers, electrochemical oxidation treatment is one of the most effective surface treatment methods. It can introduce different types of reactive functional groups as well as enhance surface roughness, thus it can substantially improve interfacial bonding strength [75]. The electrolyte solutions used for electrochemical oxidation can be divided into acid solution, alkaline solution and ammonium salt solution [31, 76].

Surface electrochemical oxidation of carbon fiber is accomplished with a series of apparatus, usually including a surface treatment bath, washing batch, and drying oven. When finishing electrochemical oxidation, a washing bath full of deionized water is used to remove the adsorbed electrolyte on the carbon fibers. After that, the treated carbon fibers will be dried in an oven. There also may be a sizing device at the end of the process. The entire procedure is shown in the following Fig. 2.4.

However, this technique also demonstrates its own drawbacks of reducing the tensile strength of the carbon fiber while improving the interfacial bonding [77]. For examples, researchers like Guo et al. [78] claimed that interfacial bonding strength could be increased by 26% while tensile strength could be reduced by 8%. This may be due to the fact that electrochemical oxidation treatment leads to partially damage the outside of carbon fiber, and core part of the fiber is exposed. There are also some researchers such as Liu et al. [75] who proposed that tensile strength can be improved (by 17.1%) with

Figure 2.4 Schematic of equipment for electrochemical treatment [75].

optimal processing conditions and procedures. By doing so, the mechanically weak boundary layer on the surface of carbon fibers can be removed while the structurally ordered sheath region of carbon fiber surface wouldn't be damaged. In the meantime, crack growth could be resisted, because additional crystalline boundaries would be generated, and the graphitic crystalline structures could be refined.

2.3.2.3 Wet chemical treatment method

Because other treatments always cost a lot of money and consume high energy, a more cheap and convenient method is necessary. Acid treatment is one of the most widely used wet oxidative methods. The common approach is to heat carbon fibers in acid solution and then wash them until PH value becomes neutral. After this chemical treatment, some activated chemical groups can be generated, and many other chemicals can also be introduced onto the carbon fibers to further improve the mechanical properties. For example, carbon fibers were modified with nitric acid by Kim et al. [79] to introduce hydroxyl and carboxyl groups on the surface. These carbon fibers were then treated with an isocyanato silane compound, 3-isocyanatopropyltriethoxysilane (IPTS) to incorporate trialkoxy groups. Results showed that mechanical properties of the composites improved significantly. Researchers Peng et al. [80] used poly (amido amine) as the bridge to connect carbon fibers and CNTs or graphene oxide. As a result, a

hierarchical reinforcement consisting carbon fiber and CNTs or graphene oxide (GO) was developed. The interfacial shear strength of the composites increased 111%.

However, to get better interactions between carbon fibers and polymer matrix, strong chemical conditions are usually used. As a result, the own property of carbon fiber is affected, and tensile strength deteriorates significantly. To solve the problem, researchers also have made a lot of efforts. For example, Wei et al. [81] tried to use aqueous ammonia to replace acid. By doing so, the surface roughness increases without introducing active functional groups on the surface of carbon fiber. The results revealed that the treated CFs showed better compatibility with both polar and weak polar solvents.

2.3.2.4 Gas phase oxidation method

Another treatment that has potential to be scaled-up for industrial production is to oxidize carbon fiber in ozone at high temperature. Fu et al. [82] treated carbon fibers in ozone at 160 °C for 5 minutes with the results that mechanical properties of carbon fiber cement composites increased. Jin et al. [9] put pitch-based carbon fibers in an ozone environment with high temperature and kept the pressure at 0.4 MPa. The carbon-carbon composites showed increased mechanical properties. Vautard et al. [6] picked continuous treatment which is based on a gas phase thermo-chemical approach and compared it with conventional and commercial electro-chemical surface treatment. The thermo-chemical surface treatment generated homogeneously hydroxyl groups and carboxylic acid functionalities at the surface of carbon fibers. When reinforcing epoxy, the adhesion between carbon fiber and matrix increased greatly.

2.3.2.5 Chemical vapour deposition method

Carbon nano-materials possessing high specific surface areas and nano-scale micro-structure attract most of attention of researchers. One of the most commonly used methods is to grow CNTs on fibers by chemical vapour deposition [83]. Some researchers made CNTs grow on the surface of carbon fibers and single-fiber/epoxy composites were studied to learn the role of CNTs in transferring load at interface. The results showed that the nano-reinforcement improved load transfer because of the stiffening of matrix. Some other researchers used fiber pull-out and push-out tests to characterize the composites with CNTs grafted carbon fibers. The results showed 60% increase of IFSS in fiber pull-out tests, and no big changes were found in fiber push-out tests [84]. Zhang et al. [85] used single fiber microdroplet tensile test to test the IFSS and reported a 150% improvement in carbon epoxy composite with CNTs grafted carbon fibers. The mechanisms of the improvement were found to be the existence of chemical bonding, Van der Waals bonding, mechanical interlocking and surface wetting. Sager et al. [13] adopted single fiber-composite fragmentation test. They coated carbon fibers with randomly oriented and radially aligned CNTs using CVD method. They reported 77% and 11% increase of IFSS for randomly and radially aligned CNTs, respectively.

When improving interfacial property, a disadvantage also comes along that the tensile strength of carbon fiber reduces a lot. Zhang et al. [86] reported that the tensile strength of CNT-grafted carbon fibers degraded nearly 40% because of the introduction of mechanical defects during CVD process. Sager et al. [13] also reported decrease of fiber tensile strength about 30% and Young's modulus about 10%. There is also paper

showing the increase of tensile property after grafting CNTs onto the carbon fibers. However, the paper doesn't show the IFSS during the process [87].

2.3.3 Effect of nano-fillers modified matrix on IFSS

Another way to improve the interfacial adhesion between reinforcement and matrix is to modify polymer matrix. Multi-scale phase reinforced composites produced by addition of nano-fillers to standard fiber reinforced polymers have a tremendous potential. Firstly, the nano-fillers give composites additional functionality. These effects are potentially attainable in low mass fraction regime. Secondly, the performance and application range of composites can be improved after integrating nano-fillers into the existing systems. The potentially lighter weight and multi-functionality of hierarchical composites promises to have a direct impact on sustainability in the near future [14]. The basic idea is to disperse nano-fillers into matrix to get the best performance from the additions. When adding nano-fillers into standard fiber reinforced polymer composites, a hierarchical composite is formed. As a result, more functions are added, and interlaminar properties are improved for these composites.

Reasonable attention has also been given to use MWCNTs as secondary reinforcement in matrix to improve the mechanical properties of hybrid composites. Kim [88] studied low content of CNTs in epoxy of 0.3% improved 18% flexural strength and 11% fracture strain when compared with the composites without CNTs. Karapappas et al. [89] reported that mode I and mode II fracture toughness can be improved obviously when CNTs were added at the concentration of 0.5% and 1.0% by weight.

At the meantime, CNTs can also be treated to achieve better adhesion with polymer matrix. Carbon nanotubes can be functionalized by oxidation [90], by non-covalent methods [91], or by covalently bonding an organic functionality [92]. After treatment, the introduced functionalized groups on the surface of CNTs can react with polymer matrix and then make the adhesion between CNTs and matrix stronger. Park et al. [93] functionalized CNTs with acid, as shown in Fig. 2.5. The CNTs were treated in acid solution at a concentration of 30 wt% for 10 min at 50°C in an oven. Then the treated CNTs were dried for 3 days at 60 °C in a vacuum oven. M. T. Kim [94] treated CNTs with both acid and silane. The silane treated composites' flexural modulus increased by 34% and strengths increased by 20% when compared with those only acid treated composites.

Figure 2.5 Schematic of the processes used for acid treatment [93].

Figure 2.6 Schematic of the processes used for dispersion of the CNTs [93].

However, there is one obstacle making CNTs reinforced polymer hard to be utilized, which is the dispersion of large amount of CNTs into polymer matrix. A lot of work has already been done to disperse CNTs uniformly into matrix and sonication, and shear mixing technique is the most commonly used methods among all of methods [94] .

Different researchers developed their own methods to disperse CNTs into polymer matrix according to different conditions. Park et al. [93] used acetone and water as solvent to help dispersion, as shown in Fig. 2.6. They firstly dissolved CNTs into solvent and sonicated for 2 h. Then epoxy was poured into the solution and sonicated for 18 h in an enclosed beaker. To get rid of the solvent, they sonicated the mixture at room temperature for 2 h in an open beaker and at 35°C for 3 days. After that, the residual solvent was eliminated in a vacuum oven at 50 °C for another 3 days. The last step was pouring the curing agent into the mixture. Kim et al. [94] adopted a much easier way. They only stirred CNTs at 700 rpm for 30 min to disperse CNTs into epoxy matrix.

Godara et al. dispersed MWCNTs into epoxy at a concentration of 0.5 wt% using calendaring equipment. This method is said to be very effective in the exfoliation of CNTs from their pristine bundle micro-structure. Wong et al. [95] used toluene as solvent to disperse CNTs into polystyrene. CNTs were added into the solution of polystyrene and toluene, and the mixture was stirred for 1 h and sonicated for another 1 h to get good dispersion.

Nano-particulate fillers enable proper enhancement as a result of the large interface available to matrix. Several techniques to modify nano-particle surfaces have been identified. For example, layered silicate clays were modified by exchanging inorganic cation with a positively charged organic compound [96]. Graphite nano-flakes were functionalized by oxidation of the grapheme plane [97], or by a coating and compounding method [98].

2.4 Interlaminar properties of CFRP laminate

2.4.1 Interlaminar shear strength

Interlaminar shear strength can be obtained using short beam shear test in according to ASTM D 2344D. Laminate composites were made into beam and tested as shown in Fig. 2.7. The interlaminar shear strength value can be calculated in following equation

$$\tau_{\max} = \frac{3P_{\max}}{4bt} \quad (2.4)$$

where $P_{\max}$ is the maximum compression load at fracture, b is the width of the specimen and t is the thickness of the specimen. Because of the simplicity of the test method and

Figure 2.7 Horizontal shear load diagram (Flat laminate) [99].

minimum complication in specimen preparation, short beam shear test has become one of the most popular methods to determine the interlaminar bond quality of composites. It has been most widely used to assess the effects of fiber surface treatments, fiber-matrix compatibility for the development of new fiber or matrix systems, etc.

However, this test has its own drawbacks because of the loading nose with small diameter. The inherent problems are associated with stress concentration and non-linear plastic deformation. To avoid this, thick specimen should be manufactured, and four-point bending should be used to replace three-point bending [100]. This is because load can be shared by the two noses so that the stress concentration can be alleviated [101].

The interlaminar shear strength of carbon fiber-epoxy composites can be improved through a number of mechanisms [102]. For example, the presence of oxides on the surface of the fiber can form hydrogen bonds with the amine hardener of the matrix. Similarly, the polar groups on the surface of the fiber can also improve ILSS results from the increased van der Waals adhesion between fiber and matrix. ILSS can also be improved by increasing the surface area of fiber, which causes improved mechanical interlocking of fiber and matrix. Jang and Yang [103] chose plasma method

to treat carbon fiber surface and found the generated micro-pittings allowed more interpenetration between carbon fibers and polybenzoxazine. As a result, the interlaminare shear strength increased by 73% after 3 minutes plasma treatment. Similar results were obtained by other researchers [104, 105].

2.4.2 Mode I interlaminar fracture toughness

The procedure of testing G_{IC} is specified in ASTM D 5528. One of the most common used specimens is DCB specimen, as shown in Fig. 2.8. The advantages of the DCB test are simple specimen geometry and stable crack growth. Both unidirectional and multidirectional lay-ups can be used for the experiments. Besides the configuration for the DCB geometry, another width tapered DCB (WTDCB) specimen is also employed, which is first devised by Wang [106]. The advantage of this figure is that strain energy release rate could be maintained constant, and there is no need to monitor crack length throughout the test. However, the disadvantages are also obvious that flexural modulus should be measured separately, and the specimens are complex to prepare. A lot of researchers have tried to analyse the experimental data differently, and the methods can be commonly divided into two main categories, which are compliance and energy methods.

The matrix toughness is important to the mode I interlaminar fracture toughness of composites. It is reported by Bradley [107] and Jordan et al. [108] that increasing the fracture toughness of matrix would lead to the improvement of delamination fracture energy. This is because the size of the plastic deformation and non-linear viscoelastic zone increased. As a result, more loads were distributed away from the crack tip. However, constraint provided by the fibres restricted the size of the plastic deformation

zone [109], and the translation efficiency was low from high matrix fracture toughness to composites fracture toughness. Bradley [107] reported that increasing matrix fracture toughness above 70 J/m^2 resulted in significant increases in composite G_{IC} , but higher matrix fracture toughness ($> 400 \text{ J/m}^2$) resulted in a small improvement of composite G_{IC} . Jordan et al. [108] found that mode I delamination toughness increased monotonically with increasing the resin fracture toughness up to 2000 J/m^2 , above which a much smaller increase in mode I delamination toughness is noted.

Some references have shown that values of interlaminar fracture toughness were closely related to specimen thickness. However, other references have shown a negligible dependence. Davies et al. [110] reported that a 50% improvement of interlaminar fracture toughness resulted from a 67% increase in thickness for IM6/PEEK specimens. But, Davies also found that there was only a 10% increase in toughness for AS4/PEEK with the same thickness increase [111].

Another important phenomenon in measuring mode I fracture toughness is fiber bridging, especially for a unidirectional beam. Fiber bridging occurs as the delamination progresses along the length of the beam [112], which increases the energy required to propagate the delamination. Therefore, the interlaminar fracture toughness measured in the presence of fiber bridging may be artificially high and hence not a generic material property for the composite [113]. However, the initiation value of G_{IC} can be considered to be accurate because it is not affected by fiber bridging [114].

2.4.3 Mode II interlaminar fracture toughness

Pure mode II interlaminar fracture testing can be performed using both ENF specimen and end loaded split (ELS) specimen. However, ENF test is more widely used. The ENF specimen is similar to three-point flexure specimen, and the only difference is that a pre-crack should be generated at the mid-plane before testing. Even though the test method is easy to perform due to its simple configuration, there are also several problems with the method. Among them, the most important one is unstable crack propagation so that it is difficult to monitor crack during propagation [115]. As a result, this test can only be used to determine initiation values but not resistance curves [116]. In addition, the effect of friction can't be ignored, and this resulted in the question whether mode II data obtained could be regarded as apparent values [117].

Some attention has been given to determining the loads and displacements of delamination initiation, which are required to calculate the G_{IIC} values [111, 118]. The G_{IIC} may be calculated using the loads and displacements obtained from three ways: i) the maximum loads at which unstable delamination growth occurs; ii) the deviation from linearity of the load-displacement curve; iii) the intersection of the load-displacement curve with a line representing a 5% increase in initial compliance [118]. For brittle composites, there is a non-linear portion of the load-displacement curve prior to unstable crack growth [118]. This non-linear portion may be due to the formation of microcracks or damage ahead of the delamination front, prior to coalescence of these cracks into delamination growth [113]. Another possible reason of the deviation from linearity is the delamination growth initiates at the center of the delamination front. The values of

fracture toughness obtained from load and displacement at the deviation from linearity are more conservative than that obtained from the maximum loads.

The value of mode II fracture toughness is also affected by many factors. Srivastava and Hogg [119] studied glass woven roving/polyester composites, which were modified with particles of polyethylene and aluminium tri-hydrate. The G_{IIC} increased from 1250 J/m² (unfilled) to 1450 J/m² to 1850 J/m², which resulted from adding aluminium tri-hydrate and polyethylene particles, respectively.

Effect of rate of testing also has effects on the final mode II fracture toughness of composites. Blackman et al. [120] conducted mode II tests on carbon fiber reinforced composites over a range of cross-head rates from 1.67×10^5 m/s¹ to 10 m/s¹. It was found that G_{IIC} of thermoplastic composites decreased from 2500 J/m² to 2000 J/m² at high rate of loading. However, a slight increase was observed from 700 J/m² to 800 J/m² for the epoxy composite.

Through-thickness reinforcement has potential to enhance the G_{IIC} obviously. Through-thickness reinforcement can enhance the G_{IIC} obviously. Lalit and Yiu-Wing [121] used Kevlar threads as through-thickness reinforcement to study their effects on carbon/epoxy composites. Results showed that that G_{IIC} increased from 1300 J/m² to 2350 J/m² when compared with the composites without Kevlar threads through thickness. The improvement was due to the development of a bridging stitch-thread zone behind the crack tip. It was also reported by the same authors that G_{IIC} was improved approximately 80% for a stitch density 4 st/cm² and 3.5-fold for a stitch density 12 st/cm².

Figure 2.8 Double Cantilever Beam Specimen: (a) with piano hinges and (b) with loading blocks [122].

2.4.4 Mixed-mode interlaminar fracture toughness

In most cases, delamination doesn't occur in a pure mode but may be a combination of different modes. Therefore, a valid mixed mode failure criterion must be established. The standard mixed-mode bending (MMB) test is the most commonly used method to get mixed-mode fracture toughness because it can vary the mixing ratio of mode I and mode II fracture toughness [123]. For example, Ozdil and Carlsson [124] adopted this method to test the fracture toughness of glass/polyester composites. There are also a lot of researchers developing other configurations to calculate mixed-mode fracture toughness. SCB test was invented by Reyes and Cantwell [125], which is similar to ELS specimen. Yoon and Hong [126] invented single-leg bending (SLB) test and Davidson et al. [46, 127] also did a large number of works about the test. In addition, Tracy et al. [128] modified the SLB test and proposed single leg four point bend (SLFPB) test. What's more, Albertsen et al. [44] and by Korjakin et al. [43] introduced the mixed-mode flexure (MMF) test. At last, the cracked-lap shear (CLS) test should also be mentioned [129]. Configurations of selected testing methods are shown in Fig. 2.10.

Standards are currently available for mixed-mode bending tests on unidirectional laminates. However, in most cases, multidirectional laminates are also commonly used in the real applications, where delamination often occurs at the interfaces between differently oriented plies. Choi et al. [130] investigated the fixed ratio mixed mode test on carbon/epoxy unidirectional and multidirectional specimens. It was found that intraply damage occurred in the latter. However, it was still possible to obtain true initiation interlaminar fracture toughness, which was 65% higher than those of unidirectional specimens. Furthermore, because of the low toughness values reported, the area method seems not suited for data reduction [131]. Pereira and Morais [132] performed the MMB tests on glass/epoxy multidirectional specimens. Results showed that the modified beam theory data reduction method gave accurate predictions of specimen compliances.

2.5 Metal-composite interfacial properties

2.5.1 Surface treating methods of metals

2.5.1.1 Sandblasting

Before bonding to composites, titanium is often mechanically treated to produce a clean surface and increase the surface roughness. Abrasive and grit blasting is a process whereby a stream of abrasive material is forcibly propelled against a surface in high pressure to achieve certain objectives. Some typical operations under this category include wet abrasive blasting, micro abrasive blasting and bead blasting [133]. However, abrasion and grit blasting techniques are not enough for surface treatment alone. When combining together with other treatments such as chemical and electrochemical treatments, strong bonding strength can be achieved.

2.5.1.2 Chemical etching

In chemical etching, acid treatment is one of the common used methods to etch titanium. There are a number of acid mixtures have been used to treat the surface of titanium. However, in most cases, the dry strengths are adequate but durability is poor [133]. Another problem is that hydrogen may pick up as a result of these treatments. But this problem can be solved by using alkaline instead of acid solutions [134].

Another common used etching solution is alkaline. Initially, the alkaline peroxide etching was implemented around 36h at room temperature, which is too long for industrial applications. Proper heating to 50-70 °C was used to shorten the treating time up to 20 minutes [135]. The treatment may cause metal to be etched or oxidized, and it is depended on the concentration of sodium hydroxide and hydrogen peroxide. For example, some researchers used sodium hydrogen peroxide etching to grow an oxide layer which is 2 µm thick and stable up to 200 °C [136].

2.5.1.3 Plasma treatment

Plasma spraying surface treatment heats chemical powder to molten state after which spraying it onto titanium surface rapidly. The treatment is environmental-friendly and does not pose any imminent hazards. Some other advantages of this form of surface treatment includes insensitivity to surface contamination, low processing costs and suitable for repairs [137].

High bonding strength comparable to good chemical surface treatments has also been recorded after successful plasma spraying surface treatment [137]. When increasing temperature, titanium joints show better properties after plasma-sprayed treatments. Ramani

et al. [138] sprayed silicon onto titanium, and results showed that surface tension and surface roughness increased together with bonding strength and durability.

2.5.1.4 Anodization

Anodization is one of the most promising methods because it can design micro-structural of titanium surface easily and adjust the element of the generated oxide layer. As a results, it may yield the best bonding strength and durability [24, 26, 27, 139]. Different anodization techniques were developed to treat titanium, which mainly includes chromic acid anodization and hydroxide anodization [27].

Some researchers claimed that chromic acid anodization can improve micro-roughness significantly, and the produced oxide thicknesses are 40 and 80 nm under 5 and 10 V, separately [134]. What's more, it is demonstrated that bond durability and bond strength are remarkably improved, and they are high enough for further treatments.

In comparison with chromic acid anodization, hydroxide-based electrolyte is more environmentally friendly because it uses less hazard chemicals [26]. Some researchers chose the sodium hydroxide as electrolytes and measured the adhesive bonding [140]. The adhesive bonds showed high strength and kept relatively high strength even when exposed to high temperature, moist and other stressed conditions. Matz [139], Garcia et al. [141] and Mertens et al. [24] also reported similar results. They used NaTESi (NaOH+Na-tartrate+EDTA+Na₂SiO₃) as electrolyte, and the oxide layer exhibited a good bonding strength to polymer matrix as well as long-term durability. He et al. [26] reported that anodizing temperature also had great influence on the micro-structure and mechanical properties of Ti6Al4V. After anodized under 0 °C, 25 °C and 40 °C, the apparent shear strength of the anodized alloy bonded with epoxy were improved by

217.7%, 225.0%, and 317.2%, respectively. What's more, this kind of solution could be used multi-times and was quite environmentally friendly.

2.5.2 Single-lap shear strength

There are several test methods to measure the shear properties of metal-composite material, such as the notched beam shear method, the notched plate shear method, and the thick-adherend shear test method. However, the most widely used adhesive bond test specimen is the single-lap tension test. The procedure of testing apparent shear strength of single-lap-joint specimen is specified in ASTM D 1002. In the experiment, the test specimen shall be cut from test panels and form the shape as shown in Fig. 2.9.

The single-lap joint is the most common joint used mainly due to its simplicity and efficiency. However, one of the problems associated to this joint is the fact that the stress distribution (shear and peel) is concentrated at the ends of the overlap [142]. Various techniques have been adopted by researchers to improve the efficiency of the single-lap joints. These include altering the adherend geometry [143], adhesive geometry [144], and spew geometry [145].

The thickness of adhesive has an important effect on the shear strength [146]. The lap joint strength increases when the bondline gets thinner [147]. However, the reason for this phenomenon is still not clear. Adams et al. [148] thought thicker bondlines contained more defects such as voids and microcracks. Crocombe [149] explained that the plastic spreading of the adhesive along the overlap was severer with increased adhesive thickness. Grant et al. [150] explained this phenomenon from another point of view

Figure 2.9 Form of test specimen for single-lap shear test [151].

recently. He believed that there was an increase in the bending stress since the bending moment has increased. The generated bending stress was the reason of the reduced shear strength.

The effect of adherend thickness is also important because of two reasons [152]. Firstly, when strength of adherend is low, the adherend becomes stronger and less likely to deform plastically with increased thickness. Secondly, when strength of adherends is high, a thicker adherend may lead to the decrease of joint strength, which is due to an increase of the bending moment.

Surface treatment is another parameter that can significantly affect the shear strength. For example, anodization can improve the shear strength obviously. He et al. [26] investigated the anodization effects on the shear strength of anodized titanium alloy bonded with epoxy. With increasing the anodization temperature from 0 °C to 40 °C, the shear strength increased up to 317.2%.

2.5.3 Mixed-mode interlaminar fracture toughness

The mixed-mode interlaminar fracture toughness of metal-composite material can be obtained using the same methods as CFRPs. In these tests, single cantilever beam test is the most commonly used one to characterize the degree of adhesion between the

composite and metal plies [2, 125, 153]. This geometry yields mixed-mode I/II loading (tension/shear) conditions at the crack tip in the sample.

The mixed-mode interlaminar fracture toughness of metal-composite material depends on the adhesion between metal and composites. Reyes and Cantwell [125] introduced a maleic-anhydride modified polypropylene interlayer at the bi-material interface to improve the fracture toughness. Results showed that G_c was 3500 J/m^2 , which was even higher than tough thermoplastic based composites such as carbon fibre-reinforced PEEK. German et al. [154] obtained similar results by using a hot dip zinc surface treatment on the DP500 steel and incorporating an interlayer based on modified polypropylene at the interface between the composite and metal plies. The fracture toughness increased from 600 J/m^2 to 1300 J/m^2 after treatment.

Loading speed is also important to the measured mixed-mode interlaminar fracture toughness. German et al. [154] adopted SCB test to measure the interlaminar fracture toughness of thermoplastic composite-metal hybrid laminates at different loading speed of 1, 10 and 100 mm/min. They found that G_c of the hybrid laminates increased from 1000 J/m^2 to 1500 J/m^2 with increasing crosshead displacement rate. Reyes and Cantwell [125] investigated the G_c over a wide range of loading rates (from 0.1mm/min to impact loading) of a glass fiber-reinforced polypropylene FML. The results showed that the interfacial fracture toughness initially increased with the crosshead displacement rate up to 100 mm/min before reducing again at higher displacement rates. It was because there were competing failure mechanisms occurring in the crack tip region.

2.5.4 Axial compressive strength of pipe

The procedure of testing axial compressive properties of composite pipe is specified in ASTM D 695-10, as shown in Fig. 2.11. In the experiment, the test specimen shall be cut from wound tubes, and form the specimens with same diameter as tube and length. The compressive strength should be calculated by dividing the maximum compressive load with the cross sectional area of specimen.

The axial compressive strength of composite pipe can be improved by combining with another material. Some researcher investigated the axial compressive strength of glass fiber-reinforced plastic short pipe, and found that the bearing capacity of the composite pipe can be heightened obviously by confining CFRP sheets outside [155]. For the glass fiber-reinforced plastic pipes of the same wall thickness, the ultimate axial compressive stress increased with the layers of the CFRP sheet. When 8 layers CFRP sheets were used, the axial compressive strength increased from 353 MPa to 722 MPa.

The axial compressive strength of pipe could also be affected by environment. Deniz et al. [156] investigated the effects of seawater on the compressive strength of impacted glass/epoxy composite pipes. After up to 12 months immersion, the axial compression tests were performed after impact tests. The results showed that compressive strength generally reduced with increase in seawater immersion time.

However, literature on compression test of metal-composite material is quite limited. Peng et al. [157] adopted this method to characterize the mechanical properties of aluminium pipes wrapped with CFRPs. By this compression method, axial compressive properties were well measured. It was proved that outer CFRP layers were helpful to enhance the axial compressive strength and stiffness of aluminium pipes. The

yield load and maximum load capacity increased up to 139.8% and 154.6%. Besides that, buckling stability of pipes could also be characterized using longer pipe specimens [158].

Figure 2.10 Illustration of loading configurations of selected methods [159].

Figure 2.11 Form of test specimen for axial compression test.

2.6 Hygrothermal effects on interfacial properties

2.6.1 Theories of moisture uptake kinetics

Environmental conditioning is believed to comprise of physical, chemical, mechanical, physico-chemical and mechano-chemical phenomena. Moisture may penetrate into polymeric composite materials by diffusive and/or capillary processes. Both reversible and irreversible changes in mechanical properties of thermosetting polymers are known to occur as a result of water absorptions [160].

The moisture absorption depends on many factors, such as relative humidity, environmental temperature, polymer chemistry and so on [161, 162]. Although a number of papers have been published on water sorption in composite systems, further study is still required in order to be understood the real working mechanism [163-165]. The common used models for water penetration through a composite matrix are either based on Fick's law or involve Fickian-based phenomenological approaches. The Fickian transport of moisture in polymers or polymer composites is described by

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (2.1)$$

This equation is known as the general diffusion law or Fick's second law of diffusion (Fick's law, for short). C (kg/m^3) is the moisture concentration, t (s) the time and D (m^2/s) is the diffusion coefficient or diffusivity of the moisture in polymers (in a 3D system). However, Fick's law may not be appropriate to describe moisture absorption behaviour of composites. For example, WAN et al. [166] investigated moisture behaviour of 3D braided carbon fiber-epoxy composites. Results showed that absorbed

moisture slightly decreased mechanical properties of the C3D/EP composites. Contrary to unreinforced epoxy, the moisture absorption behaviour of the C3D/EP composites cannot be described with Fick's law of diffusion, probably because of the presence of voids and/or 3D fiber structure.

The absorbed water has significant effects on the final performance of composite in their long-term utilization. The resulting hygrothermal forces and residual stresses may be sufficiently large enough to influence the failure of laminated composite. Hydrothermal aging may also introduces chemical and structural changes in resin matrix. The aging-induced new-phase at interphase is more mobile than matrix because it has its own glass transition at a lower temperature [167-170]. As a result, this hygrothermal effect should not be neglected in modern design analysis and lifetime estimation of composite structures [160]. For instance, Luo et al. [171] investigated the moisture absorption behaviour of three-dimensional braided carbon fabric composites with different conditions. It was found that moisture absorption behaviour and loses of mechanical properties were interface dependent. It was proposed that the roles of interfaces encompass two combined competing effects of withstanding migration of moisture molecules and resisting the leaching of low-molecular-weight matters.

2.6.2 Effects of absorbed moisture on matrix dominated properties

For marine and offshore application, one of the biggest issues is that interface must be able to resist degradation due to moisture absorption as well as maintain the mechanical properties even under hygrothermal environment [172]. The state of composite interface could influence the nature of moisture diffusion and affect

mechanical properties reduction. The degradation is not only influenced by moisture but also by temperature [160].

The environmental action can limit the usefulness of polymer composites by deteriorating their mechanical properties during service. The most common damage modes of composites are matrix cracking, delamination growth and fiber fracture. There has been a great need to quantify the environmental influence on the degradation of mechanical properties of fiber/polymer composites. At the same time, understanding of the moisture diffusion process in polymeric materials can help to identify the location of damage, analyse the mechanical degradation and predict the residual strength and service-life of FRP structures.

Environmental exposure causes reduced interfacial stress transmissibility as a result of three factors: matrix plasticization, chemical changes and mechanical degradation [167, 173, 174]. Among all failure modes, delamination is a critical one, which occurs when the resultant transverse shear force exceeds a threshold value. Low interfacial shear strength may be the reason of initiation and propagation of delamination. The interfacial separation results from the delamination may lead to premature buckling of laminates, excessive intrusion of moisture and stiffness degradation. In short-term treatment of the specimen, damage growth and premature failure occurs due to delamination. However, for long-term, this may lead to load-bearing layers for different environmental factors [175].

A number of researchers have already done a lot of investigation on the hygrothermal effect on the interfacial properties of hybrid composite systems. Cauch-Cupul et al. [176] adopted single fragmentation test to assess the quality of fiber-matrix

interphase . They concluded that the role of moisture uptake on the residual stresses is considered to be important when considering the effect deterioration of the interfacial shear properties.

Ray [160] concluded that higher temperature can increase moisture uptake rate and modify delamination nucleation stress. It is not only the absorbed moisture but also under what conditions it diffuses into the specimen that characterizes the interfacial degradation phenomena. Selzer and Friedrich [177, 178] found that moisture decreased the properties dominated by matrix or interface due to the ductility of matrix and loss of shear strength. However, the influence of water on the fiber-dominated values, as well as on the properties of thermoplastic material, was not detectable.

2.7 Summary

CFRP-Ti becomes a promising choice to replace metal riser for deep-water oil exploration and production, because it combines excellent specific strength, stiffness, and fatigue properties of composites with superior machinability and toughness of metals. As the weakest part in the hybrid system, the interface has profound influence on the final performance of CFRP-Ti composites. To achieve better adhesion of the hybrid composites, many strategies have been developed. They can be basically divided into three main categories: surface treatment of carbon fibers, modification of matrix with nano-fillers and surface treatment of titanium. In this process, a number of difficulties would be encountered, such as reduction of tensile strength, uneven distribution of nano-fillers, environmental pollution and so on. According to the present situation, there is still a great demand of developing new treatment methods to improve the interfacial properties of the hybrid composite system in a more efficient way.

In addition, interface also affects the hygrothermal aging behaviours of composites, and stability of interfacial region is crucial to the CFRPs' lifetime performances, especially in deep-sea application. Therefore, sufficient resistance to the negative influence from moisture attack is one of the key issues in development of CFRPs for deep-sea applications, which necessitates understanding the effects of moisture on the interfacial properties.

To evaluate the interfacial properties of the hybrid composites, a number of mechanical test methods have been developed from micro to macro-scale. Different techniques are chosen to be used for different applications based on their advantages and disadvantages. However, until now, the mechanical and other properties of CFRP-Ti composites in hygrothermal environment have not yet been studied to quite an extent. It is of great use to obtain these benchmark data to refine the design and prediction of CFRP-Ti composites used for marine application.

Chapter 3 Materials and Experiments

3.1 Materials

The metal plates used are Ti6Al4V alloy (Grade 5) with thickness of 1.62 mm from Titan Engineering Pte Ltd. The titanium tubes (Grade 9) were also provided by the same company with outer diameter of 50.8 mm and thickness of 1.25 mm. Commercially available HexTow IM2C carbon fibers, with an average diameter of approximately 5.2 μm , were used as the primary reinforcement. The epoxy matrix, Epolam 5015 resin, is a mixture of Bisphenol F and Bisphenol A resins supplied by Axson Technologies. The Epolam 5015 hardener consists of isophoronediamine and polyoxypropylenediamine. (3-glycidyloxypropyl) trimethoxysilane coupling agent was obtained from Sigma-Aldrich. Nanocyl NC7000 multiwalled carbon nanotubes were used as the secondary reinforcement. The average diameter and length of NC7000 CNTs are 9.5 nm and 1.5 μm , respectively. Seawater was simulated by dissolving sea salt (SIEM Trading PTE Ltd) in tap water to make a 3.5% salinity solution. All chemicals in this study were used without further purification unless otherwise specified.

3.2 Preparation of specimens

3.2.1 Preparation of coating for carbon fibers

Fig. 3.1a illustrated the chemical structure of (3-glycidyloxypropyl) trimethoxysilane. This kind of silane coupling agent can be hydrolysed to produce silanol groups [179] (Fig. 3.1b), which can react with C-OH groups coming from the sizing material on the surface of carbon fibers and form chemical bonds on one side [179-182]. On the other side, epoxide groups in silane coupling agent can be cross-linked with the

Figure 3.1 (a) Chemical formula and (b) hydrolysis of (3-glycidyloxypropyl) trimethoxysilane coupling agent.

epoxide groups in epoxy matrix with the aid of amine hardener [179]. By this way, the polymer matrix and carbon fibers are tightly bound to each other through the silane coating. In addition, some silanol groups that do not participate in the aforementioned reaction condense with themselves.

A mixture of ethanol and water with weight ratio of 95:5 was used as solvent for silane coupling agent. (3-glycidyloxypropyl) trimethoxysilane was added into the solvent to yield a 2% final concentration. In order to facilitate hydrolysis of silane coupling agent, the PH value of solution was adjusted to 5 using acetic acid. The solution was ultrasonicated in a bath sonicator (Fisher Scientific, Model: FB15051, shown in Fig 3.2a) under power of 280 W for about 30 minutes to reach a homogeneous state. The introduction of MWCNTs with loading of 0.05 wt% and 0.1 wt% into the solution is performed through a two-step procedure: i) CNTs were added into the solvent of ethanol and water (weight:weight = 95:5), and then ultrasonicated for 30 minutes using a Misonix 3000 sonicator under 45 W; ii) the suspension was mixed with the silane coupling agent following the same method as the above mentioned. To facilitate the dispersion of MWCNTs in the silane coupling agent, before being mixed with the silane coupling agent,

the MWCNTs were oxidized with a nitric acid and sulphuric acid solution. 75 ml concentrated nitric acid was mixed with 225 ml concentrated sulphuric acid in a three-neck flask and 3g of MWCNTs was added to the mixture. The mixture was then sonicated for 30 minutes in order to produce a uniform suspension. After sonication, the mixture was heated to 90 °C and refluxed for 1 hour with continuous stirring. The slurry was then poured into a beaker containing 2000 ml of deionized water and was left to stand overnight. After the precipitate had settled, the supernatant water was removed, and this washing process was repeated three more times. Following this, the precipitate was poured into a dialysis bag and soaked in deionized water for three days, with the water being changed frequently. Finally, a freeze-dry method was used to obtain the final oxidized CNTs. Carbon fibers were soaked in the silane coupling agent (with or without MWCNTs) for several minutes followed by drying at 110 °C for 20 minutes. Afterward, the fibers were carefully kept from disturbance of strong airflow or physical touch before the deposit of resin droplet.

The incorporation of MWCNTs into epoxy resin was performed following a three-step procedure: i) CNTs was added into acetone prior to ultrasonication for 30 minutes using a Misonix 3000 sonicator under 45 W; ii) The mixture was then processed by a IKA T18 Ultra-Turrax homogenizer (Fig. 3.2b) at speed of 15000 rpm for 30 minutes in an ice bath; iii) Afterward the mixture was added into epoxy resin, homogenized for 1.5 hour, and then mechanically stirred for 4 hours at 55 °C to remove the solvent completely. Two nano-composite matrices containing 0.05 wt% and 0.1 wt% MWCNTs were prepared.

Figure 3.2 Setup for dispersion: (a) ultrasonicator and (b) homogenizer.

3.2.2 Sample preparation for microbond test

Fig. 3.3a shows the schematic diagram of a specimen for microbond test. A piece of carbon fiber was attached onto a rectangular paper frame (8 mm $\times$ 40 mm) with a hole in the middle. A resin droplet was then deposited on the fiber and cured in situ at room temperature for 24 hours followed by the post-curing at 80 $^{\circ}$ C for 16 hours. Before the test, the lower side of paper frame was cut to free the lower end of carbon fiber.

Figure 3.3 Schematic illustration of microbond test, not to scale.

Both fiber diameter and microdroplet dimensions were required for the analysis of the microbond tests. The diameter of the fibers was measured using FE-SEM and the dimensions of epoxy droplets were measured under optical microscope.

3.2.3 Preparation of CFRP laminates using VARTM procedure

Carbon-epoxy composites were manufactured using Vacuum Assisted Resin Transfer Moulding (VARTM) process. The composites were created using 8 layers of carbon fiber sheets with a layer of Teflon film placed in between the 4th and 5th layer in the mode I and mode II fracture toughness samples to introduce a preliminary crack. Peel-ply was added above these layers, and finally an infusion mesh was added on top of the peel-ply to aid the wet out of the fibers. The epoxy resin was fed into the vacuum bag with a PVC hose and infusion spiral until fully distributed within the layers. This set up can be seen in Fig. 3.4a and b. The laminate was left to cure at room temperature for 24 hours and then post cured at 80 °C for 16 hours. The average thickness of the samples was measured to be around 3.0 mm.

Figure 3.4 (a) Schematic illustration of VARTM procedure and (b) actual fabrication of CFRP composites using the VARTM process.

3.2.4 Surface treatment of titanium alloy

To treat titanium surface, Ti plates were firstly ground and polished. Then, they were sandblasted for 20 seconds using alumina powder with particle size of 50-100 μm . The plates were laid flat during the process to minimize the residual stress and strain in the titanium, and the sandblasted plates were chosen as controlled samples for comparison purpose. After that, some titanium alloys were anodized according to previous work [26]. The electrolyte was prepared from the solution of NaOH (7.5 M), $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ (0.2 M) and EDTA (0.1 M). The anodization was conducted at 40 $^{\circ}\text{C}$ for 15 minutes using a DC power, which generates voltage of 15 V.

3.2.5 Preparation of CFRP-Ti laminates

The CFRP-Ti laminates were also manufactured using VARTM process. The laminates were manufactured by stacking 4 plies of carbon fiber cloth onto a 1.62 mm thick titanium plate with a layer of Teflon film placed at the composite-Ti interface to introduce a preliminary crack for tests. The laminates were left to cure at room temperature for 24 h after being wet by epoxy and then post cured at 80 $^{\circ}\text{C}$ for 16 h.

3.2.6 Filament winding of CFRP layers on Ti lined hybrid risers

In filament winding process, fibers travel through a resin bath which is filled with epoxy resin and are rolled over a rotating mandrel at $\pm 55^{\circ}$ to form 3 helical layers. Then a hoop layer which is 90° to mandrel is formed at the outer surfaces. The winding machine is shown in Fig. 3.5a. This wet filament winding method is more commonly used in comparison to prepreg type winding. Advantages of wet winding method are low cost,

Figure 3.5 (a) Filament winding machine and (b) rotational machine for curing.

short winding time and resin production can be altered easily in order to satisfy the requirements.

For curing of composite pipes manufactured by filament winding, the pipes were also placed at room temperature for 24 hours and then put into oven at 80 °C for another 16 hours to post cure. Due to the convex shape of pipes, low viscosity resin systems flow along gravitational forces forming areas of high fiber volume fraction and low fiber volume fraction. Thus the geometry of pipes requires constant rotational movement during curing in order to achieve a homogeneous fiber matrix, and the rotational machine designed for curing is shown in Fig. 3.5b.

3.3 Mechanical tests

3.3.1 Interfacial shear strength between single fiber and matrix using microbond method

Microbond test was carried out using an in-house developed tester equipped with a 2.45 N force load cell, as shown in Fig. 3.6a. The microvise is made from aluminium,

and two blades are mounted on the top of the microvise. A screw passes through a side of microvise to control the distance between the two blades. The bottom of the microvise is mounted onto the X-Y direction travelling stages. The specimens are clamped by a fixture that was fixed on an actuator. By adjusting the position of X-Y travelling stages and the distance between two blades, the droplet is blocked by the blades while the fiber remained straight. Contact between fiber and blade is identified when the fiber is curved. Then release the stress of screw a little bit to make sure droplet is blocked while there is no friction between fiber and blades. All of the observation can be achieved by a removal Zeiss stereo microscope with the magnifying power of 100 $\times$, which is shown in Fig 3.6b.

The fiber was pulled between the blades of microvise at 1 $\mu\text{m/s}$. The average interfacial shear strength τ , was determined using the equation below, assuming that the interfacial shear stress keeps constant along the fiber:

$$\tau = \frac{F}{\pi D l} \quad (3.1)$$

where F is the maximum pull out force, D is the fiber diameter, l is the embedded length, which is in a range of 40 – 60 μm . A total of 20 – 30 valid data were collected for each composite system in order to offset the scattering of measured results.

Figure 3.6 (a) Micro-tensile test machine for IFSS and (b) microscope for microbond test.

3.3.2 Interlaminar properties of CFRP laminates

3.3.2.1 Mode I interlaminar fracture toughness

The Mode I interlaminar fracture toughness of the samples was determined in accordance with the ASTM D5528-01. The dimension of composite laminates for DCB tests was 157.5 mm (length) $\times$ 25 mm (width) with the starter crack length of 57.5 mm. To prepare the samples for loading, the edges of the samples were coated with a thin layer of water-based correction fluid ahead of the insert, and vertical lines were drawn every 1 mm in order to aid the visualization of crack propagation. The double cantilever beam test was performed using Instron 5569 universal testing machine at crosshead speed of 2 mm/min. The testing sample is illustrated in Fig. 3.7a. The modified beam compliance theory was used to calculate Mode I interlaminar fracture toughness using the following equation:

$$G_{Ic} = \frac{3P_c \delta_c}{2B(a + \Delta)} \quad (3.2)$$

where G_{IC} is the Mode I interlaminar fracture toughness, P_c is the critical loading value, δ_c is the deflection value, B is the specimen width and a is the crack length, Δ is correction factor to account for rotation of the DCB arms. The correction factor is determined experimentally by generating a least squares plot of the cube root of compliance ($C^{1/3}$) as a function of delamination length, where C is δ_c / P_c .

The crack initiation value of $G_{IC(init)}$ is defined using the load and deflection measured at the point at which delamination is visually observed on the edge. As to the

Figure 3.7 Illustration of sample for: (a) mode I interlaminar fracture toughness test; (b) mode II interlaminar fracture toughness test; (c) interlaminar shear strength test.

propagation fracture toughness, G_{IC} usually increases firstly and then reaches a plateau. The crack propagation value $G_{IC(prop)}$ used here is the average of the plateau values.

3.3.2.2 Mode II interlaminar fracture toughness

The dimension of composite laminates for ENF tests was 70 mm (length) $\times$ 10 mm (width) with the starter crack length of 20 mm and the effective span of 60 mm. To determine the Mode II interlaminar fracture toughness (G_{IIC}) of samples, ENF test was performed using an Instron 5569 universal testing machine with crosshead speed of 2 mm/min at room temperature. The testing sample is illustrated in Fig. 3.7b. The Mode II interlaminar fracture toughness was determined for each specimen using the following equation [183]:

$$G_{IIC} = \frac{9a^2 P_c \delta_c}{2B(2L^3 + 3a^3)} \quad (3.3)$$

where a is the crack length, P_c is the critical loading value, δ_c is the specimen deflection value, B is the specimen width and L is half of the span length. Since in the ENF test, the crack growth is unstable, only crack initiation $G_{IIC(init)}$ values can be obtained.

3.3.2.3 Interlaminar shear strength

Interlaminar shear strength of the samples was determined in accordance with the ASTM D2344/D2344M–00 standard using three-point short beam shear test. Dimension of composite laminates for SBS tests was 18 mm (length) $\times$ 9 mm (width) in size. The test was performed using an Instron 5569 universal testing machine at a crosshead speed

of 2 mm/min. The testing sample is illustrated in Fig. 3.7c. The ILSS values were determined using the following equation:

$$ILSS = 0.75 \times \frac{P_m}{b \times h} \quad (3.4)$$

where P_m is the maximum load, b is the specimen width and h is the specimen thickness.

3.3.3 Mixed-mode interlaminar fracture toughness of CFRP-Ti laminates

The interlaminar fracture toughness of CFRP-Ti laminates was obtained through SCB tests. The specimen geometry is shown in Fig. 3.8. Nominal width was 25 mm and initial crack length (a_0) was 50 mm. The SCB specimen was clamped in a steel fixture at one end, leaving a minimum length of 55 mm available for crack growth. The edge of each specimen was covered with a thin layer of white correction fluid and marked at 1 mm increments from the tip of the starter. Specimens were tested at 2 mm/min on an Instron universal testing machine (model 5569).

The interfacial fracture energy from the SCB tests was evaluated as follows [184]:

$$G_c = \frac{P^2}{2B} \frac{dC}{da} \quad (3.5)$$

where P is the load, B is the width of specimen, C is the compliance and a is the crack length.

In addition, the specimen compliance can be expressed in the following form:

$$C = C_0 + ma^3 \quad (3.6)$$

Figure 3.8 Illustration of sample for single cantilever beam test.

where C_0 and m are experimentally determined constants. Then equation 3.5 can be expressed as follows:

$$G_c = \frac{3P^2ma^2}{2B} \quad (3.7)$$

G_c value was defined using the load and deflection measured at the point at which delamination is visually observed on the edge.

3.3.4 Lateral and axial compressive properties of CFRP-Ti risers

The compressive properties of the CFRP-Ti risers were obtained through different test methods: lateral and axial compression tests. To get the axial compressive strength of CFRP-Ti risers, the procedure of testing was in accordance with ASTM D 695-10, as shown in Fig. 3.9b. In the experiment, test specimens were cut from wound tubes with length of 25.4 mm. For the lateral compressive tests (at right angles to the longitudinal axis, as shown in Fig. 3.9a), the specimen size was the same, with the diameter becoming the height. A minimum of 5 specimens were tested at 1.3 mm/min on an Instron universal testing machine (model 5569).

For axial compression test, compressive strength was calculated by dividing the maximum compressive load carried by the specimen during the test by the original minimum cross sectional area of the specimen:

$$\sigma = P_{\max} / A \quad (3.9)$$

where σ is the average axial compressive strength, $P_{\max}$ is the maximum compressive load, A is the cross-sectional area,

$$A = \frac{\pi}{4}(OD^2 - ID^2) \quad (3.10)$$

and ID and OD are the average inner and outer diameters, respectively.

For lateral compression test, fracture is mostly like to occur at the contacting points of pipe and loading plates, where stress is the largest. The compression strength can be obtained from the curved beam theory if material is homogeneous. However, the CFRP-Ti pipe used here is composed of three different materials, and it is difficult to calculate the accurate stress at the contacting point. In this research, a rough calculation method is used, where average lateral compression strength is obtained by dividing the maximum load by the longitudinal cross-sectional area. The cross-sectional area is expressed as follows:

$$A = L \cdot (OD - ID) \quad (3.11)$$

and L is the length of specimen, ID and OD are the average inner and outer diameters, respectively.

The lateral pipe stiffness was tested according to ASTM D2412-11 using compression test. The specimen geometry is shown in Fig. 3.9a, and the difference from

lateral compression test is the specimen size and testing speed. In the experiments, test specimens were cut from wound tubes with length of 160 mm. A minimum of 3 specimens were tested at 12.5 mm/min on an Instron universal testing machine (model 5569). The value of pipe stiffness was obtained by dividing the force per unit length of specimen by the resulting deflection in the same units at the prescribed percentage deflection.

Calculate the pipe stiffness, PS, for any given deflections follows:

$$PS = (F / \Delta y)(1 + \Delta y / 2d)^3 \quad \text{kPa} \quad (3.12)$$

where F is the force per unit length, Δy is the measured change of the inside diameter in the direction of load, d is the average of the inside diameters.

Figure 3.9 Illustration of sample for: (a) lateral compression test/pipe stiffness test; (b) axial compression test (not to scale).

3.4 Materials characterizations

3.4.1 XPS and DMA

The chemical bond on the surface of carbon fiber was checked by XPS, which was conducted on an Axis Ultra spectrometer (Kratos Analytical) using a monochromated Al K α X-ray source (1486.7 eV) operating at 15 kV. The pressure in XPS sample analysis chamber was about 10^{-7} Pa during the recording of spectra. The glass transition temperature of epoxy matrix was verified by DMA, which was conducted on TADMA Q800 dynamic mechanical analyser in single cantilever mode. The multi-frequency strain test was run for each sample at amplitude of 15 μ m and frequency of 1 Hz. The temperature was recorded between 30 $^{\circ}$ C and 150 $^{\circ}$ C. From the measurements of DMA tests, the temperature at which the $\tan\delta$ curve shows a maximum peak is recorded as the glass transition temperature for the composites specimen.

3.4.2 SEM and Contact angle

The surface topography of carbon fibers was characterized using field emission scanning electron microscope (JEOL JSM 6700F) equipped with an EDX-S detector. EDX-S analysis was operated at 10 kV, and backscattered electron imaging was conducted at 5 kV. Four similar areas were selected for EDX-S analysis to get an average value. The contact angle between epoxy and titanium was measured with Kyowa contact-angle meter using epoxy droplet with volume of 4 μ L as the indicator, and photo interval was 0.2 s.

Chapter 4 Interfacial shear strength between surface treated carbon fiber and epoxy matrix under long-term moisture condition

4.1 Overview

In this chapter, a novel method to deliver MWCNTs into interphase was developed, which has following advantages: i) Much less CNTs are required; (ii) the incorporation procedure is easy to perform compared to dispersion of CNTs in epoxy resin; and (iii) the coating can be directly applied onto the as-received fibers. These merits provide the coating-modification method great potential to scale up from research laboratory to industrial manufacturing. MWCNTs were first dispersed in silane coupling agent, and then the solution was applied to the as-received carbon fiber wrapped with commercial sizing in order to form a nano-composite coating. Interfacial shear strength between carbon fiber and epoxy matrix was evaluated using microbond testing technique. The reinforcement mechanisms were analysed according to the characterization of surface morphology and chemical composition. A comparison of reinforcing efficiency of MWCNTs was performed between our method and conventional CNT-based modification of matrix. Then the carbon fibers with deposited droplets of epoxy resin have been immersed in de-ionized water and simulated seawater for about four months. The long-term effects of moisture on the interfacial shear strength of the CFRPs were also evaluated through single fiber microbond test. The mechanisms of property degradation were explored based on the SEM characterization of the fracture surfaces and

Table 4.1 Seven composite systems prepared for comparison.

Sample code	Description
CF/EP	Carbon fiber reinforced neat epoxy matrix
CF-SL/EP	Carbon fiber with silane coating and neat epoxy matrix
CF-SL-0.05%CNT/EP	Carbon fiber with silane coating containing 0.05 wt% MWCNTs and neat epoxy matrix
CF-SL-0.1%CNT/EP	Carbon fiber with silane coating containing 0.1 wt% MWCNTs and neat epoxy matrix
CF/EP-0.05%CNT	Carbon fiber without coating and epoxy matrix doped with 0.05 wt% MWCNTs
CF/EP-0.1%CNT	Carbon fiber without coating and epoxy matrix doped with 0.1 wt% MWCNTs
CF-SL/EP-0.1%CNT	Carbon fiber coated with silane coating and epoxy matrix doped with 0.1 wt% MWCNTs

XPS characterization of chemical composition of carbon fiber surface. In this work, seven composite systems were made for the comparison purpose, as listed in Table 4.1.

4.2 Surface morphology of carbon fibers and matrix

Fig. 4.1 shows the SEM micrographs of the carbon fibers with different treatments. It can be seen that the as-received carbon fiber has very smooth surface (Fig. 4.1a), whereas the surface of the silane coated carbon fiber looks rougher (Fig. 4.1b). Fig. 4.1c shows that a considerable number of CNTs uniformly distribute on the surface of carbon fiber with silane coating containing 0.05 wt% CNTs, whereas the CNTs are heavily entangled with each other on the surface of carbon fiber with silane coating

Figure 4.1 SEM images of the carbon fibers with (a) only commercial sizing; (b) silane coating; (c) silane + 0.05 wt% CNT coating; (d) silane + 0.1 wt% CNT coating.

containing 0.1 wt% CNTs (Fig. 4.1d). According to the SEM images, the thickness of silane coating is roughly estimated to be about tens of nanometers. Fig. 4.2 gives the SEM micrograph of the fracture surface of epoxy doped with 0.1 wt% CNTs, on which the well dispersed CNTs (embedded within the matrix) are clearly visible.

4.3 Microbond tests

Fig. 4.3 shows the typical load-displacement curves for four representative composite systems (CF/EP, CF-SL/EP, CF-SL-0.05%CNT/EP and CF/EP-0.1%CNT). The load increases in a quasi-linear manner with the displacement as soon as the blade of microvisc contacts the droplet, and drops immediately after the maximum value down to a much lower but non-zero level. Such kind of sharp peak followed by non-zero force

Figure 4.2 SEM image of fractured surface for epoxy containing 0.1 wt% CNTs. The CNTs are indicated by arrows.

Figure 4.3 Typical load-displacement curves for four representative composite systems.

reading indicates that the recorded data reflects the interfacial shear debonding between resin droplet and fiber [63]. Results of peak loads and embedded area of different samples prepared are presented in Fig. 4.4. The calculation of IFSS is via the ratio of peak load to embedded area with the assumption of uniform distribution of interfacial

Figure 4.4 Microbond measured peak loads and embedded area of: (a) CF/EP; (b) CF-SL/EP; (c) CF-SL-0.05%CNT/EP; (d) CF-SL-0.1%CNT/EP; (e) CF/EP-0.05%CNT; (f) CF/EP-0.1%CNT; (g) CF-SL/EP-0.1%CNT.

Table 4.2 Interfacial shear strength of the seven composite systems.

Sample code	Average IFSS ($\pm$ std err) [MPa]	Adj.R-Squar	Increase [%]
CF/EP	84.2 $\pm$ 2.5	0.978	bare
CF-SL/EP	97.3 $\pm$ 3.5	0.961	15.5%
CF-SL-0.05%CNT/EP	106.7 $\pm$ 3.2	0.981	26.7%
CF-SL-0.1%CNT/EP	96.9 $\pm$ 2.3	0.98	14.4%
CF/EP-0.05%CNT	88.0 $\pm$ 1.9	0.98	5.3%
CF/EP-0.1%CNT	89.9 $\pm$ 1.5	0.99	6.4%
CF-SL/EP-0.1%CNT	99.2 $\pm$ 4.16	0.98	17.8%

shear stress. Here, all the raw data of peak pull-out force is plotted against embedded area. Then a squares straight line whose slope gives the IFSS is obtained, and the coefficient of correlation is also provided.

Table 4.2 gives the statistics of measured IFSS for the seven composite systems. Both of the standard errors and coefficient of correlation are found to fall in a reasonable range for microbond test. It is clear that the application of silane coating leads to a marked improvement of interfacial shear strength. The IFSS of CF-SL/EP system increases about 15.5% compared with traditional CF/EP system. Modification of silane coating with 0.05% MWCNTs results in a further increase of 9.7%. However, the reinforcing effect of MWCNTs in epoxy matrix seems relatively weak. CF/EP-0.05%CNT system and CF/EP-0.1%CNT system only give an increase of 5.3% – 6.4%

Figure 4.5 SEM images of debonding region on carbon fibers after microbond test: (a) CF/EP system; (b) CF-Silane/EP system; (c) CF-Silane-0.05%CNT/EP system; (d) CF/EP-0.1%CNT system.

over CF/EP system. But when using the silane coated carbon fibers, CF-SL/EP-0.1%CNT system shows a remarkable increase of 17.8% compared with CF/EP system.

Fig. 4.5 shows the fracture regions of four representative composite systems after microbond test. The fracture surface of CF/EP system looks smooth and clean (Fig 4.5a), whereas the fracture surface of CF-SL/EP system looks rougher with some matrix debris attached (Fig. 4.5b). In Fig. 4.5c, CF-SL-0.05%CNT/EP system shows furry fracture surface covered by considerable CNTs. It can be seen that more matrix debris sticks on the fiber. As for CF/EP-0.1%CNT system (Fig. 4.5d), though pull-out of CNTs from matrix can be seen in the remained part of droplet, the fracture surface looks quite smooth,

Figure 4.6 Schematic illustration of reinforcing mechanisms in: (a) CF-SL-0.05%CNT/EP system; (b) CF/EP-0.1%CNT system; (c) CF-SL/EP-0.1%CNT system.

indicating a relatively weak interfacial bonding between the as-received carbon fiber and CNT-doped matrix.

4.4 Reinforcing mechanisms

Fig. 4.6 gives a schematic illustration of the fiber/matrix interface of three kinds of hybrid composite systems. At a microscopic scale, fiber/matrix interface is a layered interphase consisting of sizing, coating and part of matrix. It is noteworthy that the distinguished difference of microbond testing results among the seven composite systems implies that the shear debonding failure occurs along the interface between the silane coating and matrix or between the sizing and silane coating, not along the interface

between the sizing and carbon fiber or within the sizing. Therefore, the effective interphase in this work can be defined as the region including only the silane coating and epoxy matrix nearby, as indicated between the two dash lines in Fig. 4.6a and Fig. 4.6c, or the nano-composite matrix near the sizing/matrix interface (Fig. 4.6b). The possible reinforcing mechanisms, associated with the application of silane coating and incorporation of CNTs, can be analysed in two aspects: chemical reactions and mechanical interactions.

4.4.1 Chemical reactions

The contribution of silane coating is ascribed to the chemical bonding formed between carbon fiber (sizing) and epoxy matrix, as illustrated in Fig. 4.7, where R-NH₂ represents the amine hardener. Fig. 4.7a shows that the free silanol groups (Si-OH) from silane coating can react with the C-OH groups from the commercial sizing of carbon fiber, and form Si-O-C bond between coating and sizing. Additionally, some Si-OH groups react with each other to form polysilanol depositing in the silane coating. On the other side, a strong chemical linkage can be formed between silane coating and epoxy matrix in the presence of hardener, as shown in Fig. 4.7b.

Fig. 4.8 provides the evidences for the mechanisms mentioned above. It shows the “Carbon 1s” and “Silicon 2p” curves for the as-received carbon fiber before and after coating, which are further processed using an asymmetric Gaussian-Lorentzian sum function in a fitting program (XPSPEAK ver. 4.1). In Fig. 4.8a-b, four sub-curves associated with the functional groups of C-C, C-OH, C-O-C/Epoxy and C=O are de-

Figure 4.7 Formation mechanisms of the chemical bonding (a) between silane coating and sizing wrapped carbon fiber; (b) between silane coating and epoxy resin in presence of hardener.

convoluted, and the percentages of the four kinds of groups are listed in Table 4.3. It can be found that the percentage of C-O-C/Epoxide group on the surface of silane coated carbon fiber is 61.5% higher than that on the as-received carbon fiber. Those C-O-

C/Epoxy groups can participate in the curing reaction of epoxy resin (see Fig. 4.7b). The mechanisms illustrated in Fig. 4.7a get support from Figs. 4.8c-d. In Fig 4.8c, only one peak at binding energy of 103.3 eV corresponding to Si-O-Si bond is found on the surface of as-received carbon fiber [181]. However, two de-convoluted peaks at different binding energy in Fig. 4.7d indicate that there are two chemical states of Si on the surface of silane coated carbon fiber. Besides the peak at 103.1 eV, another peak at 101.6 eV associated with Si-O-C bond connecting sizing and silane coating can be observed [180]. It should be mentioned that in Fig. 4.8d the percentage of Si-O-C bond (21.1%) is much lower than that of Si-O-Si bond (78.9%). The reason could be related to the limited probing depth of XPS (~10 nm), which is less than the thickness of silane coating. Therefore only a small amount of Si-O-C bond can be detected in the area where the silane coating may be thin enough.

To verify the strength of Si-O-C bond, an additional test was conducted. The silane coating was directly cured on the surface of as-received carbon fiber without presence of epoxy, through the same curing process for resin droplet. Afterward, the coating was washed with ethanol in a bath sonicator under 280 W for 10 minutes. Fig. 4.9 shows the XPS survey spectra of the surfaces of as-received carbon fiber, un-washed and washed surface of silane coated carbon fiber. It is found that the washing process causes an insignificant decrease in Si percentage on the surface of silane coated carbon fiber, from 6.2% to 5.4 %. The remaining percentage of Si on the surface of silane coated carbon fiber after washing is still much higher than that on the surface of as-received carbon fiber (0.9%). Moreover, the XPS spectra of Si 2p on the washed silane coating (Fig. 4.10) show indiscernible change of Si-O-C peak (percentage of 20.2%) in

Table 4.3 Carbon 1s peak fitting results for carbon fibers with and without silane coating.

Fiber type	C-C (%) at 284.9eV	C-OH (%) at 285.6 eV	C-O-C/Epoxide (%) at 286.6eV	C=O (%) at 287.8eV
CF	61.99	9.61	26.15	2.25
CF-Silane	47.65	6.01	42.24	4.00

Figure 4.8 XPS spectra of C 1s on the surface of (a) as-received carbon fiber and (b) silane coated carbon fiber; XPS spectra of Si 2p on the surface of (c) as-received carbon fiber and (d) silane coated carbon fiber.

comparison with that on the un-washed coating (21.1%, Fig. 4.7d). The results provide indirect evidence that a strong chemical bond is formed between the silane coating and the commercial sizing on carbon fiber.

It can be observed according to the results of microbond tests that the silane coating acts as a leading role in the reinforcement of interphase compared to MWCNTs when they are dispersed in matrix. The CF-SL/EP system shows a more significant increase in IFSS (15.5%) than the two CF/EP-CNT systems with as-received carbon fibers (5.3 – 6.4%). Moreover, the replace of as-received carbon fiber with silane coated one in CF-SL/EP-0.1%CNT system leads to a remarkable further increase in IFSS (about 10.3%).

Figure 4.9 XPS survey spectra of as-received carbon fiber, un-washed and washed silane coated carbon fiber.

Figure 4.10 XPS spectra of Si 2p on the surface of silane-coated carbon fiber after washing.

4.4.2 Mechanical interactions

The reinforcing mechanisms introduced by CNTs can be elucidated from a mechanical point of view, as illustrated in Fig. 4.6. MWCNTs, when being incorporated into coating or matrix, can act as interlocking pins within the interphase and create higher friction between fiber and matrix [185, 186]. In addition, the MWCNTs were functionalized with silane, which improve the interactions between MWCNTs and epoxy resin in the interfacial region [187, 188]. This mechanism can ameliorate the stress transfer from matrix to fiber and lessen the stress concentration in the interphase. These fillers can also effectively suppress the formation and propagation of the micro-cracks in the interphase between fiber and matrix through pull-out and bridging effects [189-191], even though this effect may be minimized by the lying down shape of CNTs on carbon fibers. The collective consequence of these mechanisms manifests itself at macro-scale as the improved resistance to interfacial shear debonding.

As compared to the silane coating, which leads to more than 10% increase in IFSS, the role of CNTs incorporated into the matrix of hybrid composites is regarded secondary. CF/EP-0.05%CNT system and CF/EP-0.1%CNT system without silane coating give slight increases in IFSS (up to 6.4%). In CF-SL/EP-0.1%CNT system with silane coating, the addition of CNTs into matrix also results in trivial improvement of IFSS (about 1.9%) over CF-SL/EP system.

It is interesting that the CNTs, when dispersed in the silane coating, yield a further increase of 9.7% in IFSS. According to the mechanisms displayed in Fig. 4.6, use of nano-composite coating can be considered in principle as a method essentially equivalent to use of nano-composite matrix for the reinforcement of interphase. Both of the two methods attempt to introduce hard nano-fillers into the interphase and improve its mechanical properties. Therefore, a question emerges: what makes the reinforcing effects of the two methods so different? Namely, why the IFSS of CF-SL-0.05%CNT/EP system is higher than that of CF-SL/EP-0.1%CNT system?

Figure 4.11 Illustration of forming process of nano-composite coating: (a) before and (b) after removal of the solvent.

The discrepancy can be explained by analysing the coating process. Fig. 4.11 illustrates the forming process of nano-composite coating. In Fig. 4.11a, when the fiber is soaked in the MWCNT-doped silane coupling agent, the volume fraction of MWCNTs V_{CNT} in solution can be calculated according to

$$V_{CNT} = [1 + \frac{\rho_{CNT}}{\rho_{mat}} (\frac{1}{W_{CNT}} - 1)]^{-1} \quad (4.1)$$

where ρ_{CNT} is the density of MWCNTs, ρ_{mat} is density of solvent or matrix, and W_{CNT} is the weight fraction of MWCNTs. The density of MWCNT, epoxy matrix, and silane coupling agent solution are 1.5 g/cm³, 1.09 g/cm³ and 0.812 g/cm³, respectively. Thus V_{CNT} of CF/EP-0.1%CNT system is 0.073 vol%, and V_{CNT} of CF-SL-0.05%CNT/EP system is supposed to be 0.027 vol%. However, during the drying process, most of volatile solvent has gone, which results in a considerable reduction in the volume of formed coating. This process is accompanied with the densification of the embedded CNT forest. As a consequence, the volume fraction of MWCNTs within the interphase of CF-SL-0.05%CNT/EP system can reach a much higher value than 0.027 vol% calculated using Equation 4.1, even though some CNTs may drop off (Fig. 4.11b). To verify this mechanism and estimate the real volume fraction of MWCNTs within the silane coating, the silane coupling agent solution containing 0.05 wt% CNTs was dropped on a glass slide, followed by natural dry, as shown in Fig. 4.12. The weight percentage of CNTs within the dried silane coating W'_{CNT} can be calculated by

$$W'_{CNT} = \frac{W_{CNT}m_1}{m_2} \quad (4.2)$$

where W_{CNT} represents the weight percentage of CNTs in the solution, m_1 and m_2 are the weight of solution before and after removal of solvent. Substituting the measured data, $W_{CNT} = 0.05$ wt%, $m_1 = 1.327 \times 10^{-1}$ g, $m_2 = 2.951 \times 10^{-3}$ g, into equation 4.2, the weight percentage of CNTs in the dried silane coating is about 2.25 wt%. Notice that the CNTs are not fully embedded in the coating but grafted on it (see Figs. 4.4c-d) and assume that the embedded length of CNTs in the silane coating is about 80%, taking the density of pure (3-glycidyloxypropyl) trimethoxysilane coupling agent (1.07 g/cm^3 , very close to that of epoxy resin), the real volume fraction of MWCNTs in the interphase of CF-SL-0.05%CNT/EP system (see Fig. 4.6a) can be estimated to be 1.29 vol% using equation 4.3, which is about 18 times as high as the volume fraction of CNTs in the interphase of CF/EP-0.1%CNT system (Fig. 4.6b) and that in the nano-composite area of interphase in CF-SL/EP-0.1%CNT system (Fig. 4.6c). It means there are much more CNTs in the interphase of CF-SL-0.05%CNT/EP system than that of CF-SL/EP-0.1%CNT system. Such a difference can also be observed in Fig. 4.1c and Fig. 4.2. This factor augments the reinforcing effect of MWCNTs to a level comparable to the chemical bonding introduced by silane coating. In the case of CF-SL-0.1%CNT/EP system, the volume fraction of CNTs in the dried coating may be too high (~ 2.59 vol%) to cause the issues of CNTs agglomeration and insufficient resin impregnation, which diminish the reinforcing effect of CNTs.

Figure 4.12 Silane coating on a glass slide: (a) before and (b) after removal of the solvent.

4.5 Moisture treatment on single fiber composites

The surface treatment with silane coupling agent and carbon nanotubes on carbon fibers is proven to enhance the interfacial bonding between the fibers and epoxy matrix efficiently. Microbond specimens and pure epoxy plates were immersed in de-ionized water and simulated seawater for up to 120 days at ambient temperature. The epoxy plates were taken out and weighed periodically to estimate the water absorption of epoxy matrix. Moisture content was calculated using the following equation

$$M_t = \frac{W_w - W_d}{W_d} \times 100\% \quad (4.3)$$

where M_t is the percentage of gained moisture, W_w and W_d represent the weights of the wet sample and the dry sample, respectively.

Because CF-SL-0.05%CNT/EP shows the best performance from previous tests, 0.05% is chosen as the default concentration of CNTs in silane coating for the following

experiments. Three composite systems with different surface treatments are compared, and two moisture conditions are imposed to those composites, as listed in Table 4.4.

Fig. 4.13 shows the SEM micrographs of the carbon fibers with different treatments immersed in the two water systems. It can be seen that surfaces of as-received carbon fibers are very smooth regardless of immersion (see Figs. 4.13a-c). In Fig. 4.13c some salt from seawater deposited on the fiber surface is clearly visible. Figs. 4.13d-f show much rougher fiber surface of silane treated carbon fibers. After soaking in the two kinds of water, silane coating becomes thicker due to diffusion of water. Salt deposit is also found on the fiber immersed in simulated seawater (Fig. 4.13f). Figs. 4.13g-i show the morphology before and after immersion of the carbon fibers treated with MWCNT-

Table 4.4 Sample codes for the composite systems with two kinds of fiber surface treatment method and immersed in the two water environments.

Sample code	Fiber surface treatment	Water
CF-DIW	Non-treated	De-ionized water
SL-CF-DIW	Silane treated original CF	De-ionized water
CNT/SL-CF-DIW	CNTs modified silane treated original CF	De-ionized water
CF-SW	Non-treated	Seawater
SL-CF-SW	Silane treated original CF	Seawater
CNT/SL-CF-SW	CNTs modified silane treated original CF	Seawater

Figure 4.13 SEM images of carbon fibers immersed in de-ionized water and seawater for different time: (a) CF@0 day; (b) CF-DIW@120 days; (c) CF-SW@120 days; (d) SL-CF@0 day; (e) SL-CF-DIW@120 days; (f) SL-CF-SW@120 days; (g) CNT/SL-CF@0 day; (h) CNT/SL-CF-DIW@120 days; (i) CNT/SL-CF-SW@120 days. (Scale bar: 1 μm)

doped silane coating. CNTs are found well dispersed on the carbon fiber surface even after immersed into de-ionized and simulated seawater for 120 days. Figs. 4.14a-c compare the surface morphology of epoxy droplets before and after immersing in the two water systems. In contrast to the dry sample, which looks smooth and clean (see Fig. 4.14a), the resin droplet steeped in de-ionized water shows wrinkled surface (Fig. 4.14b), whereas the resin droplet steeped in simulated seawater seems still smooth and partially covered by salt coating, as shown in Fig. 4.14c.

Figure 4.14 SEM images of the epoxy droplets in the conditions of: (a) dry; (b) immersion in de-ionized water for 120 days; (c) immersion in simulated seawater for 120 days. (Scale bar: 10 μm)

4.6 Moisture absorption

Figure 4.15 Relative moisture gain of pure epoxy plates immersed in the de-ionized water and simulated seawater as a function of days.

Fig. 4.15 displays the relative moisture gain of pure epoxy plates, plotted against days of immersion. It can be seen that the relative mass gain in the two water systems increase in a non-linear manner with immersion time, and reach 1.90% and 1.69% respectively after 120 days immersion. It can be observed that the speed of moisture absorption slows down gradually. And the moisture absorption of epoxy immersed in de-ionized water is found more efficient than that in simulated seawater. The possible reason may be related to the ions in seawater, which are not easy to be absorbed by epoxy [29, 192]. As a consequence, they are more likely to accumulate on the surface of epoxy and form a barrier which prevents the further diffusion of seawater into epoxy. When the salt concentration inside the epoxy is lower than that in seawater, water absorption will be suppressed by the induced osmotic pressure. Furthermore, according to Fig. 4.15 the specimens in the two water systems do not reach saturation state within 120 days.

4.7 Microbond test

Fig. 4.16 gives the measured interfacial shear strengths for the three composite systems during the immersion test in de-ionized water and simulated seawater. The application of silane coating onto carbon fibers leads to an increase of 14.5% in IFSS of composites in dry air, from 83.8 MPa to 96.0 MPa. This improvement is ascribed to a strong chemical linkage formed between silane coating and epoxy matrix during curing process on one side. On the other side, the free silanol groups (Si-OH) of silane can react with the C-OH groups on the original sizing of carbon fibers and form Si-O-C linkage between silane coating and commercial sizing on fiber surface [193]. When MWCNTs are incorporated into the interphase, the IFSS is increased 11.7% further over that of SL-CF. The additional improvement is attributed to the increased friction along interface and the restrained micro-cracks propagation caused by CNTs.

It can be observed in Fig. 4.16 that the IFSS of all the three composite systems decreases with time during the immersion test. The IFSS-time curve shows a relatively steeper drop within the first 20 days, and then gradually reaches a stable level. This tendency is roughly consistent with the evolution of water absorption rate in Fig. 4.15. Fig. 4.17 shows the debonding regions of the three composite systems after microbond test. Before immersion tests, the fracture surface of CF system is clean and smooth, as shown in Fig. 4.17a. In contrast, the fracture surface of SL-CF system is rougher and some matrix debris sticking on the fiber surface (see Fig. 4.17d). For the CNT/SL-CF system, besides epoxy, some CNTs can also be found remaining on the fractured surfaces of carbon fibers (Fig. 4.17g). After the immersion test in de-ionized water for 120 days, the remaining parts of resin droplets become rougher with some micro-cracks. Their

Figure 4.16 Interfacial shear strength of CF, SL-CF and CNT/SL-CF based composites during the immersion tests in: (a) de-ionized water; (b) simulated seawater.

fracture manifests itself a flaking-off manner, as shown in Figs. 4.17b, e and h. The surface of remaining parts of resin droplets after 120-day immersion test in seawater (Figs. 4.17c, f and i) looks similar to those immersed in de-ionized water. The fracture manner of resin droplet does not change markedly in comparison to the case in de-ionized

Figure 4.17 SEM images of debonding region of specimens immersed in de-ionized water and seawater for different time: (a) CF@0 day; (b) CF-DIW@120 days; (c) CF-SW@120 days; (d) SL-CF@0 day; (e) SL-CF-DIW@120 days; (f) SL-CF-SW@120 days; (g) CNT/SL-CF@0 day; (h) CNT/SL-CF-DIW@120 days; (i) CNT/SL-CF-SW@120 days. (Magnified pictures of white rectangle area are shown at the top right corner, scale bar: 1 μm).

water. But quite a few salt particles as well as micro-flaws, such as holes and cracks, appear in the fracture region, as a consequence of seawater attack. It can be seen in Fig. 4.17 that after immersion test the debonding surface become much smoother than that

before immersion, indicating a significantly reduced interfacial bonding between carbon fiber and epoxy matrix.

The negative effects of moisture on the IFSS of composites are associated with multiple factors: 1) water molecule may weaken the interfacial bonding between carbon fiber and epoxy matrix by forming hydrogen bonds with epoxy matrix and carbon fibers, resulting in the plasticization of epoxy and deteriorated physical connection in the interphase [160]. 2) the volumetric expansion of epoxy during the immersion tests are much higher than that of carbon fiber, which may generate additional localized stress (swelling stress) along interface and reduce its resistance to shear [160]. However, the silane coating, especially the CNTs modified silane coating, as an interlayer between carbon fiber and epoxy matrix, can relieve the generated moisture stresses. On the other hand, the swelling stress of epoxy may offset the thermal stress in the interphase generated during the cooling process from curing temperature to room temperature [194, 195]. This mechanism may interpret that the three composite systems demonstrate better maintenance of IFSS in de-ionized water than in simulated seawater during the first 20 days (see Fig. 4.15). 3) the hydrolysis of chemical bonding could be formed in the interphase. When silane coupling agent is used to treat carbon fibers, the formed chemical bonding hydrolyzes and causes the long term IFSS degradations [196]. The silane coupling agent used to treat carbon fibers, acts as an interlayer, can relieve the generated residual stresses between carbon fiber and epoxy matrix. What's more, the formed chemical bonds formed in the interphase replace the previous hydrogen bonds between carbon fiber and epoxy matrix, and prevent water from weakening the interfacial properties in a more efficient way than CF. However, after a long term moisture attack,

water gets into interphase and hydrolysis of chemical bonding starts to occur. Siloxane linkage can be hydrolyzed to Si-OH until a new equilibrium is reached with the condensation of silanols [197, 198], and Si-O-C bonds between silane coupling agent and carbon fibers may also be hydrolyzed to generate Si-OH and C-OH. As a result, IFSS keeps decreasing during the long term immersion in the two water systems. However, the bonding strength of SL-CF is still higher than that of CF due to the existence of chemical bonds, even though they are partially broken. It is noteworthy that the epoxy-functional coupling agent shows superior hygrothermal resistance compared with other kinds of coupling agent, such as amino-functional coupling agent. According to the work by Choi et al. [199], the durability of epoxy-functional coupling agent treated epoxy-concrete composite is considerably superior to non-treated composite, while the amino-functional coupling agent treatment showed no positive effect during hygrothermal exposure. Furthermore, the CNTs incorporated into the silane coatings can ameliorate the stress transfer from matrix to fiber and lessen the stress concentration in the interphase [193]. It may lead to a more even distribution of internal stress. In addition, chemical reactions between the functionalized CNTs and epoxy groups can also prevent interfacial properties decreasing in moisture environment.

Table 4.5 lists the IFSS values determined at the 0th, the 20th, and the 120th day. The IFSS of SL-CF-DIW system remains 14.8% improvement at the 20th day and 12.3% at the 120th day compared with CF-DIW system. For CNT/SL-CF-DIW system, the maintained improvement in IFSS are 23.0% (at the 20th day) and 21.6% (at the 120th day), respectively. In simulated seawater, SL-CF system remains the enhancement in IFSS of 10.7% at the 20th day and 11.9% at the 120th day. For CNT/SL-CF system, the

maintained enhancements are 18.3% and 20.7% during the immersion test. The results indicate that though IFSS decreases with immersion time, the surface treatments do not aggravate deterioration of interfacial properties in both water systems. It is noteworthy that all of the three composite systems maintain more interfacial shear strength in de-ionized water than in simulated seawater in the early stage of immersion tests, though the water gain of epoxy in de-ionized water is faster than that in simulated seawater. Nevertheless, the difference becomes less and less with immersion time, and finally disappears after 100 day, which may imply that salt ions in seawater do not have additional long-term influence on the interfacial bonding of CFRP. The reason that salt ions play little role in influencing the final performance of CFRPs may be due to the neutral nature and good corrosion properties of CFRPs. For the long-term moisture treatment, the decrease of IFSS is most determined by the chemical degradation, rather than the mechanical degradation such as release of moisture stress and plasticization of matrix. However, there is no evidence showing that the salt ions are involved into the chemical deduction process. Similar phenomenon is also observed by other researchers [200-202]. Liao et al. [200] found that salt concentration did not seem to affect flexural properties of E-glass fiber reinforced vinylester matrix composite in a noticeable way. Grant et al. [201] compared transverse tensile properties of three graphite/epoxy composite materials and found little difference in the behaviour of those composites immersed in distilled water and in seawater. In the study reported by Davies et al. [202], the glass reinforced composites showed the almost same shear strength after immersion in different water systems.

Table 4.5 Interfacial shear strength of the three composite systems during the immersion tests.

Sample code	IFSS (MPa)		
	0 day	20 days	120 days
CF-DIW	83.8±11.0	76.5±7.8	73.1±10.3
SL-CF-DIW	96.0±17.8 (14.6%)	87.8±14.6 (14.8%)	82.1±14.5 (12.3%)
CNT/SL-CF-DIW	105.9±12.4 (26.4%)	94.1±16.8 (23.0%)	88.9±8.9 (21.6%)
CF-SW	83.8±11.0	75.9±16.2	73.1±12.1
SL-CF-SW	96.0±17.8 (14.6%)	84.0±12.6 (10.7%)	81.8±15.6 (11.9%)
CNT/SL-CF-SW	105.9±12.4 (26.4%)	89.8±10.8 (18.3%)	88.2±10.5 (20.7%)

Note: Values in parentheses are increased percentages using CF-DIW and CF-SW samples as benchmarks.

4.8 Summary

MWCNTs have been incorporated through two routes to build hybrid CFRP composites. It was found that both of the two hybrid composites show improved interfacial bonding compared with the common CFRP. An increase of 26.7% in IFSS was achieved by incorporating 0.05 wt% MWCNTs into silane coating on the surface of carbon fiber, whereas an 17.8% increase in IFSS was obtained by dispersing 0.1 wt% MWCNTs into epoxy matrix when using the neat silane coated carbon fiber. The analysis reveals that there are two reinforcing mechanisms working simultaneously in the hybrid composites. The chemical bonding introduced by silane coupling agent is regarded as a predominant role in enhancing the interphase. The formed silane coating provides a strong connection between the as-received carbon fiber and epoxy matrix, leading to an

increase of about 15.5% in IFSS. The secondary role of CNTs in reinforcement when they are dispersed in the matrix of hybrid composites can be promoted to the primary one by incorporating CNTs into the silane coating, yielding a further increase of 9.7% in IFSS. This change of reinforcing effect is attributed to the densification of CNTs forest grafted on fiber surface during the forming of nano-composite coating, which augment the effects of crack-bridging and interface-interlocking. Therefore, although the coating-modification method is equivalent in principle to matrix-tuning method for enhancement of the interphase between fiber and matrix, the former can achieve much higher volume fraction of CNTs in the interphase, which is usually hard to fulfill in the latter without issues of CNTs agglomeration and resin impregnation. Furthermore, coating-modification method takes advantages of cost saving, considering that i) much less CNTs are required; ii) the incorporation procedure is easy to perform compared to dispersion of CNTs in epoxy resin; and iii) the coating can be directly applied onto the as-received fibers. These merits provide the coating-modification method great potential to scale up from research laboratory to industrial manufacturing.

The interfacial bonding between the surface treated carbon fibers and epoxy matrix has been studied in the conditions imitating freshwater and marine environments. The application of silane coating led to an increase of around 15% and 12% in interfacial shear strength, before and after a 120-day immersion tests respectively. When MWCNTs were introduced into silane coating, around 12% and 8% further improvements respectively were observed before and after the immersion tests. Although the deterioration of interfacial shear strength in different composites showed a similar trend during the immersion test, the composites using the carbon fibers with silane

coating, and MWCNT-doped silane coating continuously maintained the improvement of interfacial shear strength compared to the composite using the as-received carbon fibers throughout the whole experiment. Furthermore, it was found that for each composite system, the interfacial shear strength gradually decreased to same level after 120-day immersion in de-ionized water and simulated seawater. Therefore, from a long-term point of view, one can expect that the effects of moisture in a marine environment on the degradation of interfacial bonding of CFRPs are similar to that in a freshwater environment.

Chapter 5 Interlaminar properties of surface-treated CFRPs under long-term hygrothermal conditions

5.1 Overview

A well-defined and characterised silane coupling agent together with multiwalled carbon nanotubes treating method was used to modify carbon fiber surfaces as described above. In this chapter, carbon/epoxy laminates were fabricated using vacuum assisted resin transfer moulding method and then placed under hygrothermal environment. Mode I and Mode II interlaminar fracture toughness and ILSS were obtained by DCB, ENF and SBS tests, respectively. The reinforcement mechanisms were analysed according to the characterization of fractured surface morphology and glass transition temperature variation. For easier discussion, the as received, silane coupling agent treated and 0.05 wt% CNTs modified silane treated composites are defined as CF, SL-CF and CNT/SL-CF.

5.2 Moisture conditioning

The effect of moisture absorption on the mechanical properties of each treated composite was observed by submerging each type of composite specimen in tap water held at 80 °C in a PolyScience 8305 circulating water bath for intervals of 10, 20, 30 and 60 days. At these pre-determined times, the specimens were removed from the bath, surface-dried to allow stable weights could be obtained. The weights were recorded using an electronic balance with a precision of ± 0.005 mg, and the weight gain was evaluated as a percentage of the original composite specimen weight.

5.3 DMA tests

Dynamic Mechanical Analysis was employed to determine the glass transition temperatures of the samples by assessment of $\tan \delta$ vs. temperature curve peak, as shown in Fig. 5.1. The glass transition temperatures of all three different treated composites are shown to decrease with increasing exposure time, implying that the polymeric matrices of composites are less likely to maintain their shape and strength after prolonged submersion in water as suggested by Odegard and Bandyopadhyay [203]. In fact, the absorbed water acts as an internal lubricant in the epoxy matrix, which decreases the energy barrier for chain segment movements of polymer [204, 205]. In addition, small amounts of water can destroy the hydrogen bonds in epoxy matrix and cause decreases of T_g [29, 206]. Another phenomenon is that the results of each kind of composite are quite similar.

Figure 5.1 Glass transition temperatures of different CFRP composites immersed in water for certain days.

5.4 Mode I interlaminar fracture toughness

Mode I fracture toughness was evaluated using equation 3.2 at each water exposure interval. Table 5.1 shows the dimensions of sample used for DCB tests. Fig. 5.2a shows typical load-displacement curves for three composites systems (CF, SL-CF, CNT/SL-CF). Fig. 5.3 shows typical R-curves of these three composites systems. The G_{IC} values of crack initiation and propagation for each treatment type are shown in Figs. 5.2c and d. The $G_{IC(init)}$ value shows an increase of 22.4% when carbon fibers are treated with silane, and the improvement becomes 35.4% when CNTs are incorporated into silane coating. After a 60 days hygrothermal treatment, the $G_{IC(init)}$ of the SL-CF and CNT/SL-CF specimens still show a 17.8% and 33% increase when being compared with the non-treated ones. There is no values for $G_{IC(init)}$ after 30 days treatment for CNT/SL-CF treated specimens, which is attributed to the sample preparation errors. The increase of $G_{IC(init)}$ for silane treated CFRP composites is mainly due to the increased bonding strength between fiber surface and epoxy matrix. Silane coating can react with original sizing on carbon fibers on one side and form chemical bonding with epoxy matrix on the other side [193]. The CNT/SL-CF samples provide the highest $G_{IC(init)}$ and maintain high fracture toughness even after lengthy exposure to moisture. When CNTs are incorporated, the thin layer of nanotube at the interface offers an opportunity for direct interaction both with epoxy matrix and carbon fiber when functional groups are available. Such interaction will directly affect the interphase formulation of composites, and improve fracture toughness by CNTs bridging or CNTs pull-out [189, 193]. In addition, the CNTs act as interlocking pins and could increase the friction at interphase area. The high stiffness CNTs can also ameliorate stress concentration and help stress transfer from matrix to fibers.

Table 5.1 Samples' widths of the three composite systems for DCB tests.

Samples (0 day)	Width (mm)	Samples (10 days)	Width (mm)	Samples (20 days)	Width (mm)	Samples (30 days)	Width (mm)	Samples (60 days)	Width (mm)
CF-1	25.42	CF-5	25.12	CF-9	25.64	CF-13	25.50	CF-17	25.37
CF-2	25.18	CF-6	25.34	CF-10	25.33	CF-14	25.23	CF-18	25.50
CF-3	25.22	CF-7	27.56	CF-11	25.28	CF-15	25.11	CF-19	25.27
CF-4	25.49	CF-8	25.33	CF-12	25.76	CF-16	25.15	CF-20	25.32
SL-CF-1	25.14	SL-CF-5	25.16	SL-CF-9	24.95	SL-CF-13	25.29	SL-CF-17	25.06
SL-CF-2	25.27	SL-CF-6	24.43	SL-CF-10	25.25	SL-CF-14	25.20	SL-CF-18	25.18
SL-CF-3	25.24	SL-CF-7	24.97	SL-CF-11	25.15	SL-CF-15	24.91	SL-CF-19	25.13
SL-CF-4	25.17	SL-CF-8	25.20	SL-CF-12	24.56	SL-CF-16	24.94	SL-CF-20	25.13
CNT/SL-CF-1	24.57	CNT/SL-CF-5	24.78	CNT/SL-CF-9	24.78	CNT/SL-CF-13	24.90	CNT/SL-CF-17	24.65
CNT/SL-CF-2	24.18	CNT/SL-CF-6	24.82	CNT/SL-CF-10	24.91	CNT/SL-CF-14	24.78	CNT/SL-CF-18	24.93
CNT/SL-CF-3	24.10	CNT/SL-CF-7	24.62	CNT/SL-CF-11	24.57	CNT/SL-CF-15	24.56	CNT/SL-CF-19	24.73
CNT/SL-CF-4	24.80	CNT/SL-CF-8	24.64	CNT/SL-CF-12	24.71	CNT/SL-CF-16	24.78	CNT/SL-CF-20	24.20

It can be observed in Fig. 5.2c that the $G_{IC(init)}$ of all the three composite systems decreases with time during the immersion test. The decrease is obvious within the first 10 days, and then the decreasing speed slows down. After 60 days immersion, the $G_{IC(init)}$ of CF, SL-CF and CNT/SL-CF decreases 20.2%, 23.2% and 21.6%, respectively. It should be noted that this $G_{IC(init)}$ is still higher than the dry CF specimens by 6.2%.

SEM micrographs of the fractured surfaces of carbon fibers under different treatments are shown in Fig. 5.3. It can be seen that the CF samples have very smooth surface (Fig. 5.3a), while both the SL-CF and CNT/SL-CF samples show much rougher surfaces (Fig. 5.3c) and (Figs. 5.3e and g), respectively. The smooth surface of the CF samples implies that at the point of failure, matrix is broken away from fibers due to poor adhesion. The addition of both silane and CNTs could improve the adhesive properties, and so a considerable amount of matrix remains intact after delamination. This results in higher fracture toughness values as a greater load is required to break the interfacial bonds for these samples. After 60 days exposure, the resin in the CF samples (Fig. 5.3b) and SL-CF samples (Fig. 5.3d) can be seen to have broken away and the CNT/ SL-CF samples (Figs. 5.3f and h) also show weaker bonding between the matrix and fibers when being compared with dry samples, giving a smoother appearance in the SEM micrograph. So it can be confirmed that the presence of water aids in the deterioration of composites' interfacial properties.

Fig. 5.2d shows the values of $G_{IC(prop)}$. The carbon fiber surface treatment by MWCNTs modified silane coating decreases the crack propagation fracture toughness $G_{IC(prop)}$ significantly, and hygrothermal effects on this kind of specimen are not obvious. However, under hygrothermal environment, $G_{IC(prop)}$ of the other two types of composites all increases firstly and then decreases. The crack propagation resistance $G_{IC(prop)}$ is highly influenced by the bridging effect of individual carbon fibers [207]. For the non-treated carbon fibers, they are separated heavily after DCB tests, which means fiber bridging effects happen easily (Figs. 5.3a and b). Surface modification using silane and MWCNTs reduces the effect of fiber-bridging and causes the dramatic decrease of crack

Figure 5.2 (a) Typical load-displacement curves of Mode I interlaminar fracture toughness test; (b) typical R-curves of Mode I interlaminar fracture toughness test; (c) $G_{IC(init)}$ of different CFRP composites immersed in water for certain days; (d) $G_{IC(prop)}$ of different CFRP composites immersed in water for certain days.

propagation toughness. When MWCNTs modified silane coating is applied onto the carbon fibers, the fibers are prone to be bundled together, and the bonding strength between carbon fibers and epoxy matrix improves drastically. As a result, the fibers are hard to be separated from each other (Figs. 5.3e and f), which makes fiber bridging difficult. Only silane treatment can also improve the bonding strength to some extent but not as obvious as silane plus MWCNTs treatment. So, the $G_{IC(prop)}$ value is in between the other two kinds of specimens. Under hygrothermal environment, $G_{IC(prop)}$ of CF and SL-CF specimens all increases firstly and then decreases. The CF specimens reached the paramount point faster because of their poor interfacial bonding strength. Water is easy to

Figure 5.3 SEM images of fractured surfaces of composites conditioned in water after DCB tests: (a) CF specimens before immersion; (b) CF specimens immersed for 120 days; (c) SL-CF specimens before immersion; (d) SL-CF specimens immersed for 120 days; (e) CNT/SL-CF specimens before immersion; (f) CNT/SL-CF specimens immersed for 120 days; (g) CNT/SL-CF specimens before immersion (high magnification); (h) CNT/SL-CF specimens immersed for 120 days (high magnification).

penetrate into the composites from the interface and exacerbate the bridging effect. However, too much absorbed water can also weaken the interfacial bonding strength, which may offset the bridging effect. As a result, the $G_{IC(prop)}$ decreases after certain time of immersion into water. As to the SL-CF specimens, chemical bonds generated from surface treatment may ameliorate the negative effect of water on interfacial properties and weaken the bridging effect. So the highest values of $G_{IC(prop)}$ are smaller and reached more slowly. When CNTs are incorporated into silane coating, the existence of CNTs improves the interfacial bonding between carbon fiber and epoxy matrix heavily. As a result, fibers are still bonding together even after 60 days hygrothermal treatment (as shown in Figs. 5.3e and f), and fiber bridging effects don't take place.

5.5 Mode II interlaminar fracture toughness

The mode II fracture toughness was evaluated using equation 3.3, and Table 5.2 shows the dimensions of samples used for ENF tests. Fig. 5.4a shows typical load-displacement curves for three composite systems (CF, SL-CF, CNT/SL-CF). The average values of $G_{IIC(init)}$ for each treatment and water exposure interval are shown in Fig. 5.4b. There is a clear improvement in the mode II fracture toughness of the SL-CF and CNT/SL-CF samples over CF. Before hygrothermal treatment, $G_{IIC(init)}$ of the SL-CF samples shows an improvement of 10.8% over the CF samples, whereas the $G_{IIC(init)}$ of the CNT/SL-CF samples is higher than the SL-CF samples by 19.9%. After 60 days immersion, the surface treatments still have positive effects on mode II fracture toughness. The $G_{IIC(init)}$ of SL-CF and CNT/SL-CF are higher than CF specimens by 23.7% and 40.5% respectively. What's more, After being exposed in water for 60 days, the CNT/SL-CF samples still show higher $G_{IIC(init)}$ even when compared with dried CF

samples. The decreasing trend is also very obvious. From Fig. 5.4b, it can be seen that the $G_{IIC(init)}$ decrease 28.3%, 19.9% and 24.1% for samples CF, SL-CF and CNT/SL-CF respectively after hygrothermal treatment for 60 days. The results indicate that though the $G_{IIC(init)}$ decreases with immersion time, the surface treatments do not aggravate deterioration of interfacial properties in hygrothermal environment.

The fractured surfaces after ENF tests are shown in Fig. 5.5. It can be seen that, before hygrothermal treatments, the CF samples have relative smooth surface (Fig. 5.5a), while the other two kinds of samples show much rougher surfaces (Figs. 5.5c, e and g). After being immersed into hot water, the fractured surfaces of three types of composites all become smoother than before (Figs. 5.5b, d, f and h), which implies that hygrothermal treatments have negative effects on the interfacial bonding of CFRPs. In Figs. 5.5g and h, CNTs can be clearly observed well dispersed on the surface of carbon fiber; the matrix has been peeled away from the fiber but the process is somewhat resisted by the CNTs. These results imply the bonding strength is improved after surface treatments. These images help to explain the interfacial interactions between fiber and CNTs despite the

Figure 5.4 (a) Typical load-displacement curves of Mode II interlaminar fracture toughness test; (b) $G_{IIC(init)}$ of different CFRP composites immersed in water for certain days.

Table 5.2 Samples' widths of the three composite systems for ENF tests.

Samples (0 day)	Width (mm)	Samples (10 days)	Width (mm)	Samples (20 days)	Width (mm)	Samples (30 days)	Width (mm)	Samples (60 days)	Width (mm)
CF-1	10.14	CF-9	10.31	CF-17	10.06	CF-25	10.29	CF-33	10.42
CF-2	10.07	CF-10	10.21	CF-18	10.31	CF-26	10.35	CF-34	10.40
CF-3	10.10	CF-11	10.07	CF-19	10.41	CF-27	10.30	CF-35	10.29
CF-4	10.13	CF-12	10.10	CF-20	10.42	CF-28	10.28	CF-36	10.46
CF-5	10.19	CF-13	10.27	CF-21	10.48	CF-29	10.28	CF-37	10.41
CF-6	10.02	CF-14	10.07	CF-22	10.23	CF-30	10.07	CF-38	10.34
CF-7	10.04	CF-15	9.98	CF-23	10.34	CF-31	10.53	CF-39	10.56
CF-8	10.14	CF-16	9.97	CF-24	10.35	CF-32	10.29	CF-40	10.24
SL-CF-1	9.90	SL-CF-9	10.16	SL-CF-17	9.99	SL-CF-25	10.13	SL-CF-33	9.79
SL-CF-2	9.88	SL-CF-10	9.76	SL-CF-18	9.95	SL-CF-26	10.23	SL-CF-34	9.75
SL-CF-3	9.94	SL-CF-11	10.13	SL-CF-19	10.16	SL-CF-27	10.13	SL-CF-35	10.28
SL-CF-4	9.89	SL-CF-12	10.10	SL-CF-20	9.90	SL-CF-28	10.12	SL-CF-36	10.32
SL-CF-5	9.94	SL-CF-13	10.09	SL-CF-21	10.19	SL-CF-29	10.12	SL-CF-37	9.96
SL-CF-6	9.86	SL-CF-14	9.87	SL-CF-22	10.15	SL-CF-30	10.25	SL-CF-38	10.35
SL-CF-7	9.81	SL-CF-15	10.00	SL-CF-23	10.17	SL-CF-31	10.21	SL-CF-39	9.60
SL-CF-8	9.86	SL-CF-16	9.94	SL-CF-24	9.99	SL-CF-32	10.17	SL-CF-40	10.25
CNT/SL- CF-1	9.95	CNT/SL- CF-9	10.01	CNT/SL- CF-17	10.26	CNT/SL- CF-25	10.23	CNT/SL- CF-33	10.24
CNT/SL- CF-2	10.02	CNT/SL- CF-10	10.20	CNT/SL- CF-18	10.22	CNT/SL- CF-26	10.23	CNT/SL- CF-34	10.33
CNT/SL- CF-3	9.68	CNT/SL- CF-11	10.05	CNT/SL- CF-19	10.08	CNT/SL- CF-27	10.12	CNT/SL- CF-35	10.28
CNT/SL- CF-4	10.01	CNT/SL- CF-12	10.16	CNT/SL- CF-20	10.17	CNT/SL- CF-28	9.95	CNT/SL- CF-36	10.27
CNT/SL- CF-5	10.07	CNT/SL- CF-13	10.07	CNT/SL- CF-21	10.17	CNT/SL- CF-29	10.23	CNT/SL- CF-37	10.30
CNT/SL- CF-6	9.73	CNT/SL- CF-14	10.14	CNT/SL- CF-22	9.90	CNT/SL- CF-30	10.25	CNT/SL- CF-38	9.77
CNT/SL- CF-7	9.65	CNT/SL- CF-15	10.14	CNT/SL- CF-23	10.19	CNT/SL- CF-31	10.26	CNT/SL- CF-39	10.10
CNT/SL- CF-8	9.95	CNT/SL- CF-16	10.02	CNT/SL- CF-24	10.16	CNT/SL- CF-32	10.21	CNT/SL- CF-40	10.24

Figure 5.5 Fracture surfaces of composites conditioned in water after ENF tests: (a) CF specimens before immersion; (b) CF specimens immersed for 120 days; (c) SL-CF specimens before immersion; (d) SL-CF immersed for 120 days; (e) CNT/SL-CF specimens before immersion; (f) CNT/SL-CF specimens immersed for 120 days; (g) s CNT/SL-CF specimens before immersion (high magnification); (h) CNT/SL-CF specimens immersed for 120 days (high magnification).

low CNTs loading within silane solution. The reinforcing and hygrothermal resistant mechanisms of both silane and MWCNTs are similar with the Mode I fracture toughness tests as the above mentioned.

5.6 Interlaminar shear strength

The interlaminar shear strength of the samples was evaluated using equation 3.3 for each exposure interval, as shown in Fig. 5.6b. Tables 5.3 and 5.4 show the dimensions of samples used for SBS tests. The SBS tests give accurate measures of ILSS only if pure interlaminar shear failures take place. Fig. 5.6a shows typical load-displacement curves for three composite systems (CF, SL-CF, CNT/SL-CF). Fig. 5.7a shows an optical microscope image of a sample that has undergone interlaminar shear failure in the neutral plane due to maximum shear stress which is the ideal failure mode for SBS samples. However, specimens usually encounter other types of damage before or concurrent with interlaminar shear failure, causing the specimens to fail by other than pure interlaminar shear [101, 208, 209]. Fig. 5.7b shows a mixed failure mode, whereby the onset of cracking was initiated outside of the neutral plane and propagate at a 90° orientation. This type of failure mode yields unreliable results for ILSS tests, as other failure modes are dominant over interlaminar shear. Fig. 5.6a also shows a typical load-displacement curve of interlaminar shear strength test. Only if the load drops obviously immediately after the peak load is reached, it is assumed that the specimen failed in laminar shear [208]. Here in the tests, the peak load in this kind of circumstance was then used to determine the ILSS.

The ILSS decreases continuously with the duration of submersion in the water bath. After immersion test, the ILSS of CF specimens decrease 30%, while SL-CF and

CNT/SL-CF specimens show similar decrease rate of 28.1% and 31%. The increase of ILSS for silane treated CFRPs is not obvious. That is because the shear failure strength is not only influenced by interfacial properties of CFRPs but also largely dependent on pure matrix properties [210]. Silane can only improve interfacial bonding strength to some extent, but not the epoxy matrix properties. So the effect of silane treatment is quite limited. However, the CNT/SL-CF composite system showed the best ILSS properties, which is 9% higher than the CF specimens before hygrothermal treatments. After immersion in hot water, the CNT/SL-CF samples still show a 4.3% higher ILSS than the non-treated samples. It indicates that this treatment has beneficial effects on ILSS. Three possible mechanisms of CNTs for shear strength enhancement seem to work [189]. Firstly, nanotubes act like rigid fillers, which can toughen and reinforce the epoxy matrix at the interphase area by serving as a crack arrester and prevent expansion of micro-cracking [211]. Secondly, nanotubes can improve the interfacial bonding strength of composites through the “bridging mechanism” in the resin-rich interphase area. In addition, the existence of CNTs can reduce the interlaminar stress concentration by smearing the mismatch of neighbouring plies properties.

Table 5.3 Samples' width of the three composite systems for SBS tests.

Samples (0 day)	Width (mm)	Samples (10 days)	Width (mm)	Samples (20 days)	Width (mm)	Samples (30 days)	Width (mm)	Samples (60 days)	Width (mm)
CF-1	8.91	CF-9	8.61	CF-17	9.06	CF-25	8.64	CF-33	8.81
CF-2	9.05	CF-10	9.14	CF-18	9.00	CF-26	8.98	CF-34	8.77
CF-3	9.34	CF-11	9.01	CF-19	8.77	CF-27	9.06	CF-35	9.14
CF-4	8.79	CF-12	8.81	CF-20	9.05	CF-28	8.78	CF-36	8.65
CF-5	8.75	CF-13	8.93	CF-21	8.43	CF-29	9.11	CF-37	8.77
CF-6	9.27	CF-14	8.60	CF-22	8.46	CF-30	8.80	CF-38	8.93
CF-7	9.04	CF-15	8.67	CF-23	8.71	CF-31	9.03	CF-39	9.03
CF-8	8.84	CF-16	8.79	CF-24	9.09	CF-32	8.85	CF-40	8.81
SL-CF-1	8.98	SL-CF-9	9.28	SL-CF-17	9.27	SL-CF-25	9.41	SL-CF-33	9.10
SL-CF-2	8.48	SL-CF-10	9.16	SL-CF-18	9.28	SL-CF-26	9.26	SL-CF-34	9.20
SL-CF-3	8.81	SL-CF-11	9.18	SL-CF-19	9.16	SL-CF-27	9.17	SL-CF-35	9.39
SL-CF-4	8.58	SL-CF-12	9.18	SL-CF-20	9.29	SL-CF-28	9.10	SL-CF-36	9.40
SL-CF-5	8.61	SL-CF-13	8.84	SL-CF-21	9.01	SL-CF-29	9.22	SL-CF-37	9.12
SL-CF-6	8.85	SL-CF-14	9.29	SL-CF-22	8.77	SL-CF-30	9.33	SL-CF-38	9.16
SL-CF-7	8.77	SL-CF-15	9.14	SL-CF-23	9.14	SL-CF-31	9.03	SL-CF-39	9.22
SL-CF-8	8.81	SL-CF-16	9.05	SL-CF-24	9.26	SL-CF-32	8.84	SL-CF-40	9.32
CNT/SL- CF-1	8.79	CNT/SL- CF-9	9.36	CNT/SL- CF-17	9.29	CNT/SL- CF-25	9.44	CNT/SL- CF-33	9.10
CNT/SL- CF-2	8.69	CNT/SL- CF-10	9.30	CNT/SL- CF-18	9.08	CNT/SL- CF-26	9.36	CNT/SL- CF-34	9.56
CNT/SL- CF-3	8.56	CNT/SL- CF-11	9.32	CNT/SL- CF-19	9.41	CNT/SL- CF-27	9.21	CNT/SL- CF-35	9.46
CNT/SL- CF-4	8.54	CNT/SL- CF-12	9.14	CNT/SL- CF-20	9.50	CNT/SL- CF-28	9.56	CNT/SL- CF-36	9.30
CNT/SL- CF-5	8.55	CNT/SL- CF-13	9.21	CNT/SL- CF-21	9.19	CNT/SL- CF-29	9.64	CNT/SL- CF-37	9.38
CNT/SL- CF-6	8.72	CNT/SL- CF-14	9.65	CNT/SL- CF-22	9.21	CNT/SL- CF-30	9.42	CNT/SL- CF-38	9.40
CNT/SL- CF-7	8.61	CNT/SL- CF-15	9.19	CNT/SL- CF-23	9.08	CNT/SL- CF-31	9.48	CNT/SL- CF-39	9.22
CNT/SL- CF-8	8.79	CNT/SL- CF-16	9.36	CNT/SL- CF-24	9.35	CNT/SL- CF-32	9.03	CNT/SL- CF-40	9.09

Table 5.4 Samples' thicknesses of the three composite systems for SBS tests.

Samples (0 day)	Thickness (mm)	Samples (10days)	Thickness (mm)	Samples (20days)	Thickness (mm)	Samples (30days)	Thickness (mm)	Samples (60days)	Thickness (mm)
CF-1	2.90	CF-9	2.82	CF-17	2.76	CF-25	2.91	CF-33	2.93
CF-2	2.88	CF-10	2.78	CF-18	2.79	CF-26	2.83	CF-34	2.98
CF-3	2.78	CF-11	2.73	CF-19	2.77	CF-27	2.76	CF-35	2.92
CF-4	2.72	CF-12	2.73	CF-20	2.76	CF-28	2.85	CF-36	2.93
CF-5	2.75	CF-13	2.77	CF-21	2.78	CF-29	2.85	CF-37	2.91
CF-6	2.81	CF-14	2.85	CF-22	2.81	CF-30	2.82	CF-38	2.82
CF-7	2.82	CF-15	2.76	CF-23	2.83	CF-31	2.75	CF-39	2.91
CF-8	2.80	CF-16	2.88	CF-24	2.76	CF-32	2.90	CF-40	2.93
SL-CF-1	2.82	SL-CF-9	2.83	SL-CF-17	2.91	SL-CF-25	2.93	SL-CF-33	3.12
SL-CF-2	2.76	SL-CF-10	2.86	SL-CF-18	2.98	SL-CF-26	3.01	SL-CF-34	3.07
SL-CF-3	2.87	SL-CF-11	2.99	SL-CF-19	3.02	SL-CF-27	2.95	SL-CF-35	2.97
SL-CF-4	2.67	SL-CF-12	2.90	SL-CF-20	2.98	SL-CF-28	3.01	SL-CF-36	2.98
SL-CF-5	2.77	SL-CF-13	2.97	SL-CF-21	2.95	SL-CF-29	2.95	SL-CF-37	3.02
SL-CF-6	2.86	SL-CF-14	2.84	SL-CF-22	2.94	SL-CF-30	2.94	SL-CF-38	3.06
SL-CF-7	2.81	SL-CF-15	2.88	SL-CF-23	3.00	SL-CF-31	3.07	SL-CF-39	3.11
SL-CF-8	2.80	SL-CF-16	2.93	SL-CF-24	2.95	SL-CF-32	2.91	SL-CF-40	3.04
CNT/SL- CF-1	2.96	CNT/SL- CF-9	3.14	CNT/SL- CF-17	3.01	CNT/SL- CF-25	3.08	CNT/SL- CF-33	3.21
CNT/SL- CF-2	2.94	CNT/SL- CF-10	3.00	CNT/SL- CF-18	3.05	CNT/SL- CF-26	3.10	CNT/SL- CF-34	3.08
CNT/SL- CF-3	2.97	CNT/SL- CF-11	2.99	CNT/SL- CF-19	3.03	CNT/SL- CF-27	3.07	CNT/SL- CF-35	3.02
CNT/SL- CF-4	2.82	CNT/SL- CF-12	3.02	CNT/SL- CF-20	3.04	CNT/SL- CF-28	2.94	CNT/SL- CF-36	3.24
CNT/SL- CF-5	2.84	CNT/SL- CF-13	3.13	CNT/SL- CF-21	2.98	CNT/SL- CF-29	3.10	CNT/SL- CF-37	3.08
CNT/SL- CF-6	2.92	CNT/SL- CF-14	3.02	CNT/SL- CF-22	3.01	CNT/SL- CF-30	2.95	CNT/SL- CF-38	3.05
CNT/SL- CF-7	2.86	CNT/SL- CF-15	2.99	CNT/SL- CF-23	3.08	CNT/SL- CF-31	3.08	CNT/SL- CF-39	3.10
CNT/SL- CF-8	2.96	CNT/SL- CF-16	3.07	CNT/SL- CF-24	3.03	CNT/SL- CF-32	2.98	CNT/SL- CF-40	3.10

Figure 5.6 (a) Typical load-displacement curves of interlaminar shear strength test; (b) Interlaminar shear strength (ILSS) of different CFRP composites immersed in water for certain days.

Figure 5.7 Optical microscope image of different failure modes after SBS tests: (a) interlaminar shear failure mode; (b) mixed failure modes.

5.7 Summary

Silane coating and MWCNTs were used to treat carbon fibers to compose hybrid CFRP composites. Effects of hygrothermal environment on mechanical properties of different treated CFRPs were characterized. The analysis reveals that there are two main reinforcing mechanisms in the hybrid composites: by silane and CNTs. The addition of silane coupling agent revealed an increase in all observed mechanical properties when

being compared with CF samples. It has been established that the chemical bonding played a significant role in this improvement, leading to an average increase in mode I and mode II fracture toughness by 22.4% and 10.8% compared with unmodified samples, respectively. The influence of silane surface treatment on the interlaminar shear strength was, however, not very significant due to this property was also affected by matrix properties. CNT/SL-CF composites showed greater increase in all mechanical properties than composites treated with silane alone. CNTs provided additional benefits by absorbing energy through their highly flexible elastic behaviour during deformation [189, 193]. The average mode I and II fracture toughness is improved by 35.4% and 19.9% compared with unmodified samples, respectively.

It has also been found that for each modification, exposure to water resulted in adverse effects on the glass transition temperature, ILSS, mode I and mode II fracture toughness, and these properties continually decreased with increasing exposure time. However, surface treatments can improve the hygrothermal resistance of CFRPs, and CNT/SL-CF specimens still showed the best results. The average mode I and II fracture toughness and interlaminar shear strength were improved by 33%, 40.5% and 4.3% compared with CF samples after hygrothermal treatments, respectively. The increase was because the treatment reduced the likelihood of delamination and promoted uniform load transfer between matrix and fibers even under hygrothermal environment, thus increasing the durability of composites. The improvements observed as a result of this easy modification provided the potential use of silane and CNTs modified composite laminates for large scale use in marine industry.

Chapter 6 Interfacial performance of surface treated CFRP-Ti hybrid composites under long-term hygrothermal conditions

6.1 Overview

In this chapter, titanium was well anodized (as illustrated in chapter 3.2.4) and carbon fibers were treated using MWCNTs modified silane coating to improve the long-term interfacial properties against humidity of FMLs. The hygrothermal effects on different treated hybrid FMLs were compared, and interlaminar fracture toughness was measured using SCB tests. The fractured topography of specimens was examined using SEM to determine failure modes and effects of surface treatments. Three FML systems were made for comparison purpose, as listed in Table 6.1.

Table 6.1 Three composite systems prepared for comparison.

Sample code	Description
Ti/CF	Titanium plates were sandblasted; carbon fibers were as received
Ti-Anodized/CF	Titanium plates were sandblasted and anodized; carbon fibers were as received
Ti-Anodized/CF-SL-CNT	Titanium plates were sandblasted and anodized; carbon fibers were treated using silane with 0.05 wt% CNT

6.2 Microstructure of surface treated Ti alloy

Fig. 6.1 shows the SEM images of Ti alloys after different treatments. In Fig. 6.1a, it can be seen that the sandblasted Ti alloys' surface is quite rough, and there are many sharp humps and valleys appearing. It was because the sandblasting can create macro-structured surfaces to enhance specific surface area and mechanical interlocking. After anodization, sharp edges can't be detected, and the surface became much smoother than sandblasted surfaces, as shown in Fig. 6.1b. This is because the sharp edges were much easier to be dissolved during anodizing process [212]. In Fig. 6.1c, many nano-sized pits appeared at higher magnification, due to electrochemical reactions in the electrolyte/oxide and oxide/metal interface [26]. Therefore, nano to macro-scale hierarchical structures were created on the Ti6Al4V surface through anodization. The thickness of oxide layer was measured using backscattered electron imaging. The bright white area indicated Ti6Al4V alloy, and the oxide layer was in dark grey color as shown in Fig. 6.1d. It is demonstrated that an oxide layer of a few hundred nanometers was formed after anodization.

6.3 XPS tests

To find out the chemical composition of titanium surface after different treatments, XPS experiments were carried out. The deconvoluted Ti 2p spectra for two kinds of titanium are given in Figs. 6.2a-b, and the contribution of each titanium species to the intensity of Ti 2p_{3/2} peak is quantitatively summarized in Table 6.2. The surface layer composing of TiO₂, Ti₂O₃, TiO and Ti at concentrations of 69.2%, 11.6%, 9.8% and 9.4% was detected on sandblasted Ti, which was spontaneously formed when fresh Ti

surface was exposed to air [26, 213]. After anodizing treatment, Ti and TiO disappeared while only Ti_2O_3 and TiO_2 were detected at the concentration of 47.1% and 52.9%.

Figure 6.1 Typical SEM images of Ti6Al4V surfaces after: (a) sandblasting; (b) anodization; (c) anodization at higher magnification; (d) anodization (cross-section).

Figure 6.2 Deconvoluted Ti 2p XPS spectra of Ti6Al4V after: (a) sandblasting; (b) anodization.

Table 6.2 Ti 2p_{3/2} peak fitting results for Ti6Al4Vspecimens after sandblasting and anodization.

Surface Treatments	Ti (%)	TiO (%)	Ti ₂ O ₃ (%)	TiO ₂ (%)
Sandblasting	7.4	9.9	7.8	74.9
Anodization	0	0	43.5	56.5

6.4 Dynamic wetting behaviour of Ti alloys

Good wettability is crucial for Ti alloy's adhesion with epoxy, and it is influenced by the chemistry and hierarchical structure of the metal surface. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapour interface (geometrically acquired by applying a tangent line from the contact point along the liquid-vapour interface in the droplet profile), as calculated in equation 6.1. The interface where solid, liquid, and vapour co-exist is referred to as the “three-phase contact line”.

$$\gamma_S = \gamma_L \cdot \cos \theta + \gamma_{SL} \quad (6.1)$$

where γ_S is solid liquid tension, γ_L is liquid surface tension, γ_{SL} is a solid and liquid boundary tension.

To obtain the dynamic wetting behaviour of epoxy on differently treated titanium alloys, contact angle tests were performed. From Figs. 6.3a-c, it can be seen that the contact angle of sandblasted titanium was 120.3° at 0 s and decreased with increasing contacting time. After around 100 s, the contact angle became stable gradually, and the

Figure 6.3 Epoxy contact angles on Ti surface. For sandblasted Ti: static contact angle images at time of (a) 0 s and (b) 300 s; (c) wetting angle vs. time curves. For anodized Ti: static contact angle images at time of (d) 0 s and (e) 900 s; (f) wetting angle vs. time curves.

value was 22.5 after around 300 s. As to the anodized samples (Figs. 6.3d-f), the starting contact angle was 132 °, and the value kept decreasing. It was reduced to around 5.5 °after 900 s, and the stable value was not reached. From the above results, it should be pointed out that sandblasted titanium showed better wettability at the starting point. This is because sandblasted titanium possessed higher content of TiO_2 at the surface than anodized titanium (as shown in Fig. 6.2c), and TiO_2 is more oleophilic than Ti, TiO and Ti_2O_3 . However, absorption/imbibition occurred all through the wetting process on the anodized titanium to form a solid/liquid composite at the surface [214]. Epoxy permeated

into the nano-pores induced from anodization, which resulted in decreased contact angle at the end.

6.5 SCB results and failure behaviour

The interlaminar fracture toughness was evaluated using equation 3.7 at each water exposure interval. Table 6.3 shows the dimensions of samples used for SCB tests. Typical load-displacement curves of the three FMLs are illustrated in Fig. 6.4a. All of the loads increased linearly first and then decreased gradually. Typical R-curves of the three FMLs are illustrated in Fig. 6.4b. The G_c values of FMLs after each treatment are shown in Fig. 6.4c. The interlaminar fracture toughness of Ti-Anodized/CF was 12.2 times higher than Ti/CF, and another 12.1% improvement was observed for Ti-Anodized/CF-SL-CNT. After 60 days hygrothermal treatment, the G_c values of Ti-Anodized/CF and Ti-Anodized/CF-SL-CNT specimens were still 14.2 and 24.5 times higher when being compared with G_c value of the Ti/CF. With increasing the immersion time, the overall trends of fracture toughness for all three kinds of specimens all decrease, especially in the first 10 days. After treated in hygrothermal environment for 60 days, G_c of CN, SL-CN and CNT/SL-CN decreases 66.8%, 61.8% and 42.9%, respectively. There was an increase of G_c for Ti-Anodized/CF-SL-CNT specimens at the 60th day, which may be because the G_c value didn't decrease after certain time hygrothermal treatment and was fluctuating around a certain stable value due to experimental error.

The increase of G_c for Ti-Anodized/CF system is due to the increased bonding strength between the titanium surface and epoxy matrix after anodization. Even though the Ti/CF samples have more sharp edges and higher roughness at titanium side, the bonding strength is still lower than the Ti-Anodized/CF. It is consistent with our previous

research, which demonstrated that shear strength between titanium and epoxy was highly improved after anodization process [26]. This is because nano-scale structures generated from anodization can increase the specific area of anodized titanium alloy (shown in Fig. 6.1c) and then enhance the mechanical interlocking between epoxy matrix and titanium plates. In addition, the lone pair electrons can be transferred from amine groups in epoxy to metallic center in TiO_x [215-217]. As a result, the organo-metallic complex is generated between epoxy matrix and oxide layer of titanium to enhance the bonding strength. In the meanwhile, the oxide layer anodized under 40 °C was strong itself and possessed good bonding property with metal substrate [26]. However, it should be noted that the metallic oxide layer has potential to be dissolved together with chemical reaction [215, 218, 219]. The oxide layer on sandblasted titanium was quite thin, which was typical within 10 nm, while the anodized oxide layer was much thicker as aforementioned. So the interfacial chemical bonding strength of Ti/CF is much lower than the Ti-Anodized/CF samples due to dissolving of the thin oxide layer.

The Ti-Anodized/CF-SL-CNT samples show the highest G_c and maintain the highest value even after lengthy exposure to moisture. This is because silane coupling agent can react with both carbon fibers and epoxy matrix and act as a connector in between the two materials [193]. (3-glycidyloxypropyl) trimethoxysilane can produce silanol after hydrolysis, which forms chemical bond with hydroxyl on the sizing of carbon fibers on one side. In addition, the functional group containing epoxide group can be cross-linked with epoxy matrix under the action of hardener to produce a chemical bond [193]. When oxidized CNTs are incorporated, the nanotubes form a kind of overcoating at the interfacial area, which can interact with carbon fibers as well as epoxy

Figure 6.4 (a) Typical load-displacement curves of single cantilever beam test; (b) Typical R-curves of single cantilever beam test; (c) G_c of different fiber metal laminates composites immersed in simulated seawater for certain days.

matrix. As a result, the fracture roughness of FMLs is improved due to the CNTs bridging or CNTs pull-out effects [189, 193]. In addition, CNTs act as interlocking pins and could increase the friction at the interphase area. The high stiffness CNTs can also essential to ensure efficient load transfer from matrix to fillers, which helps to reduce stress concentrations and improves overall mechanical properties.

Table 6.3 Samples' widths of the three composite systems for SCB tests.

Samples (0 day)	Width (mm)	Samples (10 days)	Width (mm)	Samples (30 days)	Width (mm)	Samples (60 days)	Width (mm)
Ti/CF-1	23.76	CF-5	23.97	CF-13	23.83	CF-17	23.78
Ti/CF-2	23.92	CF-6	23.86	CF-14	23.88	CF-18	25.88
Ti/CF-3	23.91	CF-7	24.01	CF-15	23.91	CF-19	23.86
Ti/CF-4	24.01	CF-8	23.91	CF-16	23.92	CF-20	23.93
Ti- Anodized/CF-1	23.87	SL-CF-5	23.96	SL-CF-13	23.90	SL-CF-17	23.83
Ti- Anodized/CF-2	23.86	SL-CF-6	23.86	SL-CF-14	23.85	SL-CF-18	23.82
Ti- Anodized/CF-3	23.76	SL-CF-7	23.92	SL-CF-15	23.81	SL-CF-19	23.88
Ti- Anodized/CF-4	23.89	SL-CF-8	25.61	SL-CF-16	23.86	SL-CF-20	23.84
Ti- Anodized/CF- SL-CNT-1	24.92	CNT/SL- CF-5	25.20	CNT/SL- CF-13	23.74	CNT/SL- CF-17	25.20
Ti- Anodized/CF- SL-CNT -2	23.86	CNT/SL- CF-6	25.20	CNT/SL- CF-14	24.65	CNT/SL- CF-18	25.15
Ti- Anodized/CF- SL-CNT -3	24.92	CNT/SL- CF-7	25.09	CNT/SL- CF-15	24.91	CNT/SL- CF-19	25.18
Ti- Anodized/CF- SL-CNT -4	25.11	CNT/SL- CF-8	25.08	CNT/SL- CF-16	24.93	CNT/SL- CF-20	24.96

Figure 6.5 Fracture surfaces of Ti/CF conditioned in simulated seawater after SCB tests: (a) composite side before immersion (remained epoxy is indicated by arrow 1); (b) titanium side before immersion; (c) composite side immersed for 120 days; (d) titanium side immersed for 120 days and (e and f) correspond to the EDX-S results of the areas of A and B.

To determine the failure modes, the SEM images of the fractured surfaces of titanium and composites under different treatments are compared and shown in Figs. 6.5-6.7. It can be seen that the Ti/CF samples have relatively smooth surface on both sides (Figs. 6.5a-b), and the morphology was quite similar even after hygrothermal treatment

(Figs. 6.5c-d). Only very limited epoxy can be found peeled off composite side and attached onto the titanium plate, as indicated by arrows in Fig. 6.5b. From EDX test results (Figs. 6.5e-f), there is no titanium atom on the CFRPs side, and carbon atom also can't be found on the titanium side in the selected area (within white rectangle). It can be deducted that almost all fracture happens in between epoxy matrix and titanium alloy. The reduction of fracture toughness is because water penetrates into Ti-epoxy interface and weakens mechanical interlocking bonds. Both sides of the Ti-Anodized/CF samples show much different surfaces topography compared with the Ti/CF specimens (Fig. 6.6).

Figure 6.6 Fracture surfaces of Ti-Anodized/CF conditioned in simulated seawater after SCB tests: (a) composite side before immersion; (b) titanium side before immersion; (c) composite side immersed for 120 days; (d) titanium side immersed for 120 days. (bare titanium is indicated by arrow 1, carbon fiber and epoxy are indicated by arrow 2)

On the composite side, besides epoxy matrix, bare carbon fibers were also found (Fig. 6.6a). On titanium side, bare titanium as well as carbon fibers and epoxy can all be detected (indicated with arrows in Fig. 6.6b), which means that it is a kind of mixed-mode failure. The failure happens in three different ways: epoxy-Ti interface, epoxy-carbon fiber interface and pure epoxy. When being compared with the Ti/CF samples, it can be concluded that titanium has better bonding performance with epoxy after anodization treatment. After 60 days hygrothermal treatment, less bared carbon fibers can be detected on the composite side (Fig. 6.6c), and the fractured titanium surface became clearer and less epoxy remained on it (indicated by arrows in Fig. 6.6d). This demonstrates that water is absorbed more through the interface between epoxy and metal, which will weaken the interaction between titanium and matrix. However, because of the nano-structure and organo-metallic complex induced by anodization, the bonding strength between epoxy and titanium is still higher than Ti/CF samples. Both fractured surfaces of Ti-Anodized/CF-SL-CNT samples (Fig. 6.7) were quite similar with those of Ti-Anodized/CF. On the composite side (Fig. 6.7a), both carbon fibers and epoxy matrix can be found, while on the titanium side (Fig. 6.7b), bare titanium, carbon fibers and epoxy can all be detected. After being immersed in hygrothermal environment for 60 days, more epoxy can be found on the composites side (Fig. 6.7c) and the titanium side becomes clearer with less epoxy remained (Fig. 6.7f). When comparing the fractured surfaces of Ti-Anodized/CF with Ti-Anodized/CF-Si-CNT after 60 days hygrothermal treatment, it is shown that fewer carbon fibers were left on the titanium sides, while more bare titanium area were exposed (Fig. 6.6d and Fig. 6.7f). Another phenomenon is that CNTs can be found on both surfaces of composites side (Fig. 6.7b) and titanium side (Fig.

Figure 6.7 Fracture surfaces of Ti-Anodized/CF-SL-CNT conditioned in simulated seawater after SCB tests: (a) composite side before immersion; (b) composite side before immersion at higher magnification; (c) titanium side before immersion; (d) titanium side before immersion at higher magnification; (e) composite side immersed for 120 days; (f) titanium side immersed for 120 days. (CNTs are indicated by arrow 1)

6.7d). The addition of silane and CNTs improved the adhesive properties and resisted the separation of fiber and matrix, resulting in higher fracture toughness values. This is because greater load is required to separate carbon fibers away from epoxy matrix due to chemical bonds induced by silane and highly flexible elastic behaviour of CNTs. By examining the fracture surface in Fig. 6.7b, it should be noticed that, on the composites side, the failure happened in both pure epoxy and interface. However, the fracture surface was relative smooth and not so much hackle markings can be found. So it can be deducted that the fracture happened more in tensile opening mode than in-plane shear mode.

6.6 Summary

Optimized anodization method was used to treat titanium plates, and MWCNTs modified silane coating was used to treat carbon fiber. Effects of hygrothermal environment on mechanical properties of different FML systems were characterized. The analysis reveals that surface treatment on titanium alloy is of the most importance to improve the interlaminar fracture toughness of FMLs. 1222% improvement was achieved from SCB tests when compared with the Ti/CF samples. In addition, surface treatment on carbon fibers also had some effects on the interlaminar properties. The fracture toughness was about 12.1% higher than Ti-Anodized/CF specimens. It has also been found that for each modification, exposure to water resulted in adverse effects on the interlaminar fracture toughness values, and these properties continually decreased with increasing exposure time. However, surface treatments can improve the hygrothermal resistance, and Ti-Anodized/CF-SL-CNT specimens still showed the best results. The improvements are mainly because of anodization, which can create nano-structured metal surfaces to

help physical connection and generate oxide layer to react with epoxy by forming organo-metallic complex. In addition, the MWCNTs modified silane treatment can also provide chemical interaction between carbon fibers and epoxy, reduce the likelihood of delamination and promote uniform load transfer from matrix to fibers even under hygrothermal environment. The improvements observed as a result of this easy and environment-friendly modification provides the potential use of the treated fiber metal laminates for large scale industrial application.

Chapter 7 Surface treatment effects on the compressive properties of CFRP-Ti risers

7.1 Overview

In this chapter, titanium pipe was well anodized (as illustrated in chapter 3.2.4), and CFRP-Ti risers were manufactured using filament winding method. The surface treatment effects on lateral and axial compressive strength and pipe stiffness were characterized. The fractured surfaces of specimens were examined using optical microscope to determine the failure modes. Finite elements analysis was used to characterize the stress distribution of pipes, and the simulated results were compared with the experimental results. Two CFRP-Ti risers were made for comparison purpose, as listed in Table 7.1.

7.2 Lateral compressive strength of CFRP-Ti risers

The lateral compressive strength was evaluated using equations 3.9 and 3.11. Table 7.2 shows the dimensions of samples used for lateral compression tests. Fig. 7.1a shows typical load-displacement curves for two different kinds of CFRP-Ti risers. The loads increased linearly first and then dropped suddenly. The compressive strength values of sandblasted and anodized Ti lined risers are shown in Fig. 7.1b. The lateral compressive strength of A-CFRP-Ti was 10.3 MPa and 37% higher than that of S-CFRP-Ti (7.5 MPa).

Table 7.1 Two composite systems prepared for comparison.

Sample code	Description
S-CFRP-Ti	Titanium pipes were sandblasted
A-CFRP-Ti	Titanium plates were sandblasted and anodized

Table 7.2 Samples' dimensions of the two CFRP-Ti systems for lateral compression tests.

Samples (0 day)	Mean outer radius (mm)	Thickness (mm)
S-CFRP-Ti-1	25.44	2.39
S-CFRP-Ti-2	25.36	2.48
S-CFRP-Ti-3	25.47	2.50
S-CFRP-Ti-4	25.32	2.50
S-CFRP-Ti-5	25.76	2.41
A-CFRP-Ti-1	25.43	2.68
A-CFRP-Ti-2	25.39	2.59
A-CFRP-Ti-3	25.42	2.64
A-CFRP-Ti-4	25.50	2.63
A-CFRP-Ti-5	25.41	2.60

The improvement in lateral compressive strength of the A-CFRP-Ti system is due to the increased bonding strength between titanium surface and epoxy matrix. Even though the S-CFRP-Ti samples have more sharp edges and higher roughness at titanium side, the bonding strength is still lower than the Ti-Anodized/CF. This is because nano-scale structures can increase the specific area of anodized titanium alloy (shown in Fig.

6.1c) and then enhance the mechanical interlocking between epoxy matrix and titanium plates. In addition, the lone pair electrons can be transferred from amine groups in epoxy to metallic center in TiO_x [215-217]. As a result, the organo-metallic complex is generated between epoxy matrix and oxide layer of titanium to enhance the bonding strength. It should be noted that the metallic oxide layer has potential to be dissolved together with chemical reaction [215, 218, 219]. So the interfacial chemical bonding strength of Ti/CF is much lower than the anodized samples due to the thin oxide layer.

Figure 7.1 (a) Typical load-displacement curves of lateral compression tests; (b) lateral compressive strength of different CFRP-Ti risers.

Figure 7.2 Optical microscope image of different failure modes after lateral compression tests: (a) S-CFRP-Ti; (b) A-CFRP-Ti. (cracks are illustrated in white rectangle)

To determine the failure modes, the optical microscope images of the cross sectional surface of two kinds of samples are compared and shown in Fig. 7.2. All delamination happened at the positions near loading plates and is vertical to the loading direction. It can be seen that the delamination (illustrated in white rectangle of Fig. 7.2a) happened in between titanium pipe and CFRP layers for the S-CFRP-Ti samples. However, A-CFRP-Ti samples didn't show delamination at the metal-CFRP interface. On the contrary, the crack (illustrated in white rectangle of Fig. 7.2b) appears within pure CFRP layers. By comparing the different failure phenomenon, it can be deducted that anodized titanium has better bonding properties with CFRPs than sandblasted ones. The metal-CFRPs interfacial bonding strength of the A-CFRP-Ti samples is strong enough to carry higher loading force and doesn't fail in the first place. Because of poor bonding strength at metal-composite interfacial area, the sandblasted samples failed at the MCI.

A finite element model is also developed using ABAQUS to predict the stress distributions of CFRP-Ti pipe under lateral compressive loading. The test specimen is modeled using standard 8-node hexahedron SC8R elements, and a compressive load of 1 kN is applied laterally to the tube. The length of tube is 25.4 mm, and it composes of inner titanium layer and outer CFRP layers. The titanium layer is 1.25 mm thick with 48.3 mm inner diameter. The outer part consists of 7 layers of CFRPs with different angles (-55° , $+55^{\circ}$, -55° , $+55^{\circ}$, -55° , $+55^{\circ}$, 90°). The thickness of each layer is 0.2 mm.

The mechanical properties of CFRP were calculated using rule of mixture and Halphin-Tsai equations. Halphin and Tsai developed their models as simple equations by curve fitting to results that are based on elasticity. The equations show that the property

of a composite could be expressed in terms of the corresponding property of matrix and fiber using the following relationships:

For longitudinal young's modulus E_l and major Poisson's ratio ν_{l2} , role of mixture gives reasonable result:

$$E_l = E_c C_f + E_m C_m \quad (7.1)$$

$$\nu_{l2} = \nu_f C_f + \nu_m C_m \quad (7.2)$$

For transverse young's modulus E_2 , in-plane shear modulus G_{l2} and transverse Poisson's ratio ν_{23} , Halpin-Tsai equation is [220, 221]:

$$\frac{M}{M_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \quad (7.3)$$

where

$$\eta = \frac{(M_f / M_m) - 1}{(M_f / M_m) + \xi} \quad (7.4)$$

in which, M = composite material modulus E_2 , G_{l2} , or ν_{23}

M_f = corresponding fiber modulus E_f , G_f , or ν_f

M_m = corresponding matrix modulus E_m , G_m , or ν_m

and ξ is a measure of fiber reinforcement of composite material that depends on the fiber geometry, packing geometry, and loading conditions. For E_2 and ν_{l2} , $\xi=2$ is commonly used and $\xi=1$ gives reasonable results of G_{l2} .

The Young's modulus and Poisson's ratio of carbon fiber are 296 GPa and 0.3. The values are 3.28 GPa and 0.35 for epoxy matrix respectively. These properties of

carbon fiber and epoxy are obtained from datasheet of materials and literature [222]. The volume fraction of carbon fiber was 30%, and the calculated mechanical properties of composites are listed in Table 7.3.

For titanium liner, Johnson-cook plasticity model was chosen, and it has the following stress expression:

$$\sigma = (A + B\varepsilon^n)(1 + C \ln \varepsilon^*)[1 - (T^*)^m] \quad (7.5)$$

where σ is the effective stress, ε is the effective plastic strain, ε^* is normalized effective plastic strain rate (typically normalized to a strain rate of 1 s^{-1}), A , B , C , n and m are materials parameters, and T^* is the non-dimensional temperature defined as:

$$T^* = \frac{T - T_{transition}}{T_{melt} - T_{transition}} \quad (7.6)$$

where T is the current temperature, T_{melt} is the melting temperature, and $T_{transition}$ is the transition temperature. Mechanical properties of titanium were obtained from published paper [223] and summarized in Table 7.4.

The stress distribution of the CFRP-Ti under lateral compression is shown in Figure 7.3. From the finite element analysis, the maximum stress under lateral loading locates at the positions where loading plates contact with tube. In longitudinal direction, stress at middle part is larger than rest area of the pipe. So, the pipe would fail at the middle firstly with increasing compressive loading. The interfacial bonding properties dominate the stress transfer capability. If the interfacial property of CFRP-Ti is not good enough, the tube would fail at the interface between titanium liner and CFRP layers in the

mode as shown in Fig. 7.2a. The tube that fails in this mode has lower compressive strength than the pipe that fails from CFRPs or titanium.

Table 7.3 Mechanical properties of unidirectional CFRPs.

Mechanical properties	CFRP
Longitudinal Modulus, E_1	178912 MPa
Transverse Modulus, E_2	17904 MPa
Poisson's Ratio, ν_{12}	0.33
Poisson's Ratio, ν_{23}	0.3
Shear Modulus, G_{12}	4932 MPa
Shear Modulus, G_{13}	4932 MPa
Shear Modulus, G_{23}	6880 MPa

Table 7.4 Parameters of titanium liner.

Parameters	Titanium
A	500 MPa
B	1168 MPa
C	0.027
n	0.63
m	1 MPa
Young's Modulus, E	120 GPa
Poisson's Ratio, ν	0.3

Figure 7.3 Stress distribution of CFRP-Ti tube under lateral compressive loading.

7.3 Axial compressive strength of CFRP-Ti risers

The axial compressive strength was evaluated using equations 3.9 and 3.10. Table 7.5 shows the dimensions of samples used for axial compression tests. Fig. 7.4a shows typical load-displacement curves for two different kinds of CFRP-Ti risers. For both kinds of samples, the loads increased slowly firstly because the samples' outer surfaces were not perfect parallel to each other. After the loads were fully applied on the whole surface area of the tubes, the loads increased linearly. After that, the increasing speeds of loads slowed down again because of the plastic deformation of samples. Finally, the loads dropped suddenly as a result of sample failure. The compressive strength values of sandblasted and anodized Ti lined risers are shown in Fig. 7.4b. The axial compressive strength of A-CFRP-Ti was 381 MPa and 6.4% higher than S-CFRP-Ti, which was 358 MPa.

Table 7.5 Samples' dimensions of the two CFRP-Ti systems for axial compression tests.

Samples(0 day)	Inner diameter (mm)	Outer diameter (mm)
S-CFRP-Ti-1	48.28	53.11
S-CFRP-Ti-2	48.36	53.01
S-CFRP-Ti-3	48.29	53.17
S-CFRP-Ti-4	48.26	53.04
S-CFRP-Ti-5	48.23	53.12
A-CFRP-Ti-1	48.04	53.24
A-CFRP-Ti-2	48.05	53.31
A-CFRP-Ti-3	48.06	53.36
A-CFRP-Ti-4	48.06	53.21
A-CFRP-Ti-5	47.99	53.33

Figure 7.4 (a) Typical load-displacement curves of axial compression tests; (b) axial compressive strength of different CFRP-Ti risers.

Fig. 7.5 shows the two kinds of samples after axial compression tests. Fig. 7.5a and b are the whole figures of tested samples. The outer CFRP layers are heavily destroyed, and the outer layers are separated from the inner ones. However, the outlooks

Figure 7.5 Optical microscope image of different failure modes after axial compression test: (a) S-CFRP-Ti; (b) A-CFRP-Ti; cross-sectional surfaces of: (c) S-CFRP-Ti; (d) A-CFRP-Ti. (cracks are illustrated in white rectangle)

of the two kinds of specimens are basically the same. The optical microscope images of the cross sectional surface of two kinds of samples are compared and shown in Figs. 7.5c-d. It can be seen that there are cracks in pure titanium for both specimens, and cracks all start from the interface between titanium liner and CFRP layers. For S-CFRP-Ti, the crack (illustrated in white rectangle) propagates along the interface in between titanium pipe and CFRP layers, as shown in Fig. 7.5c. However, the A-CFRP-Ti samples don't show delamination at the metal-CFRP interface. On the contrary, the crack (illustrated in white rectangle) travels through pure CFRP layers (Fig. 7.5d). By comparing the two different kinds of samples' failure modes, it can also be deduced that

anodized titanium shows higher bonding strength with CFRPs than those sandblasted ones. The metal-CFRP interfacial bonding strength of A-CFRP-Ti samples is strong and doesn't fail, while the sandblasted samples fail at the MCI because of poor bonding strength. The reason of the increased bonding strength is same as the above mentioned. Due to the different modulus of titanium and CFRPs, the load carried by metal and composites are different under the same deformation condition. Better interfacial bonding properties mean that more force can be transferred, and so the final axial compressive strength can be increased.

A finite element model is also developed to predict the stress distributions of the CFRP-Ti pipe under axial compressive loading. A compressive pressure of 360 MPa is applied on both ends of the tube. The mechanical properties and dimensions of the CFRP-Ti are the same as aforementioned.

Figure 7.6 Stress distribution of CFRP-Ti tube under axial compressive loading.

Figure 7.7 Stress distribution in radial direction of CFRP-Ti tube under axial compressive loading. (R1: inner radius, R2: outer radius)

The stress distribution of the CFRP-Ti is shown in Fig. 7.6. From the finite element analysis, stress is not uniformly distributed on the CFRP-Ti tube. In the longitudinal direction, the stress on the both ends and middle part is larger than other section of the pipe. The colour change of the area in red circle is due to visual effects, and the stress is uniformly distributed along circular direction. For discussion purpose, the stress through the wall of CFRP-Ti pipe at middle section is determined and shown in Fig. 7.7. From the figure, it can be seen that the maximum stress on titanium plate is 447.9 MPa, while the maximum stress on CFRP layers is 366.7 MPa. However, there is a big difference of stress (109.9 MPa) at the interface between the two materials. The interface dominates the stress transfer capability at this area, and higher interfacial bonding strength would transfer stress more efficiently from CFRPs to titanium. As a result, the final axial compressive strength of CFRP-Ti pipe would be higher with better bonding properties. This strength would keep improving with increasing bonding strength

between CFRPs and titanium pipe until the bonding strength is high enough so that stress in titanium liner or CFRP layers reaches the maximum strength limit of relative materials. From then on, the axial compressive strength would not be affected by interfacial bonding property between titanium and CFRP. Instead, the compressive strength of titanium liner and CFRP layers become the limiting factors. In other words, if the interfacial area is regarded as a special kind of material which possesses its own properties, the compressive strength of CFRP-Ti pipe depends on which part reaches the strength limit firstly: titanium liner, interphase or CFRP layers.

7.4 Stiffness of CFRP-Ti risers

The lateral stiffness of pipe was evaluated using equation 3.12. Table 7.6 shows the dimensions of samples used for pipe stiffness tests. Fig. 7.8a shows typical load-displacement curves for two different kinds of CFRP-Ti risers. The loads increased linearly first and then dropped suddenly and increase again. The figure is quite similar with Fig. 7.1a. This is reasonable because the two tests were basically the same. The only difference was the larger specimen size and higher testing speed of stiffness test, which was designed to eliminate the creep effects. The pipe stiffness values of sandblasted and anodized Ti lined risers are shown in Fig. 7.8b. The pipe stiffness of A-CFRP-Ti was 37.1 MPa and 3.3% higher than S-CFRP-Ti, which was 35.9 MPa.

The pipe stiffness for A-CFRP-Ti system is almost the same as that of S-CFRP-Ti system. This is because stiffness is an elastic property and doesn't depend on the bonding strength between Ti and CFRP. Under elastic deformation stage, the materials are supposed not to be damaged in microscopic structures. The small difference (3.3%) may be due to experimental scatter.

Table 7.6 Samples' dimensions of the two CFRP-Ti systems for pipe stiffness tests.

Samples (0 day)	Inner diameter (mm)
S-CFRP-Ti-1	48.14
S-CFRP-Ti-2	48.12
S-CFRP-Ti-3	48.08
A-CFRP-Ti-1	48.10
A-CFRP-Ti-2	48.14
A-CFRP-Ti-3	48.11

Figure 7.8 (a) Typical load-displacement curves of pipe stiffness tests; (b) pipe stiffness of different CFRP-Ti risers.

A finite element model is also developed to predict the stiffness of the CFRP-Ti pipe under lateral compressive loading. A compressive load of 1 kN is laterally applied on the tube. The interface is modelled using perfect bond, and the mechanical properties as well as the dimensions of the CFRP-Ti are the same as aforementioned, except length of the tube is changed to 120 mm.

Figure 7.9 Deformation of CFRP-Ti tube under lateral compressive loading.

The deformed shape of the CFRP-Ti is shown in Fig. 7.9. The red plate with large displacement is the loading plate, while the blue plate is fixed. From the simulation results, the inner diameter changes 0.256 mm after 1 kN load is applied. By using equation 3.12, the pipe stiffness could be calculated to be 32 MPa, which is similar to both stiffness (35.9 MPa and 37.1 MPa) obtained experimentally. It demonstrates that numerical estimations obtained from this model are in perfect agreement with the experimental results for the present benchmark.

7.5 Summary

Optimized anodization method was used to treat titanium pipes. Effect of treatment on mechanical properties of different CFRP-Ti risers was characterized. The analysis reveals that surface treatment on titanium alloy is effective to improve the lateral and axial compressive strength of CFRP-Ti risers. 37% and 6.4% improvements were achieved when comparing A-CFRP-Ti samples with S-CFRP-Ti samples. The

improvements resulted from the improved bonding strength between titanium and CFRPs. Higher interfacial properties can transfer stress between two materials more efficiently and sustain more stress. However, the pipe stiffness didn't change obviously due to surface treatment. This is because stiffness is an elastic property and doesn't depend on the bonding strength between Ti and CFRP. Under elastic deformation stage, materials are supposed not to be damaged in microscopic structures. The improvements observed as a result of this easy and environment-friendly modification provides the potential use of the treated CFRP-Ti risers for large scale industrial application.

Chapter 8 Conclusions and future work

8.1 Conclusions

Fiber-matrix interface, interlaminar interface, and metal-composite interface are critical to the overall performance of hybrid CFRP-Ti composite system. To improve the interfacial properties of the CFRP-Ti composites, two different strategies have been adopted in this work: i) modification of the interfaces in CFRPs and ii) tuning of the MCI via the surface treatment of titanium alloy. CNTs modified silane coating is used to treat carbon fibers, and anodization is adopted for titanium surface treatment. CNTs modified silane coating is used to treat carbon fibers, and anodization is adopted for titanium surface treatment. The effects of both treatments on the interfacial properties, and hygrothermal resistance of CFRP-Ti composites are discussed.

MWCNTs have been incorporated through two routes to build hybrid CFRP composites. It was found that both of the two hybrid composites showed improved interfacial bonding compared with the common CFRPs. An increase of 26.7% in IFSS was achieved by incorporating 0.05 wt% MWCNTs into silane coating on the surface of carbon fiber, whereas an 17.8% increase in IFSS was obtained by dispersing 0.1 wt% MWCNTs into epoxy matrix when using the neat silane coated carbon fiber. The analysis revealed that there are two reinforcing mechanisms working simultaneously in the hybrid composites. Firstly, the formed silane coating provided a strong connection between the as-received carbon fiber and epoxy matrix, leading to an increase of about 15.5% in IFSS. Secondly, when incorporating CNTs into the silane coating, it yielded a further increase of 9.7% in IFSS. This change of reinforcing effect was attributed to the densification of

CNTs forest grafted on fiber surface during the forming of nano-composite coating, which augment the effects of crack-bridging and interface-interlocking. Therefore, the coating-modification method can achieve much higher volume fraction of CNTs in the interphase, which is usually hard to fulfill in the matrix-tuning method without issues of CNTs agglomeration and resin impregnation. Furthermore, the coating-modification method has other advantages: i) much less CNTs usage, ii) easy to perform and iii) direct application onto the as-received fibers.

The IFSS has been measured in freshwater and marine environments through single fiber microbond tests. The application of silane coating led to an increase of around 15% and 12% in interfacial shear strength, before and after a 120-day immersion tests respectively. When MWCNTs were introduced into silane coating, around 12% and 8% further improvements respectively were observed before and after the immersion tests. Furthermore, it was found that for each composite system, the interfacial shear strength gradually decreased to same level after 120-day immersion in de-ionized water and simulated seawater. Therefore, from a long-term point of view, it can be expected that degradation of CFRPs' interfacial properties are similar in a marine and freshwater environment.

Interlaminar properties of CFRP laminates have also been characterized. The addition of the silane coupling agent revealed an increase in all observed mechanical properties when being compared with CF samples. It has been established that the chemical bonding played a significant role in this improvement, leading to an increase in mode I and mode II initiation fracture toughness by 22.4% and 10.8% compared with unmodified samples, respectively. The CNT/SL-CF composites showed greater increase

in all mechanical properties than the composites treated with silane alone. CNTs provided additional benefit by absorbing energy through their highly flexible elastic behaviour during the deformation. The mode I and II initiation fracture toughness was improved by 35.4% and 19.9% compared with the unmodified samples, respectively.

It has also been found that for each modification, exposure to water resulted in adverse effects on the glass transition temperature, ILSS, mode I and mode II fracture toughness values, but surface treatments could improve the hygrothermal resistance of CFRPs. The mode I and II initiation fracture toughness and interlaminar shear strength of CNT/SL-CF specimens were improved by 33%, 40.5% and 4.3% compared with the CF samples after hygrothermal attack. The increase is because the treatment reduced the likelihood of delamination, and promoted uniform load transfer from matrix of fibers even under hygrothermal environment.

Optimized anodization method has been chosen to treat titanium plates, and its resistance to hygrothermal environment was also characterized. The analysis revealed that surface treatment on titanium alloy was of the most importance to improve the interlaminar fracture toughness of FMLs. 1222% improvement was achieved from SCB tests when being compared with the Ti/CF samples. In addition, the surface treatment on carbon fibers also has some effects on the interlaminar properties. The fracture toughness was about 12.1% higher than the Ti-Anodized/CF specimens. It has also been found that exposure to water resulted in adverse effects on the interlaminar fracture toughness values, but surface treatments could improve the hygrothermal resistance. The interlaminar fracture toughness of the Ti-Anodized/CF-SL-CNT specimens improved by 2452% compared with the Ti/CF samples after hygrothermal treatments. The

improvements of Ti-Anodized/CF samples resulted from the created nano-structured metal surfaces and the generated oxide layer, which had potential to react with epoxy by forming organo-metallic complex.

Same anodization method has been used to treat titanium pipes. It is revealed that surface treatment on titanium alloy could obviously improve the compressive strength of CFRP-Ti risers. 37% and 6.4% improvements were achieved from lateral and axial compressive tests when A-CFRP-Ti was compared with S-CFRP-Ti. The improvements resulted from the improved bonding strength between titanium and CFRPs. Higher interfacial properties can transfer stress between two materials more efficiently and sustain more stress. However, the effects of surface treatment were quite limited for stiffness of pipes, because it is an elastic property and not depending on the bonding strength. The difference of pipe stiffness was only about 3.3% for both specimens.

The results obtained from the experiments demonstrated that the coating-modification method and optimized anodization method provided the potential use of the CFRP-Ti composite risers for large scale industrial application.

8.2 Future work

Although MWCNTs modified silane coating has been developed to improve the bonding properties of CFRPs, and a kind of optimized anodization method has also been adopted to increase the titanium adhesive strength with CFRPs, further studies are still important and should be performed in future.

1. Develop new methods to treat carbon fibers, epoxy matrix and titanium alloy so that the interfacial properties could be further improved. Finding new and easier

surface treatment methods is always a very important in the field of hybrid composite materials. The present improvement is restricted by the easy processing requirement, and the distribution of high concentrated CNTs is facing a big problem. So, other easy to separated nano-carbon fillers can be considered to replace CNTs in the future work. In addition, the fracture toughness and interlaminar shear strength are highly affected by the property of matrix. More attention should be paid on modification of epoxy matrix. What's more, epoxy is not very suitable for using under seawater and high temperature because of its nature properties. Other polymers such as BMI can be adopted to replace the epoxy and obtain better performance even under hygrothermal environment. In addition, self-healing materials may be considered to be used in healing the interfacial cracks under hygrothermal environment.

2. Due to the restriction of experimental conditions and high evaporated nature of ethanol, carbon fibers can't be treated before going through the epoxy bath to finish filament winding. It is recommended to add this step during the following research process.
3. All of the mechanical tests performed in the study are quasi-static experiments. However, in the real application, materials will be used in more hostile environment, and dynamical mechanical properties should be measured to characterize the performance of the treatments effects, such as impact testing, fatigue tests and so on.
4. In the present study, only compressive properties of CFRP-Ti risers were obtained. However, many other factors also play quite important roles in determining the

final performance of the riser. So other characterizations should be performed in the future, such as burst/collapse strength, hoop tensile strength and so on.

5. A degradation law that predicts the IFSS as a function of time could be developed based on the experimental results obtained. This will be quite useful to eliminate the laborious task of having to do many long-term tests.

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List of Publications

Journal publications:

1. **B. Yu**, Z.Y. Jiang, X.Z. Tang, C.Y. Yue, J.L. Yang. Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating. *Composites Science and Technology*. 2014;99(0):131-140.
2. **B. Yu**, Z.Y. Jiang, J.L. Yang. Long-term moisture effects on the interfacial shear strength between surface treated carbon fiber and epoxy matrix. *Composites Part A: Applied Science and Manufacturing*. 2015;78:311-7.
3. X.Z. Tang, **B. Yu**, R.V. Hansen, X.L. Chen, X. Hu, J.L. Yang. Grafting Low Contents of Branched Polyethylenimine onto Carbon Fibers to Effectively Improve Their Interfacial Shear Strength with an Epoxy Matrix. *Advanced Materials Interfaces*. 2015;2(12):7.
4. P.G. He, K. Chen, **B. Yu**, C.Y. Yue, J.L. Yang. Surface microstructures and epoxy bonded shear strength of ti6al4v alloy anodized at various temperatures. *Composites Science and Technology*. 2013;82:15-22.

Conferences:

1. **B. Yu**, Z.Y. Jiang, J.L. Yang. Hygrothermal effects on the interfacial properties of CFRP composites with surface treated fibers. *The 9th Asian-Australasian Conference on Composite Materials (ACCM-9)*, Suzhou, China, 15-17 October 2014.
2. **B. Yu**, J.L. Yang. Hygrothermal Effects on Mechanical Properties of Carbon Fiber Reinforced Polymer (CFRP) Composites after Surface Treatment. *The International Conference on Experimental Mechanics (icEM2014) in conjunction with the 13th Asian Conference on Experimental Mechanics (ACEM)*, Singapore, 15-17 November 2014.
3. X.Z. Tang, **B. Yu**, J.L. Yang. Improved interfacial shear strength between polymer and carbon fibers modified with branched Polyethylenimine. *The International Conference on Experimental Mechanics (icEM2014) in conjunction with the 13th Asian Conference on Experimental Mechanics (ACEM)*, Singapore, 15-17 November 2014.
4. X.T. Li, **B. Yu**, J.L. Yang. The effect of winding pattern and yarn size on the stress distribution of filament-wound composites. *The International Conference on Experimental Mechanics (icEM2014) in conjunction with the 13th Asian Conference on Experimental Mechanics (ACEM)*, Singapore, 15-17 November 2014.
5. **B. Yu**, J.L. Yang. Hygrothermal Effects on the Interfacial Properties of Surface Treated Metal Composite (Ti-CFRP) Laminates. To attend and oral present at the *ASME 2015 Applied Mechanics and Materials Conference*, Seattle, America, 29 June-01 July 2015.
6. **B. Yu**, J.L. Yang. Long-Term Interfacial Performance of Surface Treated CFRP Composites under Hygrothermal Conditions. To attend and oral present at the *20th International Conference on Composite Materials*, Copenhagen, Denmark, 19-24 July 2015.