

EFFECT OF SURFACE TREATMENT ON BONDING BEHAVIOR OF WET LAYUP CFRP—STEEL JOINT AND ITS HYDROTHERMAL DETERIORATION MECHANISM

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**EFFECT OF SURFACE TREATMENT ON
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Jiajing XIE

**EFFECT OF SURFACE TREATMENT ON BONDING BEHAVIOR
OF WET LAYUP CFRP-STEEL JOINT AND ITS
HYDROTHERMAL DETERIORATION MECHANISM**

A Thesis Submitted
In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Engineering

By
Jiajing XIE



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GRADUATE SCHOOL OF ENGINEERING
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CERTIFICATE

The undersigned hereby certify that they have read and recommended to the Graduate School of Engineering for the acceptance of this thesis entitled, “*Effect of Surface Treatment on Bonding Behavior of Wet Layup CFRP-Steel Joint and Its Hydrothermal Deterioration Mechanism*” by **Jiajing XIE** in partial fulfillment of the requirements for the degree of **Doctor of Engineering**.

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ABSTRACT

With the development of society, steel structures have been widely used in the construction industry in the past decade. As the service life increases, steel structures are affected by the temperature, humidity and airborne sea salt in the coastal areas, and local corrosion may occur. In order to extend the service life of steel structures, engineers have adopted various measures to reinforce the corroded parts, to maintain their structural strength. Among the many reinforcement methods, the wet resin-impregnated carbon fiber cloth layering method is widely used because of its convenient construction, easy transportation, light weight, and other characteristics.

Achieving an effective connection between carbon fiber composite materials and steel is one of the key technologies in structural reinforcement. In addition, during the service process, the adhesive and the carbon fiber composite material resin matrix are easily affected by the temperature and humidity in the external environment, and long-term effects will cause the material to age, reduce the material performance, and shorten the service life. The aging of the resin matrix will also cause galvanic corrosion between the carbon fiber composite material and the steel structure, which will have a negative impact on the structural reinforcement. Therefore, in order to improve the reinforcement effect and extend the service life of CFRP–steel joints, it is necessary to study the effects of different surface treatment methods on the performance of the composite joint, the aging failure mechanism caused by the hygrothermal action, and the galvanic corrosion phenomenon between the carbon fiber and the steel structure.

To solve the above problems, this thesis investigates the effect of surface treatments on the adhesive strength of CFRP–steel joints, as well as the aging and corrosion behavior of joints during service. Initially, the study analyzed and discussed the influence of five typical surface treatment methods on the bonding behavior of uncorroded steel surfaces through experiments, and adhesive strength and evaluated the rust removal efficiency for corroded steel of these surface treatment methods. Moreover, the effectiveness of the pre-coating process in improving joint adhesive strength is tested through experiments and discussed the influence of curing temperature on joint adhesive strength to determine the optimal construction season for better initial adhesive strength. Building upon the results of the above studies, the thesis further discussed the effect of

surface residual rust on the joint bonding performance of de-rusting corroded steel. Furthermore, the study analyzed the deterioration mechanism of joints and resin matrix under simulated aging conditions and considered the effects of temperature and moisture on the mechanical properties and durability. Finally, experimental analysis was conducted on the galvanic corrosion between CFRP and steel, the progression mechanism of CFRP peel off from the bonding surface due to corrosion was also analyzed.

The results indicate abrasive blast treatment (ABT) provided the best adhesive strength on uncorroded steel surfaces. For corroded steel, ABT has the best rust removal efficiency and adhesive strength. In cases where ABT cannot be used, rust can be removed by a combination of disc sander (DS) and wire brush (WB), but this would produce an oxidized film on the surface of steel which affects the adhesive strength. During reinforcement operations on steel structures, the pre-coating process can effectively enhance the adhesive strength of CFRP–steel joints. Furthermore, higher environmental temperatures (35 °C) can improve the curing effect of the joint's resin matrix, contributing to increased bonding strength. Among the environmental factors influencing joint aging, moisture and temperature play a primary role. Moisture ingress leads to plasticization of the joint's resin matrix, causing a decrease in tensile strength. Higher environmental temperatures promote moisture uptake, and the negative effects caused by moisture cannot be eliminated through physical dehumidification methods. Additionally, the carbon fibers exhibit anisotropic electrochemical behavior, with more severe corrosion occurring when the cross-sections of carbon fibers are in contact. Corrosion progresses through gaps formed by resin deterioration into the interior of the adhesive interface, leading to the resin peel off from the steel surface. This is especially pronounced when there is pooling of water at the degraded part of the joint, resulting in more severe galvanic corrosion.

Keywords: Steel structure, CFRP, Surface treatment method, Bonding behavior, Hygrothermal aging, Galvanic corrosion

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CHAPTER 1 INTRODUCTION

1.1 Research background

With the development of the human industrial level and the needs of social development, since the 1950s, a large number of bridges have been built around the world, with the rate of construction peaking in the 1970s[1]. To realize energy saving and environmental protection, steel bridges are widely constructed due to their short construction time and low environmental impact[2]. According to statistics, 40% of all bridges are made of steel in the United States [3]. In Japan, there are more than 50,000 steel bridges maintenance, and more than 50% of them have been in use for more than 70 years[4]. The study by Kulicki et al. confirms that corrosion of steel is one of the most serious threats to the stability of bridges[5]. The corrosion of the bridges can lead to gradual weakening, reduced structural strength and even collapse[6–8]. The annual corrosion cost accounts for approximately 3 ~ 4% of the GDP of industrialized countries[9]. Therefore, in order to extend the service life of steel bridges, corroded areas need to be descaled and reinforced.

In recent years, fiber-reinforced polymer (FRP) composites have been increasingly used in civil engineering applications. Of these, carbon fiber-reinforced polymers (CFRP) have been widely used to reinforce structures because they possess the desirable features of light weight[10], high specific mechanical properties, fatigue resistance, and high corrosion resistance[11–15]. Compared with CFRP laminates, carbon fiber fabrics are easy to transport and construct, which can effectively reduce the construction cost, and the material cost is much lower than that of CFRP laminates. During the process of reinforcing corroded structures, the carbon fiber fabric is more flexible than the CFRP laminate and can be applied to narrow or curved parts, such as pipelines and bridge piers. Therefore, the use of carbon fiber fabric to reinforce corroded structures is receiving increasing attention, and it is becoming popular as a construction material[16,17].

As early as the early 1970s, the wet layup process of carbon fiber was applied in laboratories in the United States[18,19]. Following closely, Japan and Europe began their research on the wet

layup process[20]. By the 1980s, the wet layup process had gained widespread development globally, initially being employed in the aerospace and automotive manufacturing industry[20–22]. From the 1990s to the present, Japan has consistently worked on integrating the wet layup process with other technologies to meet the diverse demands for high-performance and lightweight materials in various industries[20], the Nippon Expressway Research Institute has produced a design and construction manual on the wet-layup reinforcement methods for corroded steel members[23,24], and a guideline for the retrofitting of steel bridge piers using carbon fiber sheets has been published by the Public Works Research Institute of Japan[25]. In 2016, a company in Japan framed a peeling-less CFRP bonding method[26]. Presently, although this repair method has been applied to aging structure members in practice, there are no globally unified manufacturing and inspection specifications owing to the lack of basic research data. As shown in **Fig. 1-1**, there is a re-deterioration case of the corroded part after CFRP reinforcement (wet layup by 19-layer carbon fiber fabrics) in the vertical member of a truss bridge. The reinforced site rusted again under the CFRP layer after several years of service, whereas the bonding interface of the composite joint completely failed. This may be due to the insufficient corrosion surface treatment before pasting CFRP, there is corrosion release expansion; may also be caused by manual errors during the paste process, CFRP is not adhesive tightly, and the reinforced parts of the gap and thus the occurrence of the gap corrosion, resulting in the failure of the bonding interface. The widespread use of power tools for the de-rusting of steel members on-site is difficult to achieve a high-quality laboratory-prepared surface, which might be the main cause of premature deterioration. Poor surface conditions, low adhesion quality, and unstable curing conditions further accelerate deterioration owing to the multiple effects of environmental factors and loads. Steel-adherent interfaces present a difficult set of problems in practice, such as adhesion debonding, which is one of the potential obstacles limiting CFRP applications in civil engineering, power utilities and automotive industry, etc.[27–32]. The bond behavior between CFRP and metallic bases has been widely investigated across different fields. In previous studies, most scholars have focused on undamaged alloys or steel substrates. Li and Xu investigated the bond behavior between CFRP plates and corroded steel plates, mainly considering the effects of corrosion duration and adhesive thickness[33,34], but did not consider de-rusting efficiency or

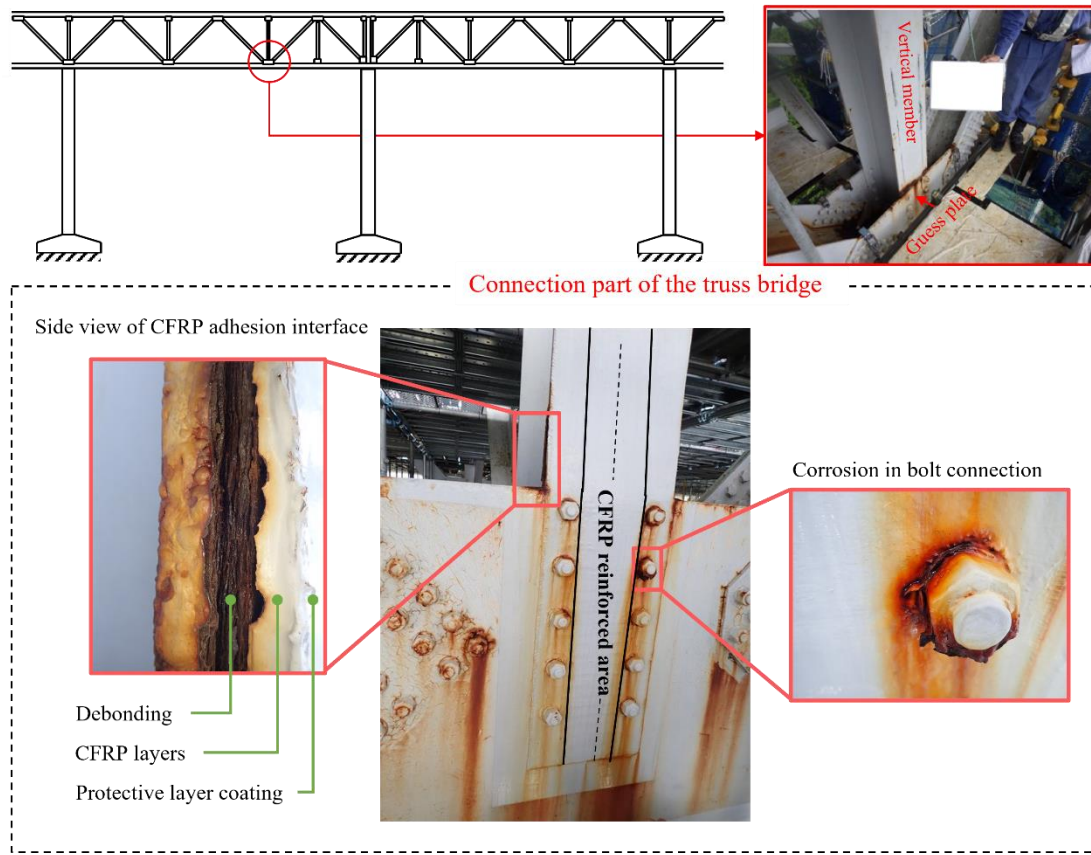


Fig. 1-1 Deterioration of adhesion interface of a CFRP–steel strengthened portion in vertical member on a truss bridge in Japan

rust residue problems. Therefore, the effects of surface characteristics and interface optimization on the bond mechanism require further investigation[35].

Besides, the CFRP interlayer resin matrix in the CFRP–steel joints serves as the polymer material. In the complex service environment of the bridge is very susceptible to temperature[36,37], humidity[38,39], ultraviolet rays[40], salt spray[41] and other environmental factors, so the mechanical properties change. Under the long-term effect of environmental factors, the aging phenomenon will occur, leading to the decline of mechanical properties, so that the premature failure of the structure, seriously affects the safety of the bridge[42]. Among them, temperature and humidity on the mechanical properties of the most significant impact, especially when the two together will make the aging more serious[43]. Therefore, studying the aging failure mechanism of composite materials under the joint action of temperature and humidity, and quantitatively evaluating the change of structural mechanical properties due to aging is an

effective way to achieve the goal of accurate prediction of residual strength after aging, which is of excellent practicability and important practical significance in engineering.

1.2 Research objectives and scope

In this study, the goal is to find a method to promote the adhesive strength of CFRP–steel joints in the corrosion area of steel structure, this method is effective, low-cost and easy to implement. Through the field project investigation, can be found that the parts which had been reinforced with CFRP would be peeled off from the surface of the steel structure with the passage of time. For this reason, the deterioration mechanism of CFRP–steel joint was investigated and discussed the influence of environmental factors and the electrochemical properties of CFRP in the deterioration process.

The main objectives of the dissertation are as follows:

- (1) Compare the several typical surface treatments used in construction, the purpose is to investigate the effect of various surface treatment methods on the surface characteristics of steel and determine which treatment provides better surface adhesive strength and which surface treatment can get the best rust removal results.
- (2) In order to optimize the construction process for better adhesive strength of the CFRP–steel joint. The effectiveness of the pre-coating process in enhancing the adhesive strength of CFRP–steel joint under the same surface treatment conditions was investigated, and the durability of the joint using the pre-coating process was tested. In addition, the effect of curing temperature on the adhesive strength of the joint was discussed by simulating ambient temperatures in summer and winter.
- (3) Utilizing de-rusted corroded steel plates, CFRP–steel joint and single strap specimens were fabricated for pull-off and tensile shear tests. A comparative analysis was conducted against specimens made from uncorroded steel treated with the same surface treatment methods. The discussion focused on the effect of residual rust and the formation of an oxide film resulting from the de-rusting process on the adhesive strength and shear strength of the joint.

- (4) Limited research has been performed on the deterioration of the new method involving wet layup CFRP reinforcement method. In order to predict the deterioration process of the strengthened area and optimizing the construction process to enhance durability and reduce costs. A hydrothermal aging test was carried out to investigate the effect of environmental factors such as moisture and temperature. The effectiveness of the physical drying method in eliminating the effects of moisture and restoring the mechanical properties of CFRP–steel joint is also discussed.
- (5) During field investigations, extensive corrosion in areas reinforced using the wet layup CFRP reinforcement method was observed. To study the corrosion behavior of the CFRP–steel joints, the anisotropic electrochemical properties of carbon fibers were investigated through electrochemical tests, and the galvanic corrosion behavior of CFRP and steel under different thicknesses of water film conditions is discussed. Moreover, the process of CFPR peeling from the reinforcement site due to corrosion was analyzed by a electrode array tests.

1.3 Literature review

With the wide application of composite structures, the durability of CFRP composites has received much attention. The key research areas are to improve the bonding strength of CFRP–steel joints, to understand the potential deterioration mechanisms, and to evaluate the remaining structural strength after long-term aging. In this section, bond behavior, environmental durability, and galvanic corrosion in joints are selected to be reviewed.

1.3.1 Bond behavior of CFRP–steel joint

Reinforcement parts of the clean degree of corrosion will affect the adhesive strength, later subsequent service life, ISO 8501-1[44] and JIS Z0313[45] classify the degree of corrosion of steel surfaces from A to D, as shown in **Table 1-1**. And the cleanliness level of corroded surfaces treated by electric power tools and blasting is shown in **Table 1-2**. The bridge maintenance manual of the USA recommends protocols for rust removal, including hammering, blasting, and knife

scraping[46] and the current commonly used surface treatment methods as shown in **Table 1-3**[47].

Table 1-1 Classification of corrosion degree of steel surface[44,45]

Degree	Surface condition of steel
A	Mostly covered with hard mill scale and very little rust
B	Rust is beginning to form and mill scale is beginning to delaminate
C	All surfaces are covered with rust, and mill scale can be easily scraped off
D	All surfaces are covered with rust and considerable erosion is observed on the bare steel surface

Table 1-2 Clean level of corroded surface treated by electric power tools and blasting

Specification	SSPC ¹⁾	ISO (SIS) ²⁾	SPSS (JSRA) ³⁾
Steel surface	Near-white blast cleaning, SP-10 (above 95%)	Sa 2.5	Sh 2, Sd 2
preparation	Power tool cleaning, SP-3	St 3	Pt 3

1) Steel Structures Painting Council

2) International Standard ISO 8501-1 (Swedish Standard SIS 05 5900-1967)

3) Standard for the Preparation of Steel Surface Prior to Painting (Japan Shipbuilding Research Association)

Table 1-3 Major methods of surface treatment[47]

Theory	Method	Introduction
Physical	Blast	Projecting abrasive material at high speed onto a treated surface to remove rust and coating films, etc., Forming a surface roughness on the steel surface.
	Power tools	Remove rust and coating film by grinding steel surfaces using tools driven by electricity or compressed air
	Hand tools	Using a power rod, hammer, wire brush, etc. Complete rust removal is difficult because it requires a great deal of labor alone.
Chemical	Pickling	A method to remove rust and oxide film on the steel surface by using acidic chemicals.
	Chemical treatment	A method that forms a phosphate film on the surface of the treated surface using phosphoric acid, etc.

Years of practical experience have taught us, it is impossible to achieve 100% rust removal on-site, and residual rust will directly affect the mechanical and durability properties of the bonding interface[48]. Corrosion damage optimization should reflect not only the change in surface geometry but also the surface cleanliness, chemical composition, and modification method[49].

Guo et al. reviewed current studies on rust removal techniques and analyzed their cleaning efficiency and environmental impact[50]. However, most de-rusting requirements are designed for repainting, wherein the adhesion interface is different from that of the composite joint. Moreover, the quantitative characterization of corroded steel plates associated with different de-rusting methods remains insufficient. Surface treatment changes the physical and chemical properties of a steel surface and can alter the strength and failure mode of the bonded joint[51,52]. However, classical Euclidean geometry methods cannot sufficiently describe the complexity of the profile characteristics of corroded surfaces[53]. Hence, the fractal geometry established by Mandelbrot[54] has gained considerable attention because it overcomes the disadvantages of conventional statistical analysis. Harris et al. reported that the measured maximum adhesive strength of a steel substrate is related to its fractal dimension[55]. Amada et al. proved that a blasted surface has fractal characteristics of self-affinity[56,57]. Xu et al. indicated that corrosion would cause a significant decrease in fractal dimension[58]. Recently, fractal dimensions have been proposed as a novel evaluation method for the representation of corroded surface topography[59].

In addition to the properties of the steel, the adhesive strength of CFRP–steel joint is also influenced by the bond area and the strength of the adhesive itself, as well as by defects within the adhesive. The defects can be divided into three categories according to their position in the bonded system: interface defects, adhesive defects, and adherends defects[60]. The typical defects in the bonded system are illustrated in **Fig. 1-2**. Like concrete[61], there is an effective bond length beyond which an extension in the bond length cannot increase the ultimate capacity of the joint. Yang et al. according to the double-lap test define that the effective bond length of the CFRP-to-steel interface may range between 135mm and 150mm[62]. Wu et al. presented an experimental and numerical study on the effects of bondline defects on the bond behavior of CFRP–steel double strap joints[63], results show the defect area affects the failure mode, the defect size has a more crucial effect on the failure mode than the defect number. When the defect

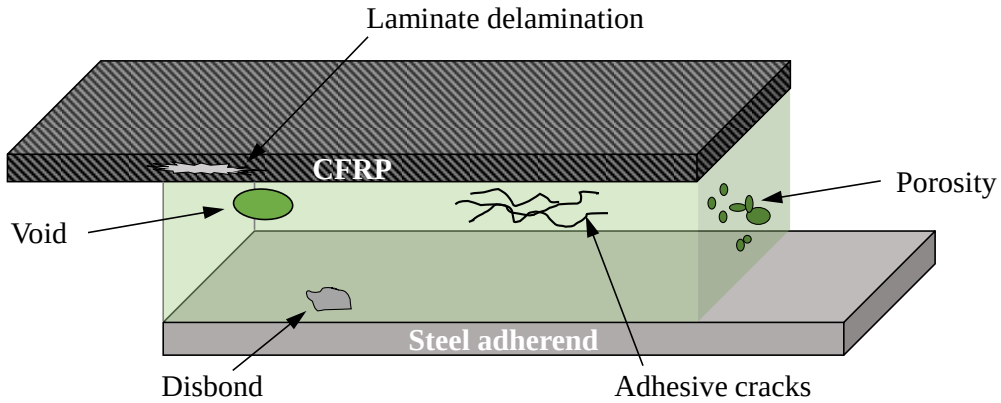


Fig. 1-2 An illustration of the typical defects in the adhesive bonded system[60]

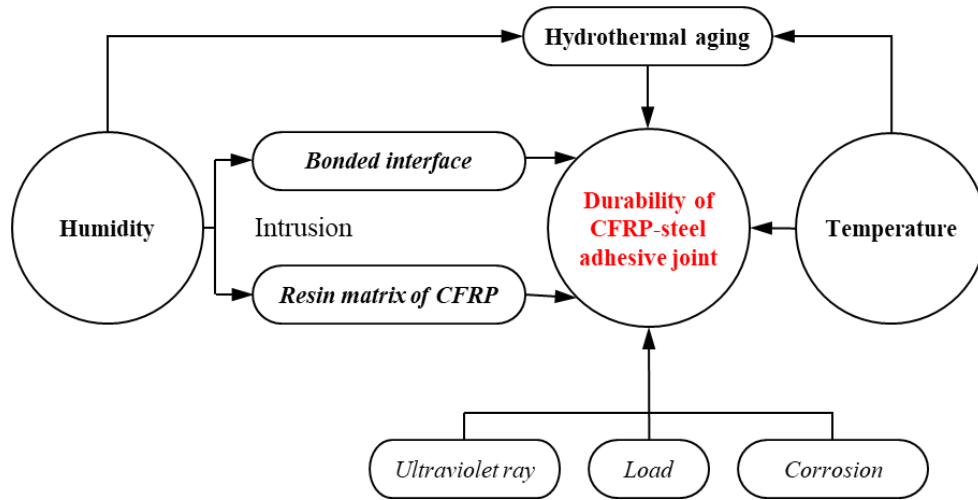


Fig. 1-3 Factors affecting the environmental durability of composite joint

area is larger than 20% of the bonded area, the dominant failure mode is steel-adhesive interface debonding.

1.3.2 Factors affecting the environmental durability of CFRP-steel joint

As shown in **Fig. 1-3**, the environmental durability of composite structures is affected by a number of factors. The influence of environmental factors such as temperature[64,65], thermal cycling[66,67], moisture[68–70], ultraviolet radiation[71], aging effects occur, leading to change in the chemical properties of the resin and a decline in mechanical performance. Among these environmental influences, moisture and hydrothermal aging are the main factors[72]. In addition,

the composite structure in service will also receive corrosion effects, corrosion and temperature, humidity and each other together to further accelerate its aging process.

1) Humidity

The resin matrix as well as the adhesive in CFRP, as polymers, are extremely molecularly mobile and permeable to all gases and liquids. CFRP reinforcement materials are highly susceptible to moisture during service, water intrusion affects the material properties of the polymer, leading to a reduction in the bond between the resin and carbon fibers and a reduction in the adhesion between the CFRP and reinforced structure[73]. According to previous studies, moisture may occur as humidity, liquid water, seawater, and other aqueous solutions, and moisture enters the CFRP or joint in three main ways: 1) diffusion from the surface layer of the resin composite to the interior, 2) wicking along the interfaces between the adhesives and adherents, and 3) absorption through the porous adherent[74]. More importantly, hygroscopic behavior is closely related to temperature[75,76]. Therefore, gaining insights into the effects of hygrothermal conditions on composites is crucial. Previous studies indicate that when moisture diffuses into the resin matrix, it can lead to defects due to plasticization, hydrolysis, swelling, and cracking[77–80]. Moisture ingress into resins typically occurs in two distinct forms: one is as free water infiltrating the material's interstitial space, thereby inducing plasticization, the diffusivity is affected by the physical properties of the material. The second form manifests as bound water, where hydroxyl groups (-OH) can engage in the formation of one or multiple hydrogen bonds with water molecules. These bonds subsequently result in material expansion, and plasticization, followed by a reduction in both strength and the glass transition temperature (T_g) of the material [81]. Moisture also penetrates further along the fibers, causing cracks within the material and penetrating the bonding interface between the composite and steel, leading to corrosion and further reducing the bonding properties[82–86]. However, the plasticization caused by moisture is reversible under certain conditions, Moy[87] et al. suggest that in the early stages of humidity-induced structural performance deterioration, damage is reversible, primarily manifested as a decrease in elastic modulus, strength, and the glass transition temperature (T_g). Upon thorough

drying, this impact can be nearly eliminated, restoring the material to its pre-humid aging performance. However, further aging leads to irreversible damage and crack formation.

Moisture absorption causes volume expansion of both the polymer matrix and the composite material, leading to moisture expansion and moisture expansion stresses. In the case of polymer/inorganic fiber composites, the rate of moisture absorption and saturation hygroscopicity of the matrix is much greater than the corresponding values for the fibers, and thus the wet swelling of the matrix is limited by the fibers. When the sum of this stress and other internal stresses frozen in the preparation of high-performance resin matrix composites is sufficiently large, cracking of the matrix may be induced[88,89]. Adamson et al.[90] investigated the thermal expansion and swelling behavior of epoxy composite systems exposed to water, and the results showed that the amount of swelling of the epoxy resin after curing was slightly less than that of the body that absorbed the water, and the rate of swelling changed with the moisture content of the polymer and changes. In addition, the thermal expansion of the cured epoxy resin after reaching the moisture absorption equilibrium was more than twice that of the dried resin.

Most studies conducted by researchers have focused on the hygroscopic properties of the polymers and the effects of moisture and temperature on the mechanical properties of CFRP-steel joints. From their results, hygrothermal aging has a significant impact on the mechanical properties of the CFRP-steel joints, with significant decreases in its tensile, compressive, and shear properties after hygrothermal aging[91–94]. However, the relationship between the moisture uptake and the degree of mechanical property deterioration is unclear, and the recoverability of the mechanical properties of the material has not been assessed. The recoverability of CFRP material properties is crucial to ensuring the durability of the material and assessing the structural strength change in the reinforced parts. If CFRP can spontaneously recover owing to changes in ambient temperature and humidity or by manual methods, the service life of the material will be significantly extended.

2) Temperature

The resin matrix in composites acts as a polymer material and the molecular mobility increases under high temperature conditions. Intermolecular chain forces and molecular motion in the

amorphous region are reflected by the glass transition temperature T_g . When the aging temperature of the adhesive is lower than T_g , its failure strength and modulus of elasticity are higher but the ductility decreases, while its performance is opposite when the temperature is higher than T_g [95,96]. Zhang et al.[97] investigated the accelerated thermal aging behavior of pure epoxy resin and carbon fiber/epoxy composites. The results showed that epoxy deterioration occurs in the surface region and the surface oxide layer protects the internal resin from further oxidation. Matrix aging is the main aging mode when the temperature is below the T_g of the pure epoxy resin, while debonding occurs at the fiber/matrix interface when the temperature is above the T_g . Wolfrum et al.[98] investigated the thermal aging behavior of two CFRPs and observed thermal and oxidative deterioration of epoxy resins by infrared spectroscopy (IR) and mass spectrometry (TD-GC/MS), with a large loss of mass and interlaminar shear strength (ILSS) after successive high-temperature aging, and the intensity of aging products, such as carbonyls, in the infrared band increased with the extension of the aging time and was correlated with the amount of oxidative product desorption.

However, the chemical reactions that occur during high-temperature aging are not entirely detrimental, as many thermoset resin products are not fully cured in manufacture, post-curing may occur when sustained at suitably high temperatures for a period of time, and the higher the temperature, the faster the rate of post-curing[99]. The positive effect of post-curing is to increase the T_g and high-temperature modulus of the material and to some extent enhance the mechanical properties of the composite structure[100]. The effect of different post-curing conditions on the toughness of fiber-reinforced composites was investigated by Tucker et al[101]. The results showed that post-curing was able to promote the completion of the cross-linking reaction in a very short period of time, ensuring the mechanical stability of the polymer while leading to the relaxation of the cross-linked network. The relaxation of the molecular network may improve the ductility of the polymer and hence its toughness.

1.3.3 Corrosion behavior of CFRP-steel joint

CFRPs have attracted considerable interest as structural engineering materials, for example, in the repair and reinforcement of steel structures. However, the possible galvanic corrosion occurring when carbon and steel are bonded is concerning, as shown in **Fig.1-4**. Notably, carbon fiber (CF) is a highly efficient cathode with a relatively noble potential in galvanic series[102]. Therefore, a significant potential difference between CFRP and metals is caused by the galvanic corrosion occurring between dissimilar materials electrically connected in the electrolyte. Galvanic corrosion of metals coupled to CFRP composites was reported decades ago; however, it has not yet been resolved[103–105]. The anodic metals of interest include steel, aluminum, and various alloys. Galvanic corrosion results in the steel, serving as the anode, being sacrificially corroded owing to its connection with the cathodic CFRP, which may lead to locally accelerated corrosion in the form of pitting or crevice corrosion. However, the galvanic corrosion characteristics are subject to specific influencing factors. Some researchers have indicated that metallic materials experience accelerated corrosion when coupled with more noble materials, which is primarily determined by the change in the local chemical environment (inside the crevice or pitting)[106]. Li et al. investigated the atmospheric corrosion of Al and Mg coupled to CFRP using friction stir blind riveting joints after a six-month exposure to a marine environment. Their results indicated that various anode metals and related corrosion products can cause significant differences in corrosion acceleration[107]. Therefore, the corrosion properties of steel members coupled with CFRP are highly related to on-site environmental factors and component form. However, limited test data are currently available for reference.

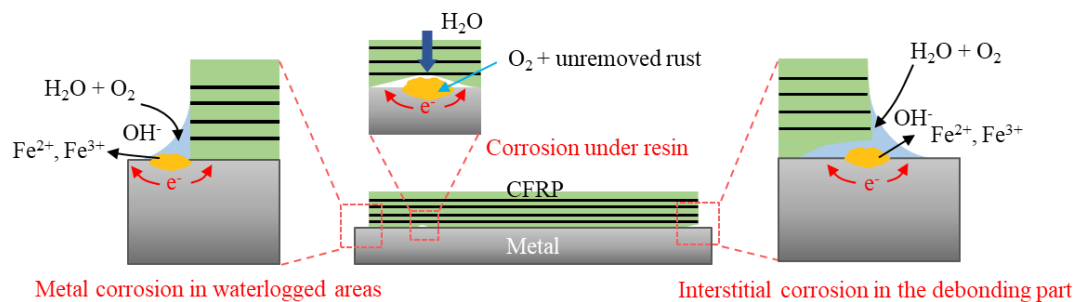


Fig. 1-4 Diagram of galvanic corrosion of metal and carbon fiber

In the field of civil engineering, CFRP-strengthened steel structures are susceptible to galvanic corrosion, particularly those used in high-humidity and wet-dry cycling environments[108,109]. High-humidity environments result in the presence of an electrolyte in the reinforced composite joint. Although an electrical insulator, such as an epoxy resin adhesive, can prevent galvanic corrosion between two materials, blocking electrical contact entirely is challenging in practice[110]. Wu et al[111]. Recommended that a layer of glass fiber sheet (GFS) be embedded in the adhesive layer to protect the CFRP-steel bonded system against galvanic corrosion, but the inclusion of GFS in the adhesive negatively affected the bond behavior between steel and CFRP. Ostapiuk et al.[112] tried to use PEO and the combination of PEO and sol-gel as a protective layer to prevent the galvanic corrosion between AZ31 alloy and CFRP, but the results showed that the PEO layer could not prevent the electrical coupling between the two, and could only slow down the formation of the electrical coupling between AZ31 alloy and CFRP in a short time. The pinhole in the CFRP and air bubbles in the adhesive layer may cause the CF filaments to make electrical contact with the steel during the reinforcement process and after hardening. In particular, this phenomenon often occurs in the case of localized strengthening methods using a continuous CF cloth with an epoxy resin wet layup on-site.

1.4 Organization and outline

The main content of this dissertation is divided into seven chapters, which are introduced in detail in chapters 1-7:

In Chapter 1, the research background and objective of this dissertation were proposed. Literature reviews relating to bond, aging, and corrosion behavior of CFRP–steel joints were summarized. The organization of the dissertation was illustrated at the end.

In Chapter 2, the interfacial bond behavior of CFRP–steel joint associations with five different surface treatments commonly used in practical construction was focused. The specimens were fabricated based on wet layup CFRP and uncorroded steel plates. The bonding effectiveness of five surface treatment methods was investigated, Surface characteristics produced by various treatment methods were compared, and qualitatively established their relation to bonding

behaviors and failure modes. The effectiveness of these surface treatments in removing rust from corroded steel surfaces is also discussed.

In Chapter 3, the effect of the pre-coating process and curing temperature on the adhesive strength of CFRP–steel joints was examined through a pull-off test. Firstly, the effectiveness of the pre-coating process to improve the bonding properties of steel surfaces after different surface treatments was discussed. The durability of the pre-coating process was also investigated through dry-wet cycle tests. Then, ambient temperatures of summer and winter were simulated, joint and CFRP laminate were fabricated at these temperatures using the wet layup process. The adhesive strength of the joint and the porosity of the CFRP laminate were compared at the two curing temperatures.

In Chapter 4, the mechanical properties of the three surface treatments selected in Chapter 2 for better rust removal were evaluated. The adhesive strength of the corroded steel surface after rust removal was discussed through a pull-off test and shear test. A comparison was made with the bonding properties of an uncorroded steel surface treated with the same methods, and the failure modes were analyzed.

In Chapter 5, the changes in mechanical properties of CFRP–steel joint as well as resin dog bones after hydrothermal aging were discussed through pull-off and tensile test. The relationship between moisture uptake and the decrease in mechanical properties was analyzed. Feasibility of restoring joint mechanical properties through physical heating for dehumidification was discussed. Additionally, the changes in the thermophysical properties of the resin matrix during the hydrothermal aging were examined, and the deterioration mechanisms of joint were analyzed.

In Chapter 6, factors influencing the corrosion behavior of carbon fiber sheet and steel were discussed through electrochemical experiments. Initially, the anisotropic electrochemical behavior of single carbon fiber was examined. On this basis, the corrosion behavior of CFRP and steel under different contact forms were discussed. Additionally, the process of CFRP peel off from the steel surface due to corrosion at the CFRP-steel joint was simulated using an electrode array. The corrosion mechanisms between carbon fiber sheet and steel were also discussed.

In Chapter 7, the work presented in this dissertation were summarized and proposed further research topics that emerged from this work.

The flowchart of work in this dissertation is shown in **Fig. 1-5**, and the main experiment list of fundamental and targeted research in this work is shown in **Table. 1-4**.

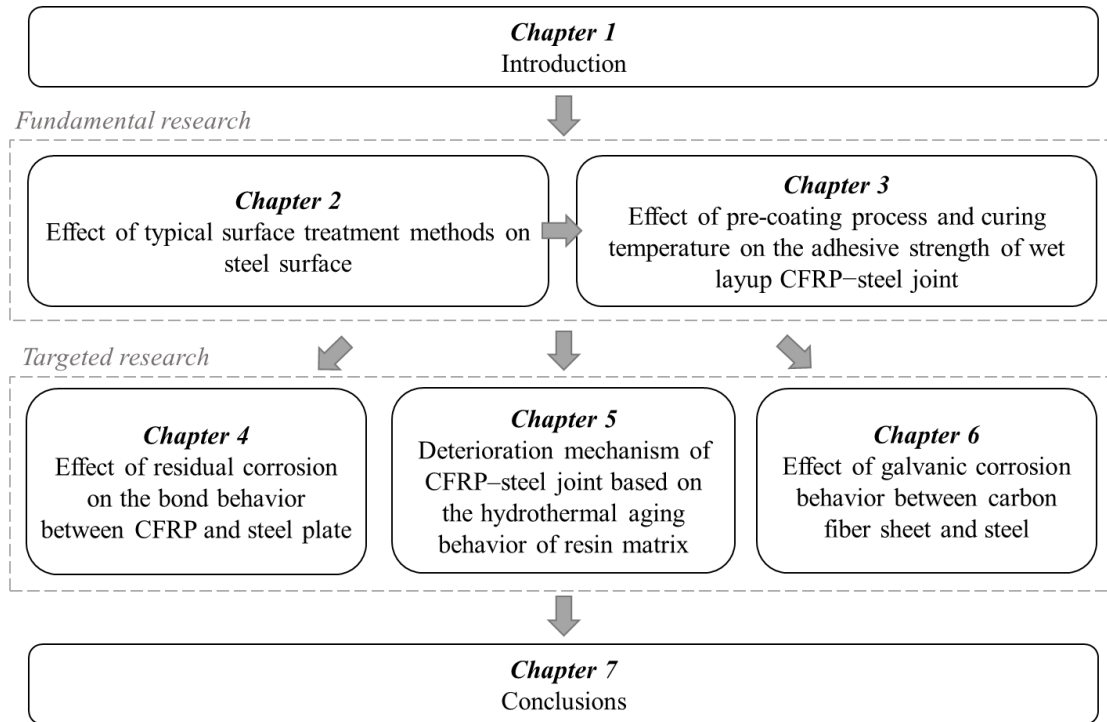


Fig. 1-5 The flowchart of this work

Table 1-4 The list of main experiments in this work

	Experiment
Chapter 2	Pull-off test, EDX
Chapter 3	Pull-off test, DSC, XRD
Chapter 4	Pull-off test, Tensile shear test
Chapter 5	Water absorption test, Hydrothermal aging test, FT-IR, DSC Pull-off test, Tensile test
Chapter 6	OCP, EIS, Galvanic corrosion test, Electrode array test

CHAPTER 2 EFFECT OF TYPICAL SURFACE TREATMENT METHODS ON STEEL SURFACE

2.1 Introduction

Carbon fiber-reinforced polymers have been widely used as reinforcements in different types of structures[113]. The bond behavior of the reinforcement system is the key to reinforcing effect and durability. In the reinforcement of steel structures using CFRP, it is common practice to perform surface treatment on the structure's surface before reinforcement to achieve better adhesive strength. With technological advancements, surface treatment methods have evolved from manual to electric tools and different surface treatment methods are employed for different areas. However, the effects produced by various treatment methods differ. This chapter analyzes and discusses several representative surface treatment methods, and through an analysis of the post-treatment surface characteristics, it summarizes the relationship between surface properties and adhesive strength. In addition, the rust removal effect of these surface treatment methods is evaluated, which provides reference and recommendations for the selection of surface treatment methods in practical construction.

2.2 Specimen preparation and surface treatment methods

Dimensions of 150 mm × 70 mm × 6 mm hot-rolled steel plates adhering to the Japanese Industrial Standards (JIS) G3106 SM490A were used in this part to investigate the effect of surface treatment on steel surface. The chemical composition of the steel is shown in **Table 2-1**.

Table 2-1 Chemical composition of the steel used in the test (mass%)

C	Si	Mn	P	S
0.18	0.19	1.33	0.014	0.003

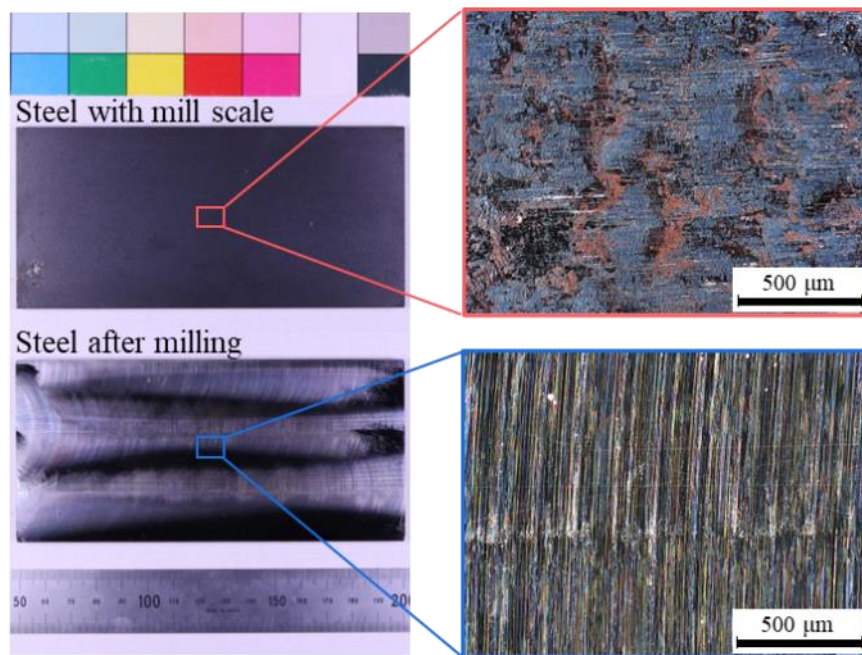


Fig. 2-1 Photograph of steel surface with mill scale and after milling

Two types of specimens were prepared for this experiment: uncorroded steel plates and corroded steel plates. The uncorroded steel plates were used to investigate the effect of different surface treatment methods on the surface characteristics of steel. The corroded steel plates were employed to evaluate the rust removal effectiveness of surface treatment methods.

To prepare the uncorroded steel specimens, hot-rolled steel plates were subjected to milling by an NV machine (cutting diameter: 50 mm, cutting speed 215 mm/min, revolutions per minute: 1369 rev./min, blade material: cermet) to remove the mill scale, obtain a smooth and even surface. Photographs of the surface before and after milling are shown in **Fig. 2-1**. After milling, wipe the surface of the steel plate with acetone to remove any milling lubricant residue on the surface, surface treatments were then carried out.

The corroded steels were prepared by the cyclic corrosion test (CCT). Before the CCT, the steel plates were first blasted with a blast machine (PB500P) to remove the mill scale from the surface (the method and criteria for the blasting process will introduce in the following), then remove the abrasive residues on the surface with a high-pressure air gun. Blasted steel plates were set in a salt spray test chamber. One side of the surface of all the blasted steel plates was exposed for 120 cycles of Cycle-D, as specified in JIS K 5600-7-9. Each cycle takes six hours and consists of 1)

atomization of salt water for 0.5 h (30 °C, RH 98%), 2) a wetting step for 1.5 h (30 °C, RH 98%), 3) a drying step with hot air for 2.0 h (50 °C, RH 20%), and 4) a drying step with warm air for 2.0 h (30 °C, RH 20%). During the CCT, the steel plates were set up at an angle of 15° to the vertical direction, based on JIS Z2371. After the CCT, the corroded steels were immediately stored in a dry cabinet before being subjected to subsequent tests.

Appropriate steel surface treatments are required to obtain the best adhesion strength between the steel and the wet layup CFRP laminate. In this section, five surface treatment methods used in practical construction are selected for evaluation. The five surface treatment methods are as follows:

- (1) Disc sander (DS): The specimen is treated by an electric rotating disc sander which is a basic electric tool for manual rust removal at remediation sites. The disc was made of SiC sandpaper (grit size 120 coarse, external diameter: 100 mm). The steel surface was rotated grinding evenly for at least 120 s.
- (2) Belt sander (BS): The specimen for which unidirectional polishing is conducted using a belt sander machine (grit size 120 coarse), one-way grinding for at least 300 s.
- (3) Wire Brush (WB): The specimen is treated by an electric rotating steel brush (diameter of steel wire is 0.5 mm) rotated grinding evenly for at least 120 s.
- (4) Bevel non-woven abrasive (BNA): An abrasive disc made of a bevel non-woven pad (external diameter: 90 mm, thickness: 13 mm) was installed on an electric rotating disc grinder and manually processed evenly on the steel surface at least 120 s.
- (5) Abrasive blast treatment (ABT): The specimen is blasted with steel grit (Mohs hardness: 10, JIS particle size index: 52.6, specific gravity: 7.4) under projectile pressure 0.7 MPa, projectile angle 60° and projectile distance 30 cm (ISO 8501-1 Sa2.5) for at least 10 s, the abrasive projection rate was 3.83 L/min.

After surface treatments, all steel plates were subjected to compressed air cleaning. The images of surface treatment tools are shown in **Fig. 2-2**, the power tool trajectory is shown in **Fig. 2-3** and treated surface photographs are shown in **Fig. 2-4**.

(a) Disc sander



(b) Belt sander



(c) Wire Brush



(d) Bevel non-woven abrasive



(e) Abrasive blast treatment

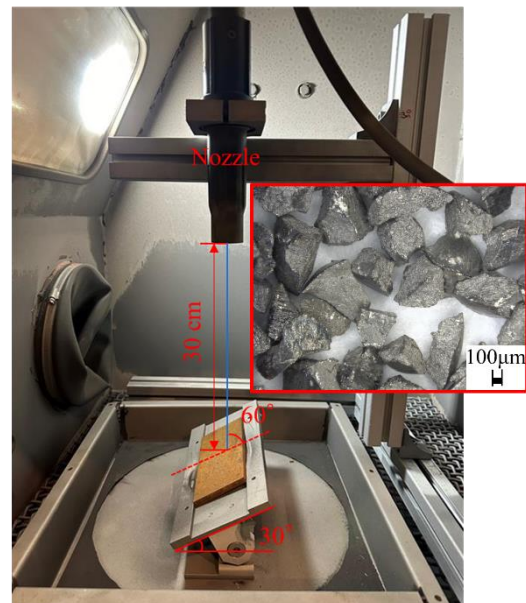


Fig. 2-2 Photographs of five kinds of surface treatment tools

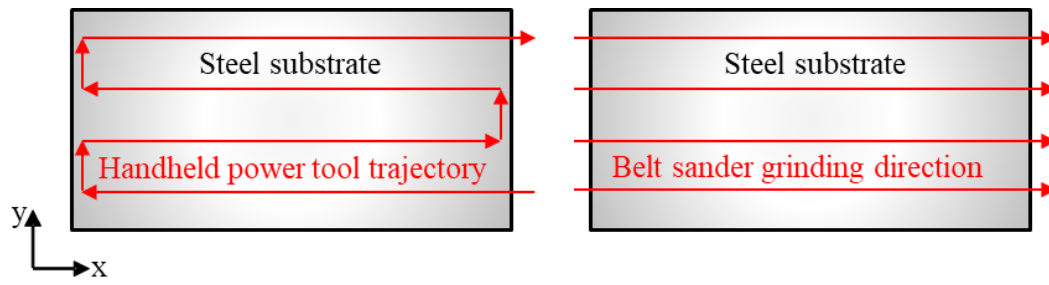


Fig. 2-3 Power tool trajectory

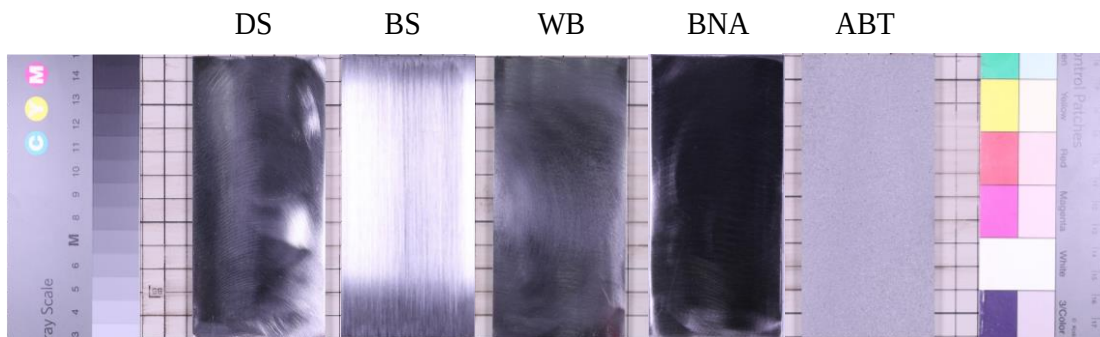


Fig. 2-4 Five kinds of prepared steel substrates

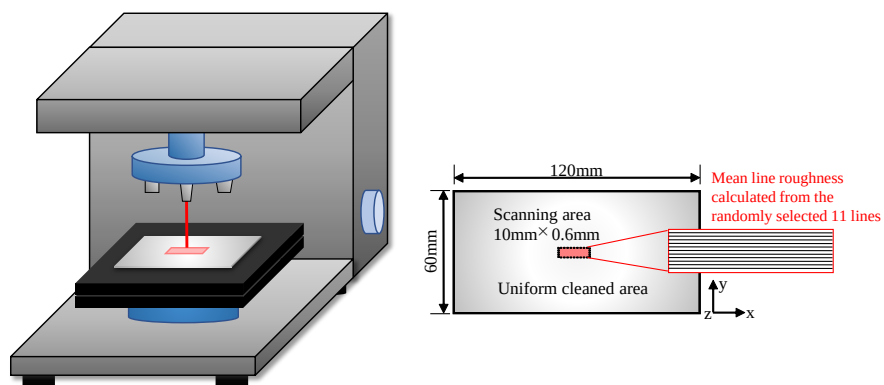


Fig. 2-5 Target area for line roughness measurement using a laser scanning confocal microscopy

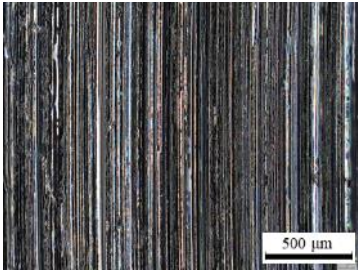
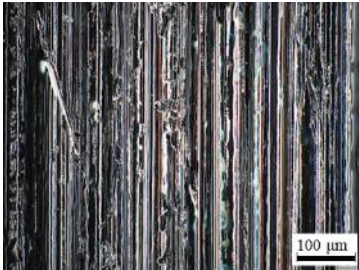
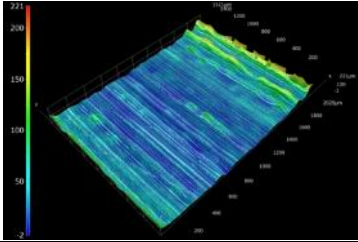
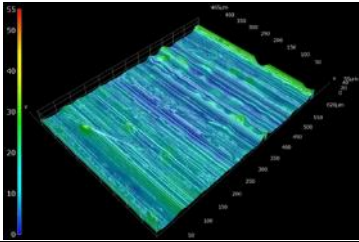
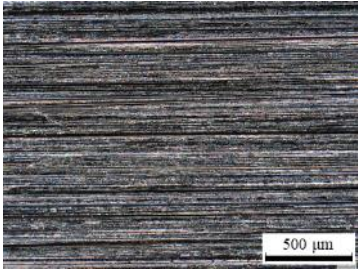
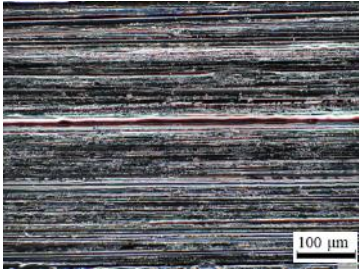
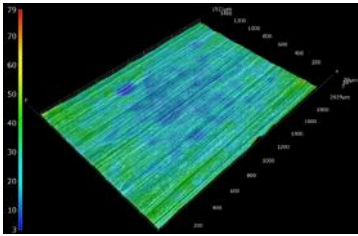
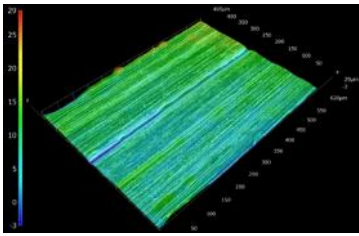
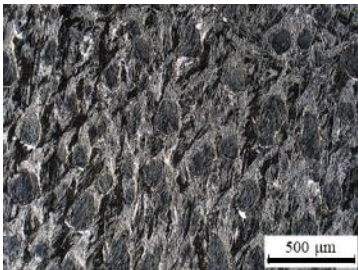
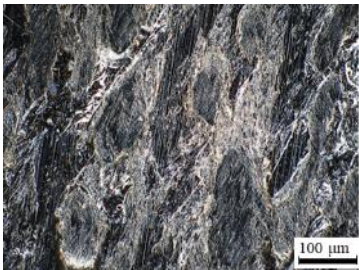
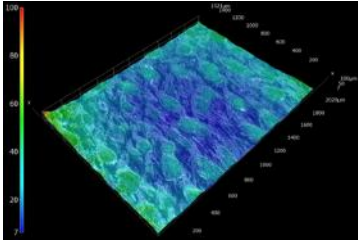
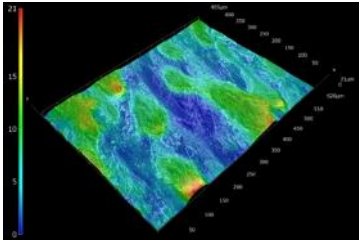
2.3 Effect of surface treatment on uncorroded steel

2.3.1 Surface properties of uncorroded steel substrate after surface treatment

To discuss the surface properties of the steel substrates after the five surface treatments mentioned above, the surface roughness of the five prepared steels was characterized via laser scanning confocal microscopy (OLS4500, Objective lens: 20x, planar resolution: 0.12 μm , z-direction resolution: 1 nm) (the following called LSCM) and a contact-type surface roughness tester (the following called CSR). The line roughness parameters were measured in a narrow area of 10 mm $\times$ 0.6 mm, the scanning area was as shown in **Fig. 2-5**, and the measurements were repeated 11 times to ensure the mean line roughness was obtained with high accuracy. Three-dimensional coordinate data of the steel surfaces were collected by LSCM over a scanning area of 20 mm $\times$ 20 mm to calculate the surface roughness. Furthermore, the treated surface was observed by optical microscopy at 140 and 500 magnifications as shown in **Table 2-2**.

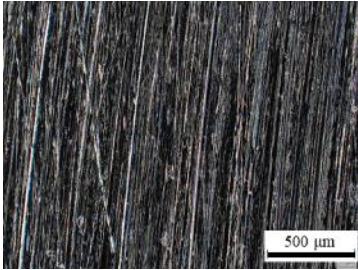
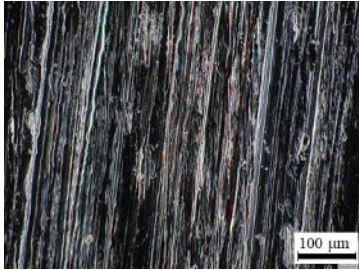
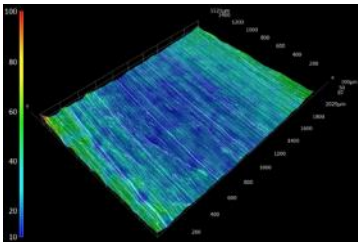
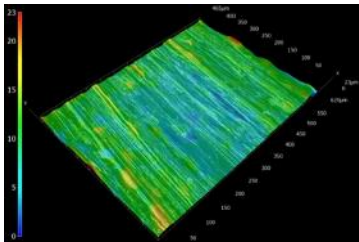
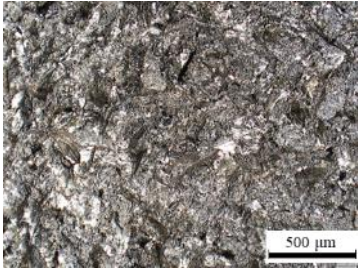
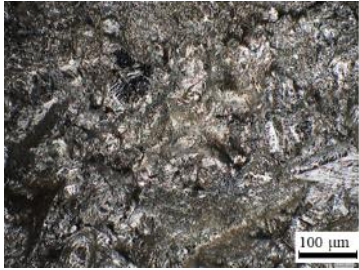
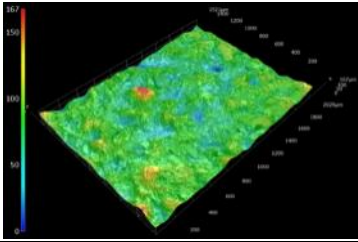
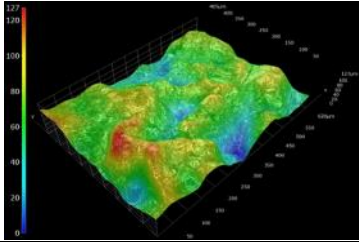
From **Table 2-2**, it can be observed that there are significant differences in surface morphology resulting from different surface treatment methods. On the steel surface treated with DS and BS, regular textures generated by unidirectional or rotational grinding were identified, with the patterns produced by BS being finer compared to DS. After WB treatment, tear-shaped indentations created by steel wire grinding were observed, and the indentations were evenly distributed. Although the surface of the specimens treated with BNA also showed patterns generated by the rotation of the grinding disk, they appeared relatively disorderly compared to DS. The surface of the specimens treated with ABT differed markedly from the surface morphologies caused by the other four treatment methods. Due to the high-speed impact of steel grit, the surface exhibited significant undulations, was extremely uneven, and specific patterns were not observed.

Table 2-2 Optical microscopy surface morphologies of five specimens

Magnification times	× 140	× 500
DS		
		
		
		
WB		
		

(Continue from last page)

Table 2-2 Optical microscopy surface morphologies of five specimens

Magnification times	× 140	× 500
BNA		
		
ABT		
		

Randomly selected line edge roughness profiles of the DS, BS, WB, BNA and ABT treated surfaces are presented in **Fig. 2-6**. As observed in the **Table 2-2**, the ABT treated specimen exhibits the most significant surface undulation, with a height difference exceeding 60 μm . In contrast, the surfaces of the remaining four specimens display relatively gentle undulations, with nearly equidistant valleys observable in the profile of the WB specimen. **Fig. 2-7** illustrates three line roughness indicators measured by LSCM and CSR.

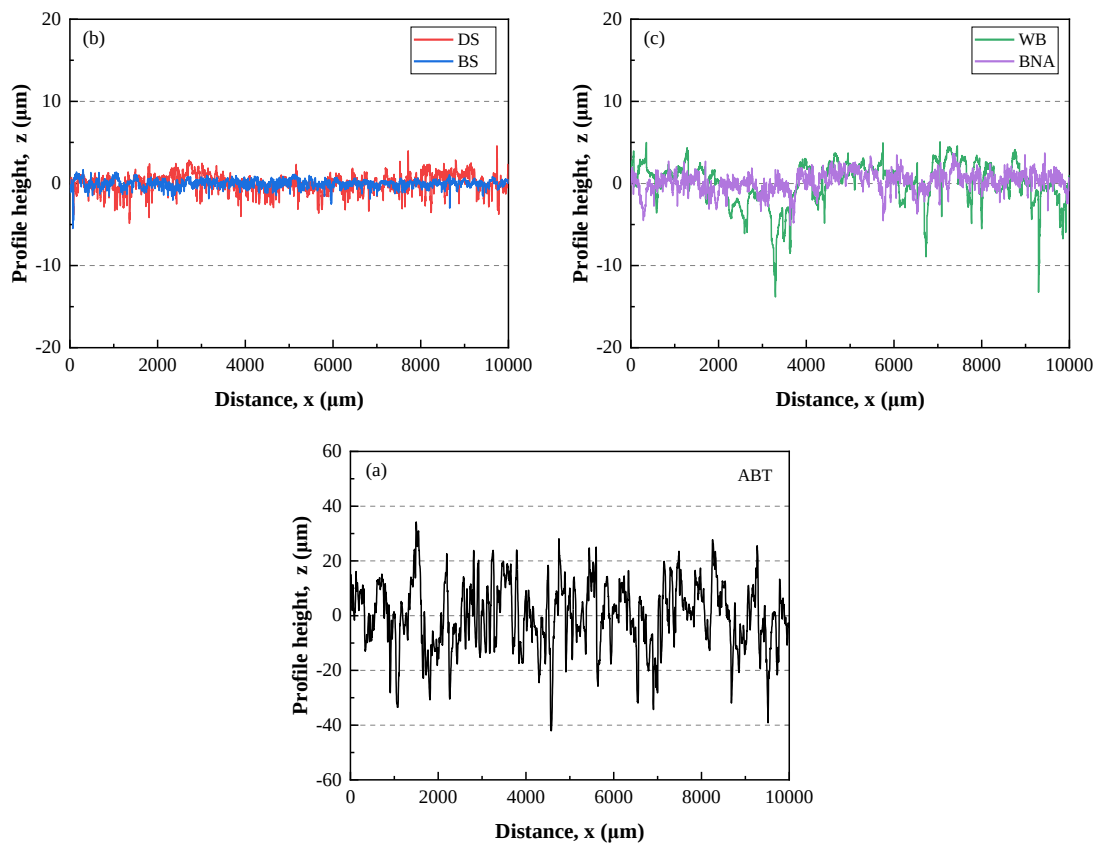


Fig. 2-6 Cross-sectional roughness of five specimens measured by LSCM

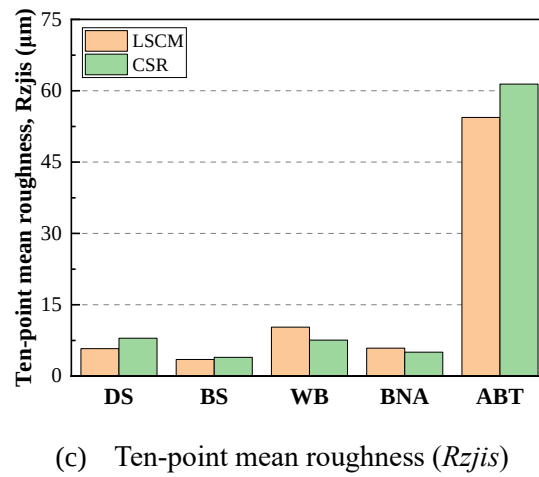
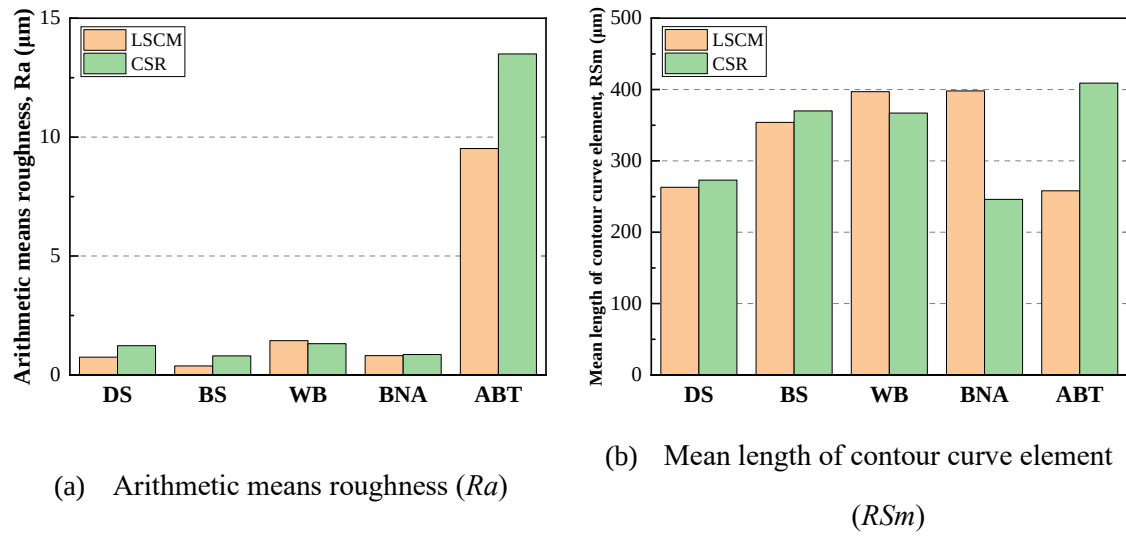


Fig. 2-7 Results of surface roughness measurement

2.3.2 Surface adhesive strength and the relationship with surface roughness

To obtain the surface adhesive strength of the five treated steel surfaces, the pull-off test was performed using a desktop tension–compression testing machine (MSC-10/500-2, Tokyo Koki Testing Machine Co., Ltd.). The tensile speed was quasi-static at 0.5 mm/min, and the Max tensile force was 10 kN. Prior to the test, the adhesive surface of the dolly (JIS H 4000 Aluminum alloy A2017, diameter: 20 mm) was uniformly sanded in one direction, The residual powder was cleaned using compressive air and tape. All steel substrates and the aluminum dolly were washed in acetone solution and dried under room conditions (23 °C and 35% RH) for 10 min. After cleaning the specimens, a two-component epoxy structural adhesive (Three Bond 2082C) with a mixture of 1:1 was used for the dolly bonding. A uniform vertical compressive stress of 0.9 MPa was applied to the dolly and maintained for 30 min to adhere it to the core area. Subsequently, the dolly specimen was cured for at least 48 h at 35 °C. All pull-off tests were repeated third to obtain the average adhesion strength. The specimen of the experiment is shown in **Fig. 2-8**.

The test results are drawn in **Fig. 2-9**. In the results, it can significantly be observed that the ABT treated surface has the best adhesive strength over 25 MPa, disc sander (DS) and belt sander (BS) treatments provided the lowest adhesive strength nearly 10 MPa, wire brush (WB) and bevel non-woven abrasive (BNA) treatments get the middle-level adhesive strength in these five types of surface treatments with approximately 15 MPa.

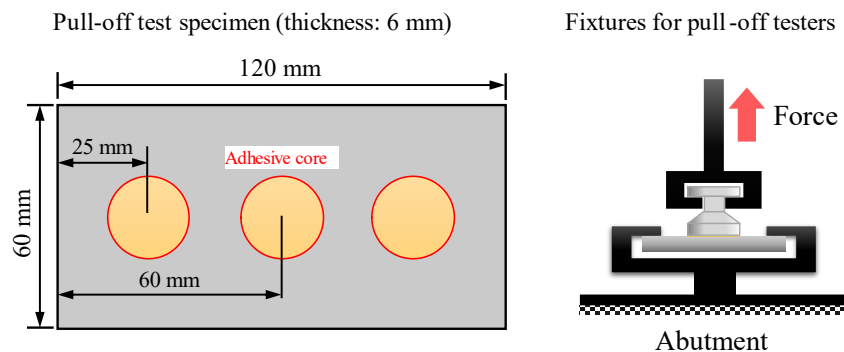


Fig. 2-8 Specimen of pull-off test

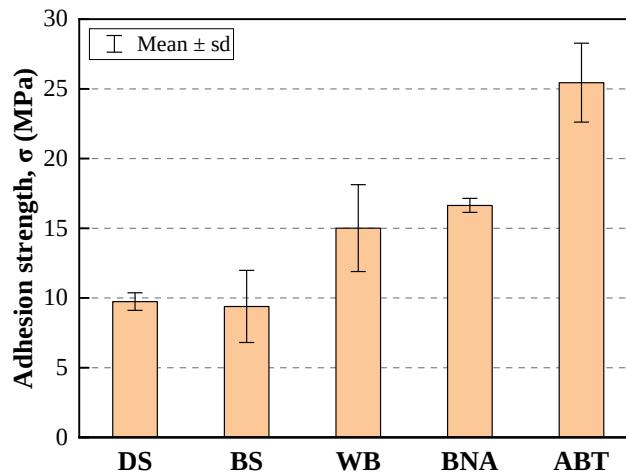


Fig. 2-9 Test result of pull-off test

Comparing the adhesion strength result and the line roughness measurement result of five treated steel surfaces, it is easy to find there is a relationship between line roughness and adhesion strength. Similar surface properties will result in similar line roughness so that the surfaces will achieve similar adhesion strength. Simply evaluating the treated surface with line roughness is not enough, it is necessary to raise the two-dimensional line roughness to the three-dimensional surface roughness for evaluation.

Three surface roughness indicators: 1) arithmetic mean height of the scale-limited surface (S_a), 2) root mean square height of the scale-limited surface (S_q), and 3) maximum height of the scale-limited surface (S_z) were calculated, Wenzel roughness factor r was also measured using LSCM according to the study by Hongru et al.[114]. The calculation results of the surface morphologies are listed in **Table 2-3**. The results show that the DS-treated specimen is slightly rougher than the BS treated specimen when rotated sanding is performed instead of unidirectional polishing. Generally, a similar surface morphology is expected regardless of the grinding direction when using an abrasive paper of identical coarseness. The correlation between the variables related to surface conditions was derived by calculating Pearson's correlation coefficients, which are shown as a color-coded matrix in **Fig. 2-10**. The Wenzel roughness factor r , and the roughness parameters, R_a , R_{zj} , S_a , S_q , and S_z , correspond to the height direction of the surface undulation, conform to the relation $BS < DS < WB < BNA < ABT$, and they all are highly correlated to the adhesive strength (correlation larger than 0.9). Concurrently, R_{Sm} corresponding to the width of the surface

undulation shows a different trend, and it has a weak negative correlation to the adhesive strength. However, the fractal dimension does not present a correlation with the surface adhesive strength, whereas it is correlated with RSm.

Table 2-3 Surface morphology calculation results of steel substrates subjected to different treatments

Surface parameters	$r=A/A_0$	Ra	RSm	Rzjis	Sa	Sq	Sz
DS	1.22	0.744	263	5.78	0.738	0.968	15.6
BS	1.20	0.377	354	3.49	0.374	0.511	11.7
WB	1.32	1.44	397	10.3	1.44	1.93	22.0
BNA	1.37	0.808	398	5.88	1.50	1.89	24.1
ABT	1.58	9.52	258	54.4	10.2	13.0	119

r : Wenzel roughness factor

A: The real surface area of the surface; A_0 : The projected surface area

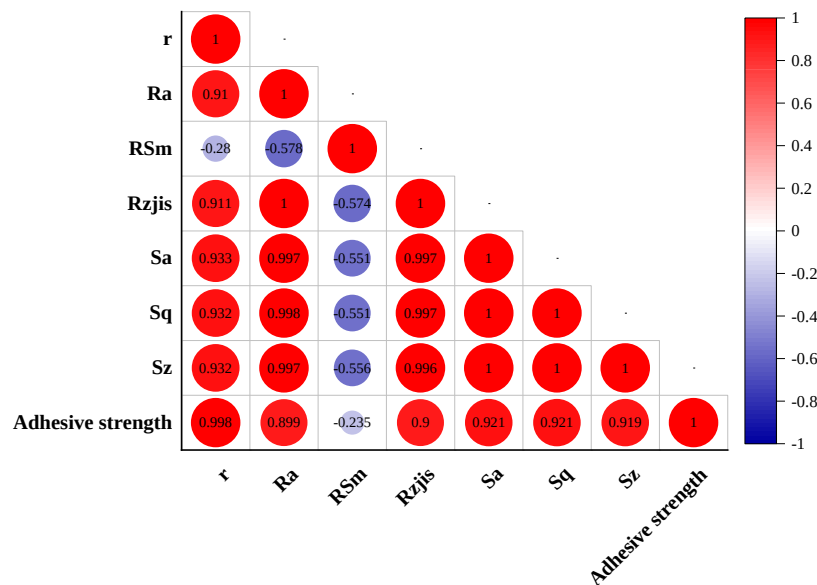


Fig. 2-10 Color scale matrix of Pearson correlation coefficients of variables related to surface morphologies

For the five surface treatment methods, Pearson correlation coefficients indicate a strong association between the Wenzel roughness factor and adhesive strength. As mentioned earlier, the actual surface area can be effectively expressed through the Wenzel roughness factor. Gent and Lai[115] argued that as long as roughness does not reduce the contact between surfaces, an increase in surface area may lead to a proportional increase in adhesion strength. Experimental results confirm that, in a specific region, the actual surface area of the blasted surface exceeds that of the other three specimens, resulting in an adhesive strength approximately 1.6-2.5 times greater than that achieved by other surface treatment methods.

2.4 Evaluation of rust removal effectiveness

2.4.1 Surface properties of corroded steel after rust removal

According to the research results mentioned above, among the five surface treatment methods, BS exhibited the lowest surface roughness and adhesive strength. Therefore, in this section, the rust removal effectiveness of the BS treatment method is not discussed but focuses on the remaining four surface treatment methods. The corroded steel surfaces and de-rusting surface by DS, WB, BNA, and ABT treatment are shown in **Fig. 2-11**. The surface textures of the de-rusting steel plates were observed using optical microscopy (VHX-1000). During the treatment process, it was observed that directly treating thick rust layers led to splattering, resulting in lower efficiency. Therefore, the surface rust layer was initially manually brushed away using a steel brush before further processing. It was also noted that, although DS treatment could swiftly remove surface rust, a significant amount of corrosion residue remained in the corrosion pits, which could not be eliminated. When using WB for treatment, the high-speed friction of the steel brush generated heat, causing the surface of the specimens to quickly turn black with the formation of an oxide film after treatment. In contrast, BNA treatment did not result in the formation of a black oxide film.

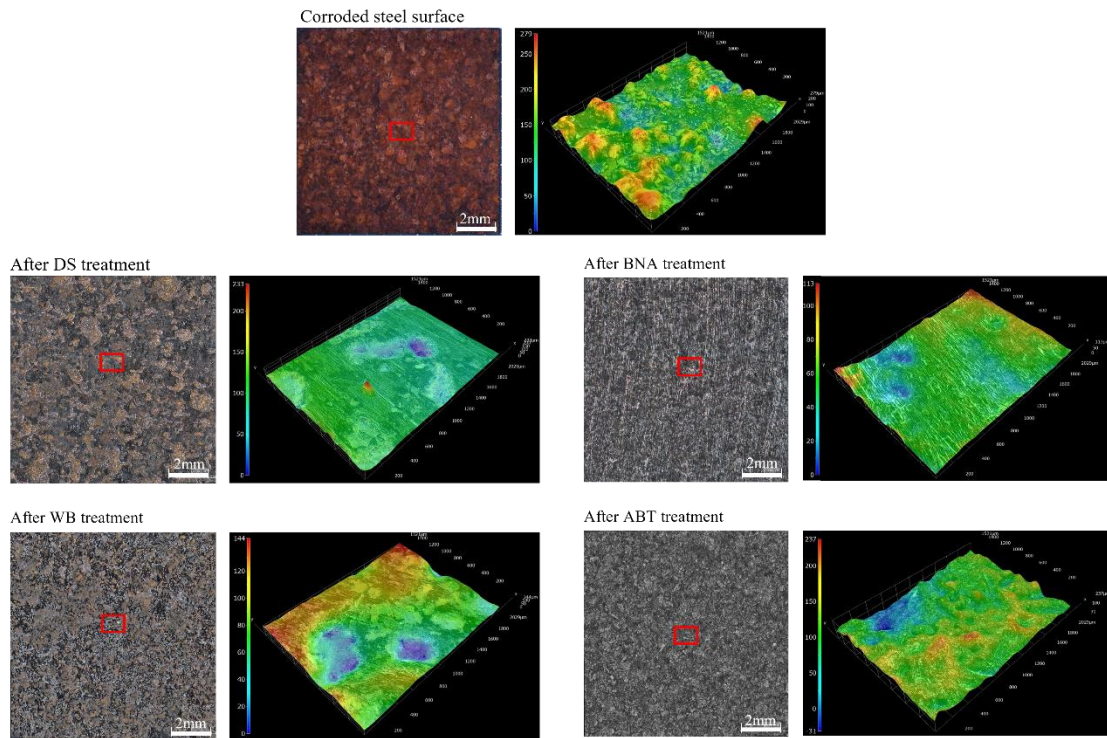


Fig. 2-11 Surface of corroded steel treated by various surface treatment methods

ABT treatment is specified in the codes of many countries and can correspond to each other. However, there are only three specifications, SSPC, ISO, and SPSS, which describe the cleanliness level of corroded surfaces treated by electric power tools. As mentioned above in **Table 1-2**. The cleaning level after blast was around Sa 2.5, and after the power tool cleaning was St 3 (Surface preparation standards ISO8501-1). A corroded specimen after the DS treatment is shown in **Fig. 2-12(a)**. According to the state description of St3 in the specifications, the surface should exhibit a pronounced metallic sheen. Obviously, DS cannot achieve the required cleaning level, that is, the amount of rust residues at pitting, when processed individually. Nevertheless, the internal rust of a large pitting can be removed after being cleared by the WB, as shown in **Fig. 2-12(b)**. Therefore, DS and WB treatments are combined for rust removal on corroded steel surfaces hereafter, while specimen ID is still denoted as WB and DS treatment is considered as a preprocessing step.

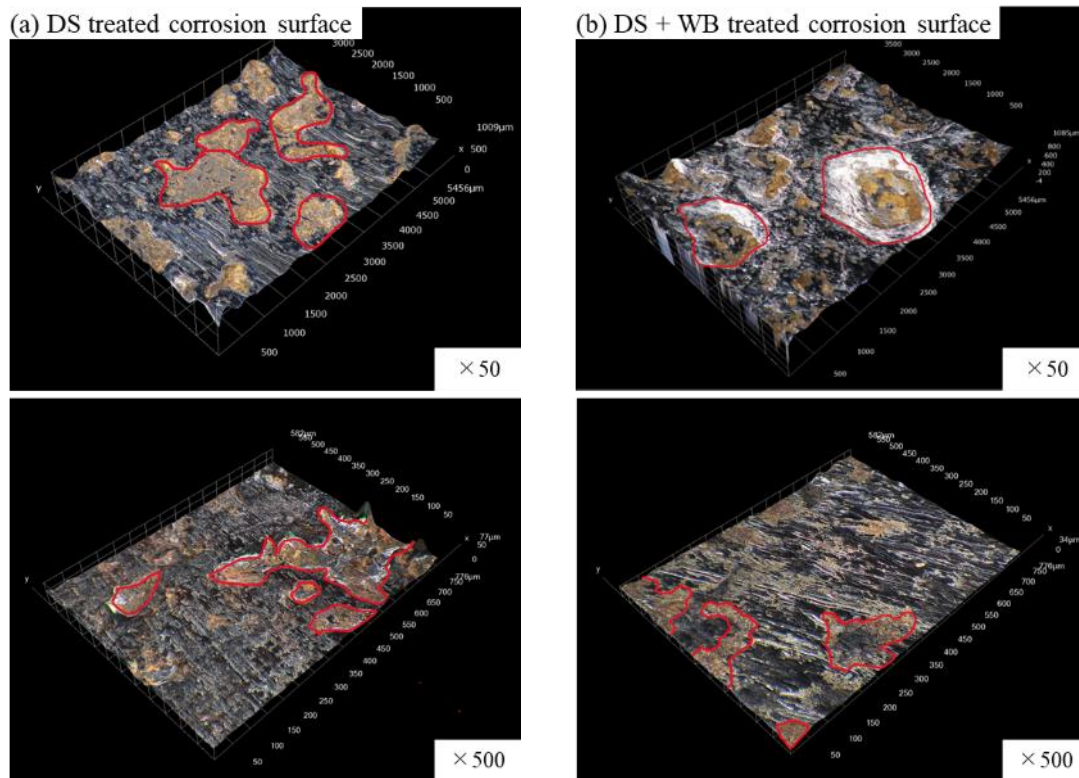
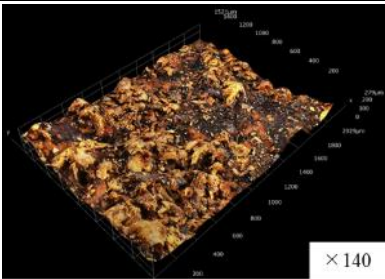
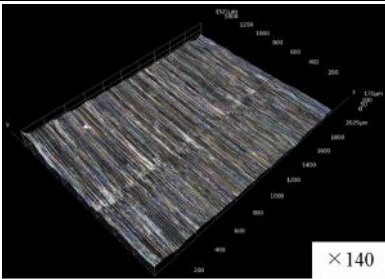
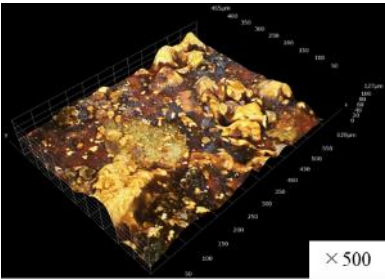
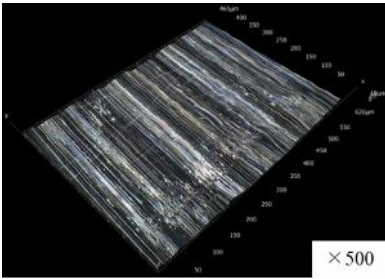
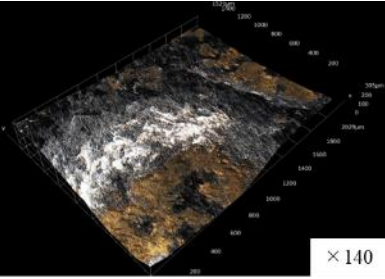
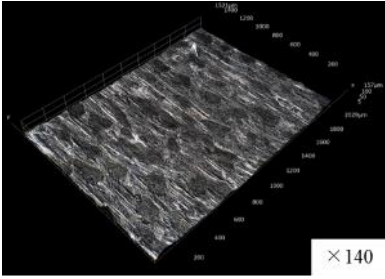
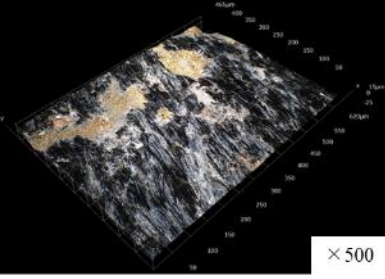
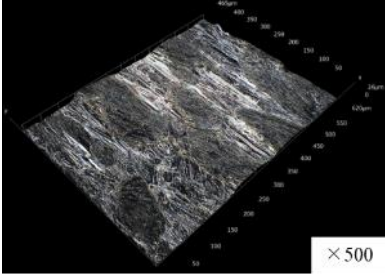


Fig. 2-12 OM photos of rust residual at pitting

In **Table 2-4**, the surface morphologies of the corroded and uncorroded steel surfaces (a) and three rust removal treatments (b) – (d) were applied to (a). After the surface treatment, the milled specimen exhibited some differences in glossiness, topography, and good surface uniformity. In addition, the corroded specimens showed that the pitting interior residue, surface uniformity, and rust distributions varied significantly owing to the different hardness and shape of the grinding materials. Rust residues at pitting in the BNA and WB cases can be seen in the images, whereas the ABT-treated surface showed a near-white steel surface and no evident visible rust. The corrosion specimen with ABT treatment showed good rust removal ability in three dimensions, whereas BNA showed good de-rusting ability on the 2D plane, as its demarcation of the pitting area is the clearest.

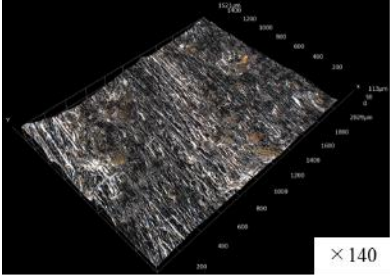
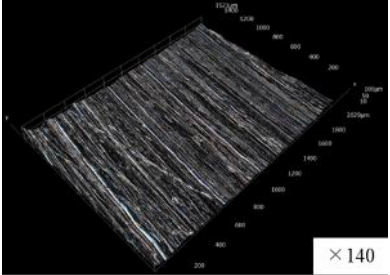
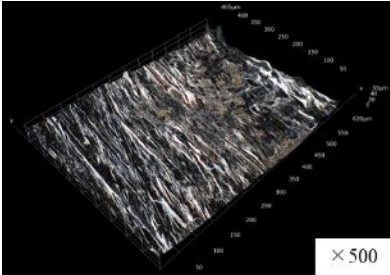
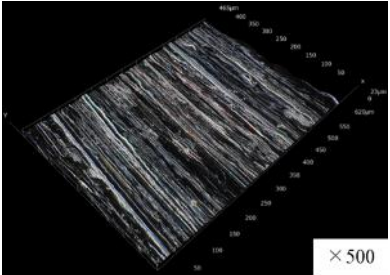
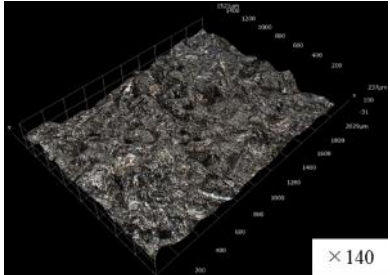
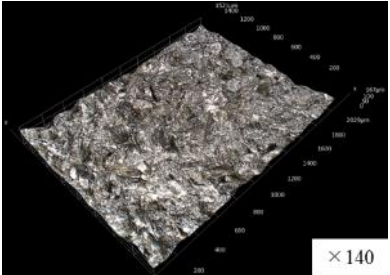
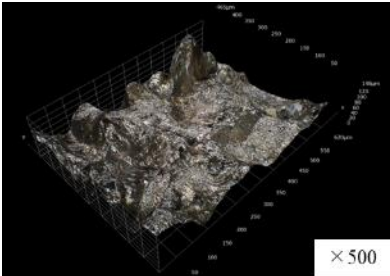
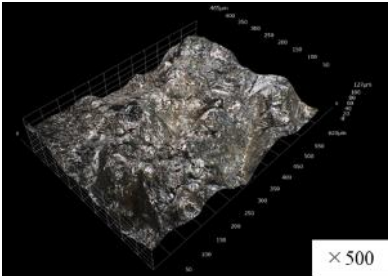
Table 2-4 OM observation on corroded steel surfaces after different surface treatments

	Corroded steel surface	Uncorroded steel surface
(a) Without surface treatment	 × 140	 × 140
	 × 500	 × 500
(b) WB	 × 140	 × 140
	 × 500	 × 500

(Continue to next page)

(Continue from last page)

Table 2-4 OM observation on corroded steel surfaces after different surface treatments

	Corroded steel surface	Uncorroded steel surface
(c) BNA	 $\times 140$	 $\times 140$
	 $\times 500$	 $\times 500$
(d) ABT	 $\times 140$	 $\times 140$
	 $\times 500$	 $\times 500$

Measurements on surface-treated corroded steel surfaces were carried out using LSCM, and the results are shown in **Fig. 2-13 (a)**. For the corroded specimens, the longitudinal variation of corrosion pits combines changes induced by different rust removal methods. The range of depth fluctuations primarily depends on the corroded surface. A comparative examination of the surface morphology of uncorroded steel (**Fig. 2-13 (b)**) obtained in section 1.3 reveals that the hills and valleys on the BNA and WB samples are quite distinct, and their profile contours are relatively

smooth curves with no significant fluctuations. The surface morphology of the ABT-treated specimen is notably more complex with more pronounced lateral fluctuations. In this case, the surface parameter describing the surface roughness and complexity were calculated: the Wenzel roughness factor r . The results are presented in **Table 2-5** and compared with the milled steel surface. As an indicator of the real area, r values for the corroded BNA, WB, and corresponding milled samples increased by 9.0%, 6.4%, and 58.4%, respectively. Regardless of corrosion, r values for BNA and WB fell within the 1.0 to 1.1 range. However, ABT treatment superimposed on the initially corroded surface significantly increased roughness and real area.

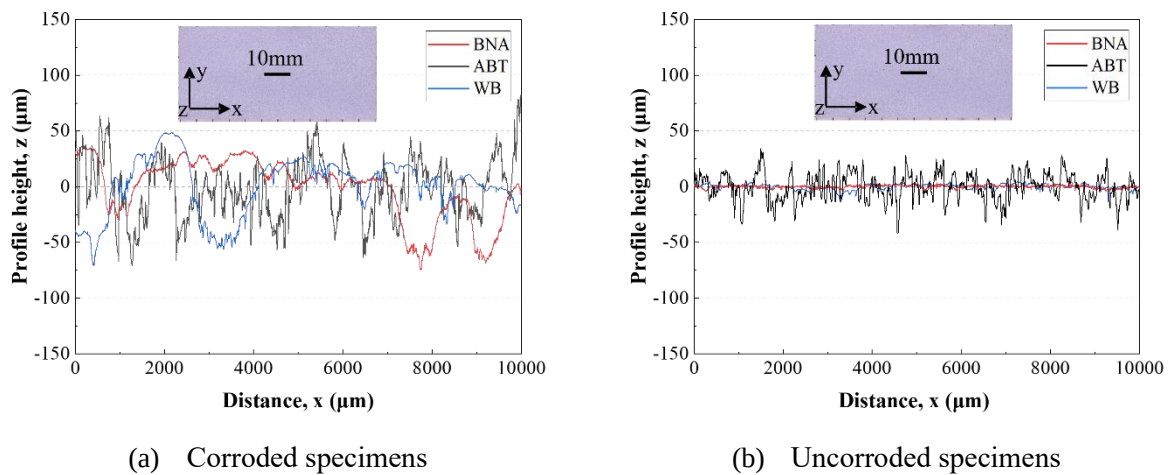


Fig. 2-13 Cross-sectional roughness profiles of specimens after surface treatment measure by LSCM

Table 2-5 Calculated Wenzel roughness factor

Specimens	Wenzel roughness factor, r		
	BNA	WB	ABT
Uncorroded steel	1.01	1.03	1.27
Corroded steel	1.10	1.10	2.01

2.4.2 Elemental analysis of de-rusting surface

1) SEM-EDX elemental analysis

During the process of treating corroded surfaces with power tools, it is impossible to completely eliminate rust products, and some residual rust traces are inevitable. The rust-removed surfaces subjected to various methods were examined using scanning electron microscopy (SEM, SU3500) in the backscattered electron (BSE) mode, under 15 kV low vacuum conditions with a pressure of 30 Pa. Energy-dispersive X-ray spectroscopy (EDX) was used to determine the elemental distribution of the corrosion products. The surfaces of the WB, BNA and ABT after rust removal are shown in **Fig. 2-14**. SEM-EDX results indicate that more chloride residues are discreetly observed on the surface of the WB specimens. Chloride ions and oxide residues are also distributed across the treated surfaces. For the BNA specimens, the boundaries between the steel base and corrosion pits are clear, with higher concentrations of oxides and salts within the pits. For the ABT specimens, the surfaces appear relatively clean with minimal residual corrosion products.

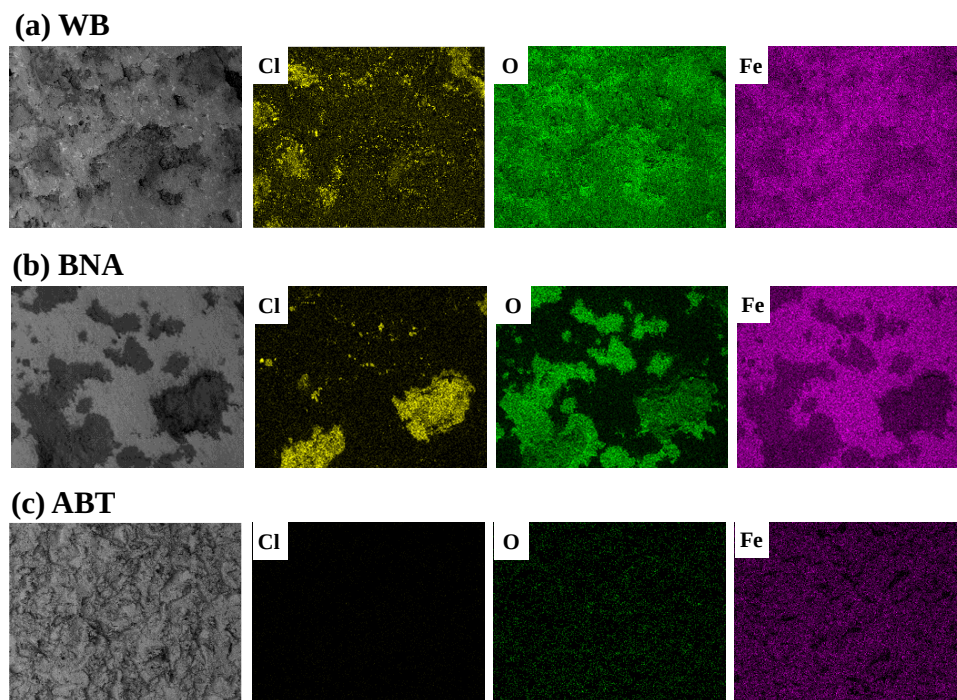


Fig. 2-14 SEM-EDX analysis on the de-rusting surfaces ($\times 50$ magnification)

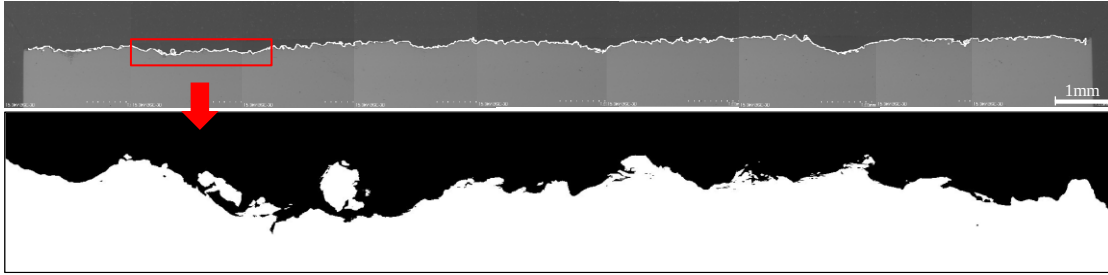


Fig. 2-15 SEM analysis on the cross-section of the de-rusting surface of corroded specimen treated by ABT ($\times 50$ magnification)

Elemental analysis of the ABT-treated specimens is depicted in **Fig. 2-14 (c)**, indicating the near absence of Cl and O residues on the surface. Moreover, the cross-section of the ABT specimen was also examined using the SEM, as shown in **Fig. 2-15**, revealing that the blast-sanded steel substrate has an irregular rough surface with cracks. This not only increases the actual bonding surface but also forms anchoring effects through crack penetration by the adhesive, further enhancing the required fracture energy.

Furthermore, previous studies have confirmed the presence of small amounts of abrasive residue on the blast-sanded steel surface, which might lead to salt and rust embedding into the substrate[48]. This aspect, however, is not addressed in this paper regarding its influence on bonding behavior.

2) XRD analysis on the oxide film

In the processes involving power tools such as WB and BNA, sparks are commonly generated due to high-speed friction, whereas ABT does not induce surface temperature changes within a short time. It is found that surface thermal oxidation occurred during the treatment of the WB specimens, resulting in a black outer layer with a reddish-brown sheen. The compositions of the oxide films were examined by X-ray diffraction (XRD, Rigaku Smart Lab) with Cu $K\alpha$ radiation, $\lambda = 1.540056 \text{ \AA}$. The X-ray diffraction was operated at 40 kV and 30 mA in the X-ray fluorescence reduction mode. A scan rate of $2^\circ/\text{min}$ was applied to record the patterns in the 2θ range of $20^\circ \sim 90^\circ$. X-ray analysis software (PDXL) was used to analyze the spectra, and the obtained pattern was matched using the database of the International Center for Diffraction Data (ICDD).

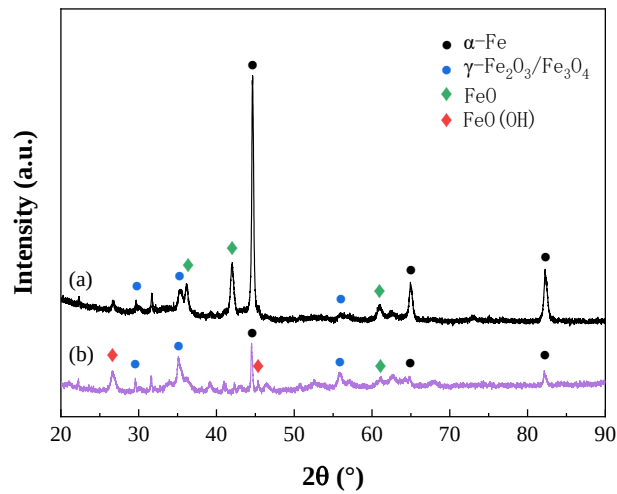


Fig. 2-16 XRD diffraction patterns of corroded samples

Table 2-6 Weight ratio of iron oxide by RIR semi-quantitative analysis

Iron oxide	WB-treated corroded	Inner rust layer of untreated corrosion
	steel	steel
α -Fe	48(2)	15(4)
FeO	34(4)	—
Fe ₃ O ₄ , γ -Fe ₂ O ₃	18(6)	31(8)
FeOOH	—	53(12)

XRD diffraction patterns of the inner rust layer from untreated corroded samples were analyzed and compared to the WB-treated surface, as depicted in **Fig. 2-16**. Besides the patterns of iron α -Fe, magnetite (Fe₃O₄), or maghemite (γ -Fe₂O₃) were also found in both untreated and WB-treated specimens. The XRD diffraction patterns of maghemite and magnetite are very similar, making it challenging to distinguish between these two compounds[116].

Table 2-6 compares the weight ratios of oxide components on untreated and WB-treated surfaces based on the Relative Intensity Ratio (RIR)[117]. Since RIR is a semi-quantitative analysis method, weight ratios less than 5% are not considered. The primary component within the rust layer is hydroxide, mainly γ -FeOOH, while magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) are also present. Furthermore, the surface of the WB-treated specimens primarily exhibits Fe₃O₄,

γ -Fe₂O₃, and a higher proportion of wüstite (FeO), with oxide components similar to those on steel surfaces cleaned with laser ablation[118].

In the natural atmospheric environment, goethite (γ -FeOOH) is the primary corrosion product, typically detected within the rust layer, and Fe₃O₄ is also commonly found[119,120]. These findings are corroborated in this study. Under high-temperature conditions, the generated γ -FeOOH dehydrates and further converts to γ -Fe₂O₃. The steel substrate can also form metal oxides with oxygen or residual magnetite, such as FeO, as shown in **Equation 2-1** and **2-2**[121]:



Hence, it is conjectured that the impact and friction generated during the WB treatment produce heat, which is transferred to the steel surface, affecting the formation of surface oxides or rust conversion. This phenomenon was not observed in the BNA and ABT-treated specimens. Moreover, the oxide scale formed on the steel surface, theoretically from the innermost layer to the outermost layer, should consist of Fe, FeO, Fe₃O₄, and Fe₂O₃[122]. Corroded brush samples reveal that epoxy resin does not directly adhere to the steel substrate but bonds to the oxide film, typically formed through heat treatment.

2.5 Summary and Findings

This chapter discusses the effect of five typical surface treatment methods on the surface characteristics of steel and the rust removal effectiveness through a series of experiments, the following summary and findings have been obtained.

- (1) The Wenzel roughness factor r , and the roughness parameters, Ra, Rzjis, Sa, Sq, and Sz, correspond to the height direction of the surface undulation, conform to the relation $BS < DS < WB < BNA < ABT$, and Pearson correlation coefficients indicate a strong association between the Wenzel roughness factor and adhesive strength.
- (2) Based on surface roughness and adhesive strength, DS, BS, WB, BNA, and ABT can be classified into three categories. The first category includes DS and BS, where the steel surfaces treated with these methods exhibit clear and regular patterns, with lower surface

roughness and adhesive strength. The second category includes WB and BNA, where the steel surfaces treated with these methods show patterns resulting from the rotation of the grinding head, but with irregular edges, higher surface roughness, and adhesive strength compared to the first category. The last category is ABT, and the steel surfaces treated with ABT exhibit a significant increase in surface roughness and adhesive strength, several times higher than the first two categories.

- (3) The rust removal efficiency is highest with ABT treatment, and the observed surface shows no apparent residual rust spots, achieving the optimal surface condition for CFRP reinforcement. In comparison, performing DS or WB treatment alone is challenging to meet rust removal requirements. However, conducting WB treatment after DS treatment can yield better rust removal results. Nonetheless, some rust residues may remain, and a black oxide film may form on the steel surface due to heat friction. BNA treatment, without generating significant heat, demonstrates good rust removal effects with minimal damage to the steel substrate and no oxide film formation. Therefore, under favorable conditions, ABT treatment is recommended as the primary choice for rust removal. In situations where ABT treatment is not feasible, BNA treatment or a combination of DS and WB treatments can be considered for rust removal operations.

CHAPTER 3 EFFECT OF PRE-COATING PROCESS AND CURING TEMPERATURE ON ADHESIVE STRENGTH OF WET LAYUP CFRP-STEEL JOINT

3.1 Introduction

The effects of different surface treatments on the uncorroded steel surface as well as on the adhesive strength of CFRP–steel joints were discussed in Chapter 2. This chapter expects to find ways to further enhance the adhesive strength of the joint based on Chapter 2, in order to obtain better initial adhesive strength and improve durability. Some studies suggested that the bond behavior between CFRP and steel also differs depending on the pre-coating process[123], dynamic load conditions[124], and modification of the adhesive by a silane coupling agent or its toughening by aramid fibers[125,126]. However, the parameters related to the bond behavior of steel structures reinforced by the resin-impregnated carbon fiber fabric wet layup system are still limited. The modification effect of a primer on different treated steel surfaces is still unknown. In addition, the deterioration mechanism of the adhesive and adhesive interface is not defined when a primer is used.

Moreover, the maintenance environment also affects the strength of the resin-impregnated carbon fiber sheet and the composite joints. Previous studies have extensively investigated the influence of curing temperature and curing time on the mechanical properties of bulk adhesive materials and joints [127,128]. However, most of these works have been focused on thermosetting adhesives and lack attention to the temperature conditions encountered in practical applications, especially in comparison to the higher curing temperatures typical of winter construction sites. Additionally, these earlier works have not explored the relationship between physical properties (such as degree of cure or glass transition temperature) and early-stage mechanical properties, particularly at low curing temperatures. Therefore, it is crucial to consider the impact of environmental temperature on the performance of CFRP in actual construction.

This chapter investigates the bond behavior of the CFRP–steel joint using the wet layup process, with a focus on improving the surface treatment of the steel substrate, the thermal properties of the resin adhesive, and the curing process of the composite. The objective is to enhance the mechanical properties and environmental durability of CFRP-steel joints by optimizing the initial manual handling and manufacturing conditions.

3.2 Pre-coating effect on adhesive interface

In conjunction with the results discussed above, the five surface treatments mentioned in the previous section were not evaluated in their entirety in this section. DS, WB, and ABT were selected for experimental evaluation based on the adhesive strengths of the treated steel surface.

3.2.1 Experimental materials and specimen

Dimensions of 120 mm × 60 mm × 6 mm hot-rolled steel plates adhering to the Japanese Industrial Standards (JIS) G3106 SM490A were used to make specimens. The unidirectional carbon reinforcing fabrics used herein named MRK-M2-20, belong to high-strength grade REPLARK™, used for impregnating by epoxy resin matrix to make CFRP laminates as wet layup system which is already used for repairing and strengthening various structures. The fabric thickness was 0.111 mm, and it had an areal weight of 0.02 g/cm². In addition, a two-part epoxy resin named XL-800 used to impregnate carbon fiber fabrics, which is recommended by the manufacturer for pairing with the carbon fabric described above. The main agent and hardener of XL-800 were mixed in a weight ratio of 4:1, and the density of the cured epoxy material was approximately 1.10 ~ 1.30 g/cm³. Following the recommendations of the supplier, the operating environment of XL-800 resin should ensure the RH is less than 85%, the curing temperature needs among the range of 15 °C to 35 °C to let the tensile, tensile-shear, and flexural strengths over 30 MPa, 10 MPa, and 40 MPa, respectively. To discuss the potential enhancement of interfacial bonding performance using primer, another two-part epoxy called E810LS, was used as a pre-coating for the steel surface. The resin and the hardener were mixed in a weight ratio of 5:2 and cured at approximately 20 °C for 6 h. Moreover, a silane coupling agent KBM-04 (denoted SCA)

Table 3-1 Material properties

Materials	Tensile strength (MPa)	Modulus of elasticity (GPa)	Density (g/cm ³)
Pitch-based carbon fiber	5,000	235	1.82
Carbon fiber fabric	3,400	230	1.82
Steel plate	568	206	7.85
Adhesive epoxy matrix XL-800	30	N/A	1.10 ~ 1.3
Primer E810LS	>1.5	N/A	1.10 ± 0.10

was added to the E810LS primer (0.5 ~ 2.0 wt%) to increase substrate adhesion and corrosion resistance. The main material properties as shown in **Table 3-1**.

CFRP–steel joint used in this part for testing adhesive strength, made of steel treated by DS, WB and ABT treatment and bonded with one layer of unidirectional carbon fiber fabric. The treated steel surface was cleaned with a high-pressure air gun to remove the residual dust. Subsequently, it was immersed in an acetone solution for 1 min of ultrasonic cleaning to remove surface grease and other impurities. The mixed resin was applied evenly to the surface of the steel substrate with a brush to moisten the surface after surface treated to avoid the formation of voids when pasting the carbon fiber. Thereafter, the resin was applied to the carbon fiber fabric using a brush to fully moisten it and then pasted on the surface of the steel plate. The composite specimens were then covered with a polytetrafluoroethylene (PTFE) film. Air bubbles were removed from the PTFE film using a metal scraper. To ensure a flat and uniform thickness for the surface of the composite specimen, a piece of tempered glass was pressed onto the surface, and a 4 kg counterweight block was placed on the glass plate. The specimen was then placed in an oven and the temperature was maintained at 35 °C for 5 d. A flowchart of the preparation process is shown in **Fig. 3-1**. Following the recommendations of the supplier, the operating environment of XL-800 resin should ensure the RH is less than 85%, and the humidity of the specimen production environment is about 50%.

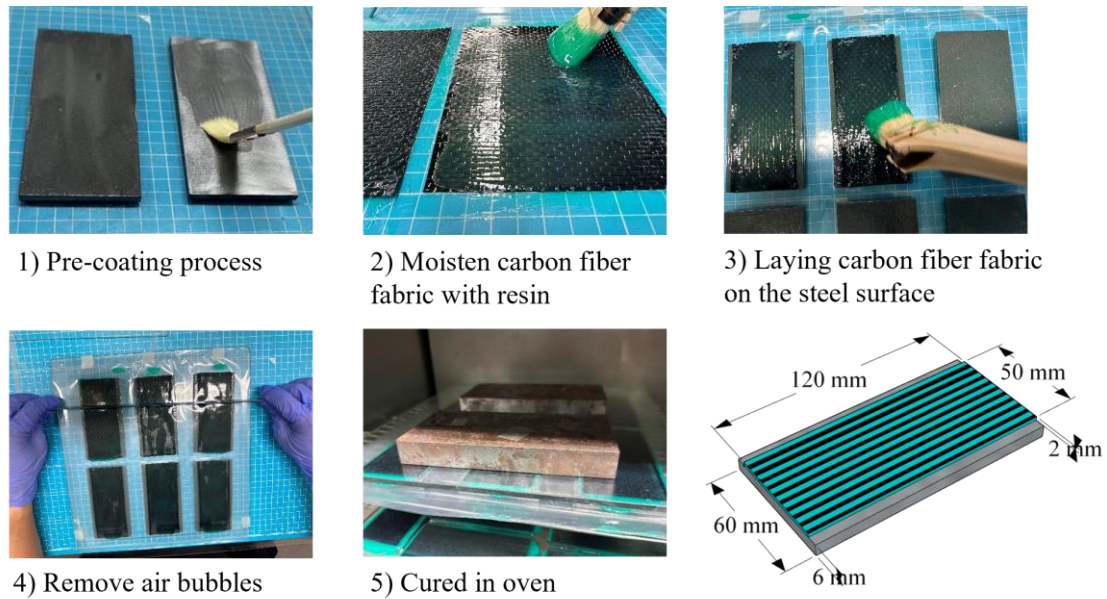


Fig. 3-1 Preparation process of CFRP–steel joint

A total of three groups were tested, and the specimen details are summarized in **Table 3-2**. Each group comprised two batches. The first group consisted of 1) three pieces of steel plates cleaned by a DS, WB, and ABT, which were subsequently directly used for dolly bonding, the results have been derived in section 2.5, and 2) three types of prepared steel plates applied with a thin primer coat, which were kept at 23 °C for 24 h and subsequently bonded the dolly to the surface.

The second group used the three types of treated steel plates that were bonded with one layer of the carbon fiber fabric and subsequently cured under 35 °C for 5 d. After the curing was completed, the adhesive layer on the top of the CFRP layer was abraded using sandpaper (#120) to roughen the core area. Finally, it was glued to the dolly under stable pressure at room temperature (0.5 h), following which constant-temperature curing (48 h) was performed, and a circular groove was drilled around the core area after the curing finished.

The aging test group considered two deterioration environments: 1) a dry–wet cyclic condition, with the specimens denoted as (C), and 2) immersion in 3.5 wt% NaCl (aq.) at ambient temperature (20 ± 1 °C), with the specimens denoted as (I). This group defaults to using one-layer wet layup CFRP specimens cured under 35 °C. All aging tests were continued for 10 d.

Table 3-2 Specimens and test condition

Test group	Condition	Coating	Specimens ID		
Steel substrate	—	—	DS	WB	ABT
	—	Primer	DS-P	WB -P	ABT -P
	—	Primer	DS-P	WB-P	ABT-P
CFRP–steel joint	—	Primer & SCA	DS-P-S	WB-P-S	ABT-P-S
	Immersion	Primer & SCA	DS-P(I)	WB-P(I)	ABT-P(I)
Aging CFRP– steel joint	Dry-wet cycle	Primer & SCA	DS-P-S(C)	WB-P-S(C)	ABT-P-S(C)

*P: Steel with primer E810LS.

*S: SCA (KBM-04) added in primer E810LS.

*All the CFRP–steel joint specimens were defaulted to using one-layer wet layup CFRP and cured under 35 °C for 5 d.

Mechanically, primers between CFRP and steel improve adhesive strength, but their durability is insufficient. To clarify the effects of moisture and dry-wet cycling on the deterioration of epoxy resin, immersion and dry-wet cycling tests were conducted. In the specimens of the deterioration test group, before the tests, a circular groove was drilled until the steel base was exposed. A silicon cover was coated at the lateral and backsides of the specimens. The circular groove acts as an artificial defect to assess the deterioration behavior at the bond interface and cross-section of the CFRP. For the dry–wet cyclic test of the aging group specimens, the test procedure referred to Condition F in JIS K 6857, as shown in **Fig. 3-2**. All specimens (I, C) were immersed in 3.5 wt% NaCl (aq.) at ambient temperature (20 ± 1 °C) for 48 h. Subsequently, the (C) specimens were exposed to drying (60 ± 3 °C, 8 h, thermo-hygrostat) and wetting (20 ± 1 °C, 16 h, 3.5 wt% NaCl (aq.)) cycles for eight days, whereas the (I) specimens were continued to be immersed for eight days. After the aging test, the CFRP surfaces were slightly dried for polishing and gluing the dolly. The specimen names are shown in **Table 3-2**.

Some adhesive epoxy as a high-viscosity epoxy adhesive may not completely penetrate the micro-fissures generated by grit blasting or other surface cleaning processes. In some cases, the micro-voids between the epoxy adhesive and the steel substrate may lead to mechanical failure or interfacial deterioration[129]. In this section, the wettability of the primer epoxy to the steel substrate was characterized by titration tests using the low-viscosity epoxy resin primer, E810L.

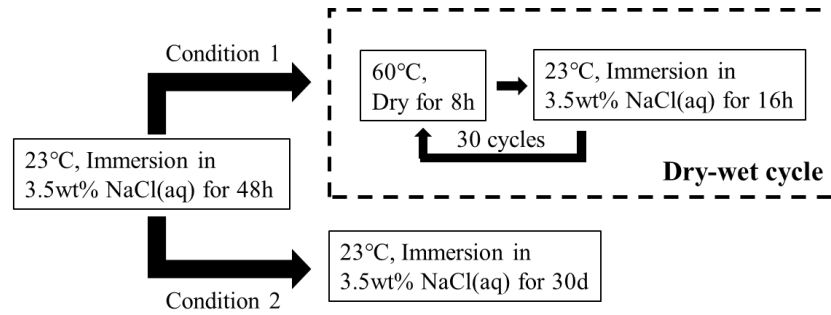


Fig. 3-2 Conditions of degradation tests

Therefore, the flow viscosity (viscosity is approximately 600 cps under 20 °C and at 300 cps under 30 °C). These tests were performed at room temperature (20 °C). Approximately 0.1 mL of a well-mixed two-part epoxy was dropped onto an ABT-treated steel substrate, and the visual variation in the coverage areas by the epoxy droplets is shown in **Fig. 3-3**. The top views of the epoxy droplets on the steel substrate surfaces show that the change in the coverage area is most rapid during the initial stage. The slumping caused by the deadweight continues for approximately 4 h until the unset resin starts to harden.

A well-flowing Primer can reduce the difficulty of applying a thin yet uniform primer layer in a dense, wetting state. After curing for 24 hours at 20 °C, the final thickness formed under all three conditions was thin and even, approximately 100–200 μm. The thickness of the ABT-treated steel samples was relatively greater than other samples due to their rough texture, which hindered the flow and leveling of the resin. All primed steel surfaces exhibited high reflectivity and smoothness, akin to a glass surface condition. To mitigate the impact of adhesive thickness and enhance the adhesive strength between the dolly and the primer surface, manual sanding with 120# sandpaper was conducted, maintaining the primer coating at around 100 μm (standard deviation (SD) ≤ 8 μm). Coating thicknesses were measured using an electromagnetic coating thickness gauge (SM-1000, manufactured by Sanko Electronics; accuracy: 1 μm; resolution: 0.8 mm). Each point was measured 11 times, with three points selected for each surface; the results are summarized in **Table 3-3**.

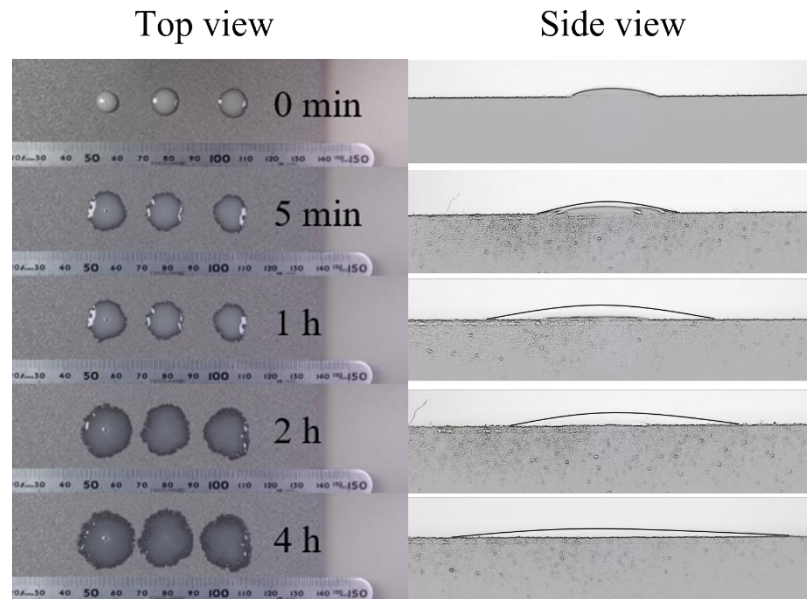


Fig. 3-3 Droplet area variation at blasted surface

Table 3-3 Mean thickness of primer coating

Surface condition	DS			WB			ABT		
Measuring spot	No.1	No.2	No.3	No.1	No.2	No.3	No.1	No.2	No.3
Thickness after curing (μm)	194	174	188	177	183	155	203	236	207
Thickness after polish (μm)	107	95	98	94	96	95	103	100	98

3.2.2 Adhesion strength with and without pre-coating

Pull-off tests were conducted on steel plates with and without primer coatings, and the test results are presented in **Table 3-4**. The failure mode for each steel specimen was an adhesive failure at the steel/adhesive interface, with a minor amount of adhesive residue. However, the predominant failure mode for all primed specimens was a cohesive failure, with a small area of steel detachment. Photographs of the steel fracture surfaces are provided in **Fig. 3-4**.

By enhancing the epoxy resin's wetting ability on the steel substrate, primer pre-coating significantly improves the adhesive strength between the steel surface and the reinforcing material, exceeding 20 MPa in all cases. The enhancement rates for the DS and WB specimens are

Table 3-4 Pull-off test results on steel substrate with and without primer

Specimen ID	Steel substrate		Steel with primer E810LS		Enhancement rate
	Adhesive strength (MPa)	COV	Adhesive strength (MPa)	COV	
DS	9.74	6.5%	20.3	18.0%	108%
WB	15.0	20.8%	25.3	15.7%	68.6%
ABT	25.4	11.1%	25.1	18.0%	-1.20%

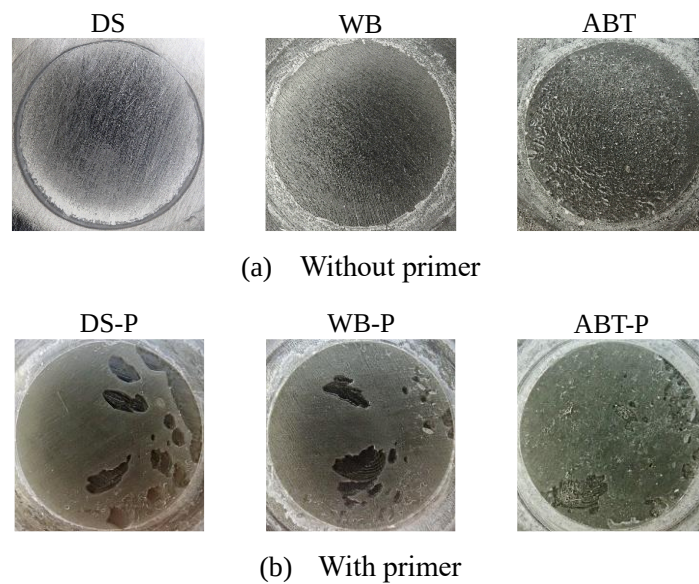


Fig. 3-4 Failure modes of steel specimens

approximately 108%, and 69%, respectively. Adhesive strengths for ABT specimen with and without primer coatings are similar, with a slight 1% reduction likely attributed to the increased total epoxy thickness resulting from the primer and die adhesive bond. Furthermore, within the primer-coated groups, the adhesive strength of the DS specimen is approximately 20% lower than that of the WB and ABT specimens. This indicates that different surface treatments can still influence the interfacial adhesive strength even when using a primer. In reinforced steel structures, the use of low-viscosity primer or other pre-coatings can alter and reduce instances of steel surface delamination, though adhesive strength may vary.

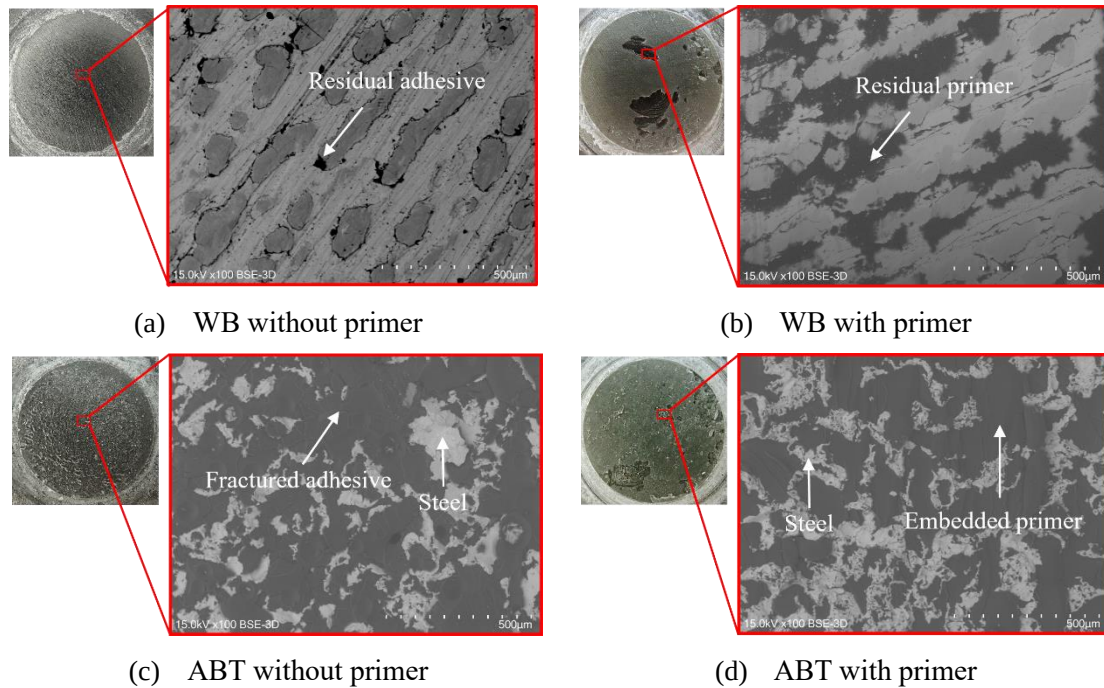


Fig. 3-5 SEM micro photos of exposed steel substrates of specimens after pull-off test

To distinguish differences between the WB specimens and the ABT specimens, the exposed steel substrates were observed under a scanning electron microscope (SEM). The backscattered electron (BSE) images are depicted in **Fig. 3-5**. **Fig. 3-5 (a)** displays a limited amount of residual adhesive surrounding elliptical marks generated by the steel brushing impact. **Fig. 3-5 (b)** reveals a residual primer area consistent with the surface texture of the steel brushing, indicating that the resin has deeply penetrated the grooves created by the steel brushing. However, no significant differences were observed between the ABT and ABT-P specimens. **Fig. 3-5 (c)** and **Fig. 3-5 (d)** illustrate that both adhesive and primer are embedded into the rough steel substrate due to the anchoring effect of the ABT process.

As shown in **Fig. 3-6 (a)**, comparing the adhesion strength on steel substrate, it is clear that ABT treatment can bring greater adhesion strength among the three surface treatments, and the WB is greater than DS. This is because of their different surface roughness as mentioned in section 2.3. As the experiment employed uncorroded steel, surface treatment does not lead to the formation of an oxide film. Therefore, surface roughness is the primary factor affecting adhesive strength. The adhesion strength of the interface was improved after the surface pre-application of

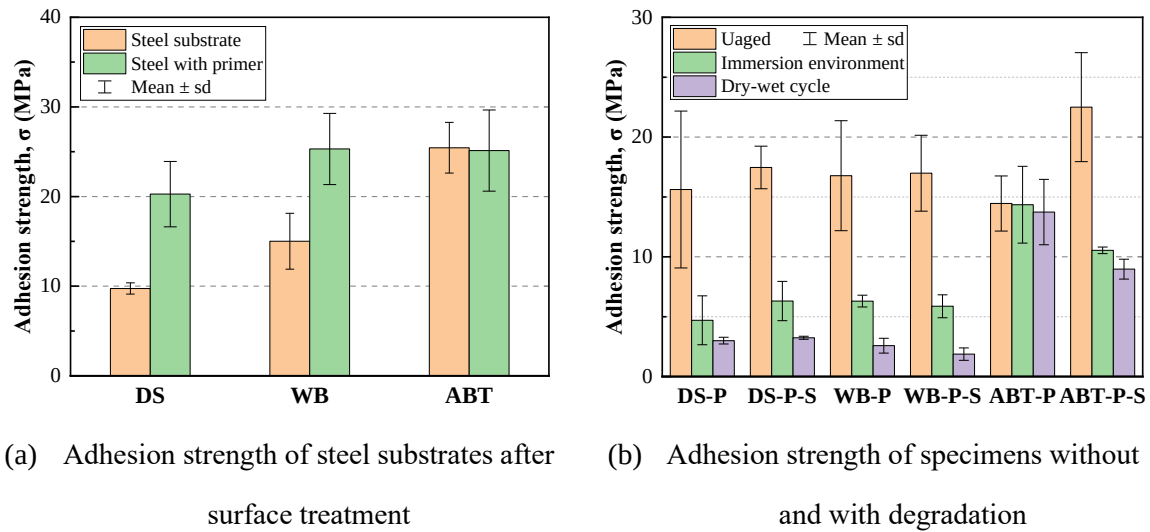


Fig. 3-6 Results of the pull-off test

primer. As shown in **Fig. 3-6 (b)**, after mixing SCA in primer, the interfacial adhesion was improved again., by comparing the surface adhesion strength of the unaged specimens with that of the aged specimens, it can be seen that the surface adhesion strength of the aged specimens decrease significantly, with the most apparent decrease in the surface adhesion strength of the specimens under dry-wet cycle conditions. From the figure, it can also be observed that the errors for each case vary, primarily due to the inherent inaccuracies introduced during the fabrication process. The thickness of resin at each location of tensile testing and the degree of bonding between resin and carbon fiber cannot be uniformly ensured. Furthermore, specimens that have been subjected to different deterioration environments may have varying degrees of deterioration. It leads to differences in material properties, which in turn affect the magnitude of error in the pull-off test results. Consequently, as depicted in **Fig. 3-6 (b)**, the range of errors under different degradation environments also undergoes alterations.

Fig. 3-7 shows that three types of failure modes were observed in the failure interface of the deteriorated specimens: a) interface failure: delamination between steel and adhesive interface, b) cohesive failure: delamination between adhesive layers, and c) material failure: delamination between CFRP layers. Interface failure and cohesive failure were observed primarily in the no deterioration and immersion groups, while modes of cohesive failure and material failure were observed mainly in the dry-wet cycle group; it can be assumed that delamination of the CFRP

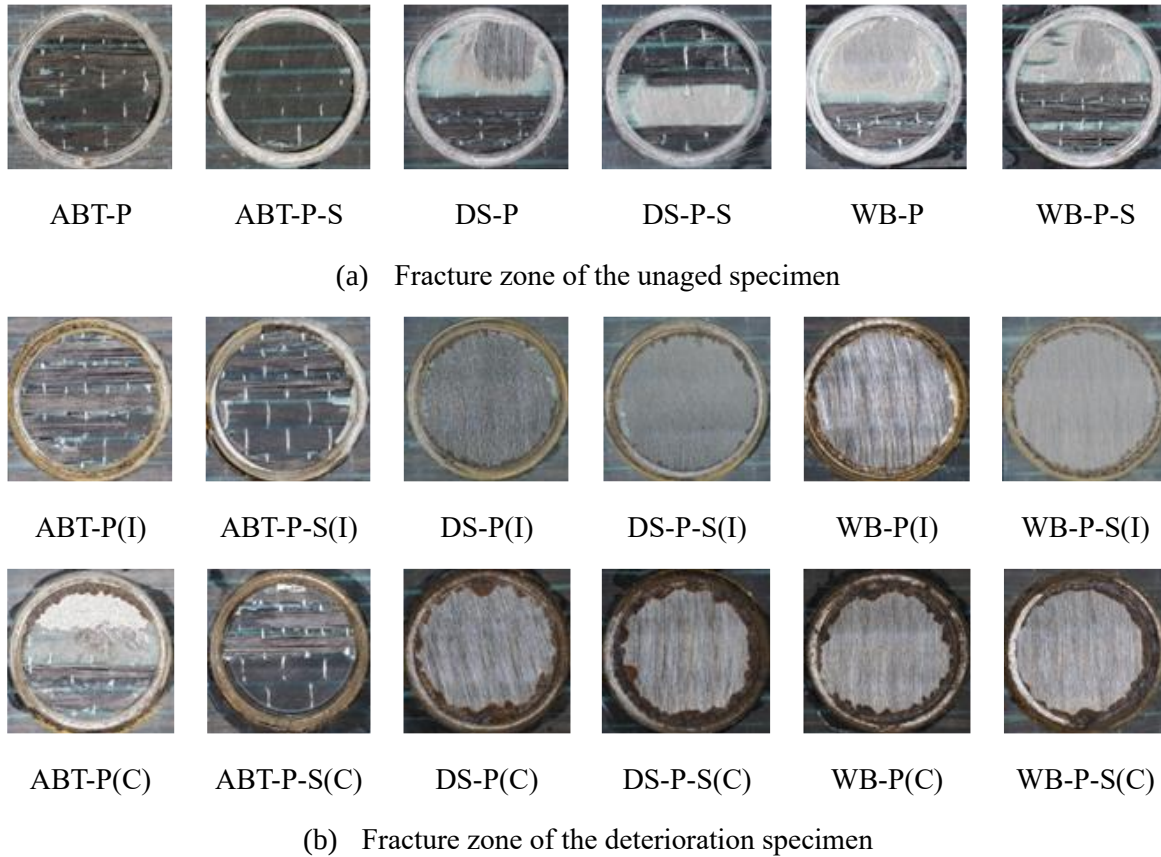


Fig. 3-7 Fracture zone of the CFRP–steel joint specimen

caused the cohesive failure and that moisture penetration contributed to this damage due to epoxy deterioration. Material failure was attributed to moisture penetration as well as corrosion of the steel base and thermal deformation differences at the interface.

The failure modes depicted in **Fig. 3-7** can explain the variations in strength observed in **Fig. 3-6 (b)** for ABT-P. Except for the ABT specimens, the aged specimens of DS and WB exhibited interfacial failure. Compared to the unaged specimens, the failure mode shifted from a combination of material and interfacial failure to complete interfacial failure, leading to a significant decrease in adhesive strength. In contrast, for the ABT specimens, regardless of degradation, complete interfacial failure did not occur; instead, the failure mode predominantly involved material delamination of CFRP. Consequently, the measured adhesive strength actually reflects the interlayer adhesive strength of CFRP rather than the interfacial adhesive strength between CFRP and the steel substrate. Due to the relatively short degradation time, the primer

and the interlayer adhesive strength of CFRP exhibited minimal variation, resulting in minor changes in adhesive strength for the ABT specimens depicted in the figure.

3.2.3 Thermal characteristics of epoxy after dry–wet cycle test

Thermal characterization of the epoxy matrix (XL-800) and the primer (E810LS) was conducted by DSC analysis (DSC 7000, Hitachi High-Tech Science). Epoxy samples, 8–10 mg, were analyzed by introducing in 4 mL aluminum crucibles, and all samples were made of pure epoxy without fibers. The data acquired from the DSC tests was correlated with the fractional conversion and the reaction rate. No isothermal measurements were performed from 0 °C to 200 °C with heating rates 20 °C/min.

First, DSC measurements of the primers with and without the silane additive were made in the uncured liquid state. The results, shown in **Fig. 3-8 (a)**, indicate that the silane additive has no significant effect on the glass transition temperature of the primer, with the glass transition temperature of the two samples being approximately 70 °C. This indicates that when the ambient temperature is below 70 °C, the primer coating is not plasticized and its mechanical properties are not reduced due to the high temperature. The results of the DSC analysis of epoxy resin in the dry and wet cycle test are shown in **Fig. 3-8 (b)**. Initially, the glass transition temperature of the

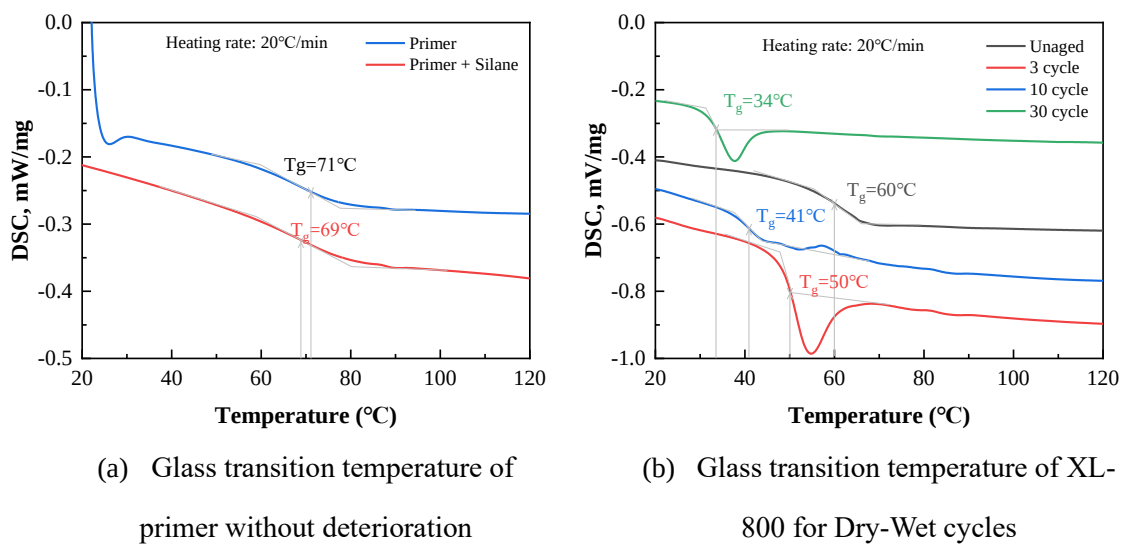


Fig. 3-8 Glass transition temperature measurement results

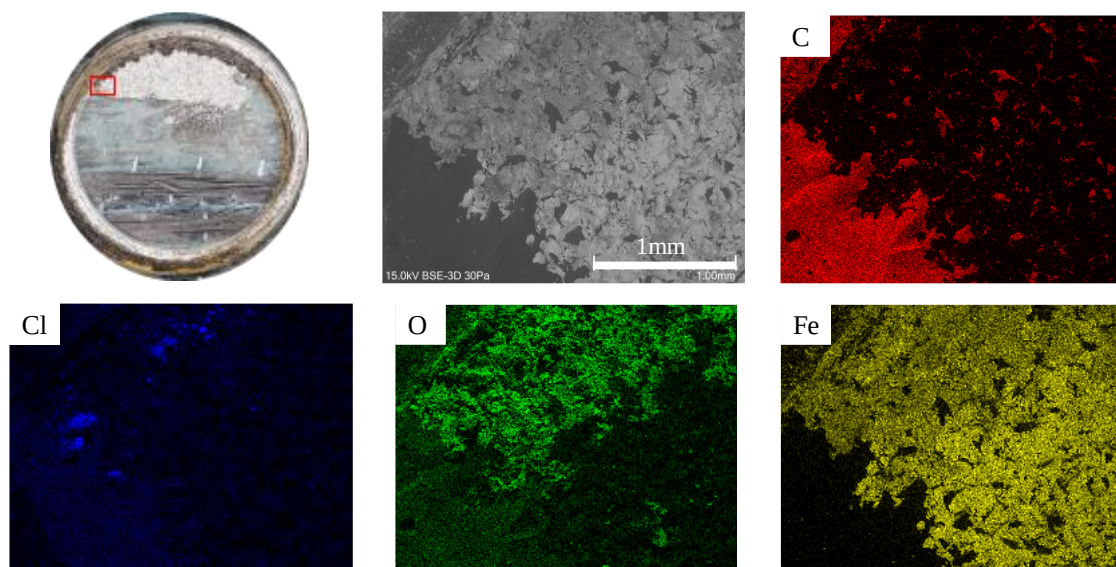


Fig. 3-9 SEM-EDX results of failure part

undegraded epoxy resin is 60 °C. As the number of dry-wet cycles increased, the glass transition temperature gradually decreased to 50 °C after 3 cycles and finally to 34 °C after 30 cycles. The decrease in glass transition temperature indicated that the internal structure of the resin was destroyed, causing delamination in the Adhesion strength test. The presence of hydroxyl groups in the epoxy, which can react with water molecules to form weak hydrogen bonds, is thought to be responsible for the breakdown[130]. Hydrophilic groups in epoxy are known to cause water uptake, leading to swelling, plasticization, and a decrease in both strength and glass transition temperature[131].

3.2.4 Elemental analysis of failure part

The determination conditions for EDX analysis were the same as in section 2.4, and the results of ABT-P (C) are shown in **Fig. 3-9**. The observation area has been highlighted by the red box. Due to the presence of carbon elements in the resin, which does not contain iron, the steel substrate appears black in the carbon element distribution image. A comparison of the distribution images of carbon and iron elements reveals that there is resin residue on the surface of this observation area. This indicates that during the curing process, the resin penetrated into the recesses created

on the steel substrate's surface by the iron sand during the blasting process. This resulted in a strong bond that resin was not pulled off in the adhesion tensile test. From the chlorine element distribution image, it is evident that over 90% of the damaged areas have a distribution of chlorine elements, with some areas showing exceptionally high concentrations, likely indicative of rust formation. It can also be observed that chloride ions have penetrated into the resin in areas with resin residue, suggesting that chloride ion penetration may be one of the contributing factors to resin deterioration in prolonged deteriorating environments.

3.3 Effect of curing temperature

3.3.1 Porosity of CFRP laminate in different curing temperature

Ambient temperature will affect the viscosity and curing process of the epoxy matrix, and basic curing information of the A/B mixed XL-800 epoxy resin is provided in **Table 3-5**. These parameters might lead to differences in the wettability of the resin to the carbon fibers, thereby causing a difference in the bond behavior. Following the supplier's recommendations, the operating environment of XL-800 resin should be between 15 °C to 35 °C, and the RH less than 85% on-site. In this part, there are two types of CFRP laminate specimens formed by the wet-layup method, one was cured at 15 °C (± 5 °C) for 2 weeks and the other was cured at 35 °C (± 1 °C) for 5 d. The dimensions of CFRP laminates were 150 mm $\times$ 60 mm of seven layers. In order to avoid the edge effect, the edge part was cut off and the CFRP was cut into 120 mm $\times$ 50 mm. The digital micrometer (accuracy 0.001 mm) was used to measure the thickness of CFRP laminates by repeated five times at each spot, and the selected spots are shown in **Fig. 3-10**. All specimens were weighed using a scale with an accuracy of 0.01 mg to obtain their weight (m_c) as the reference value. The porosity (V_p) for each specimen was calculated using **Equation 3-1**:

$$V_p = 1 - \frac{m_c}{V_c \cdot \rho_{ER}} + \frac{n \cdot \rho_f^s}{t_s} \cdot \left(\frac{1}{\rho_{ER}} - \frac{1}{\rho_f} \right) \quad (3-1)$$

Where V_p is the porosity of CFRP, m_c is the weight of CFRP, V_c is the volume of CFRP, t_c is the thickness of CFRP, ρ_{ER} is the density of epoxy (1.3 g/cm³), ρ_f is the density of carbon fiber (1.82

Table 3-5 Basic curing information of A/B mixed XL-800

Ambient temperature (°C)	15	25	30	35
Viscosity (cps)	16,000	11,300	9,630	7,360
Gel time (min)	287	92	47	31
Tactile hardening time (hrs)	13	8.5	7	5
Curing period (day)	14	7	5	5

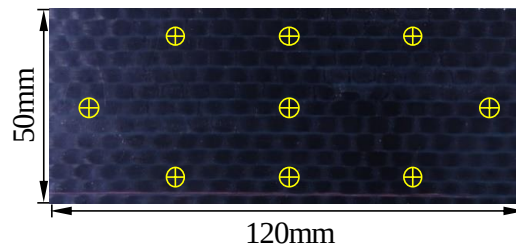


Fig. 3-10 CFRP laminate specimen for porosity calculation

Table 3-6 Porosity calculation of CFRP laminate

Curing condition	Number of layers n	m_f (g)	m_c (g)	Area (mm ²)	t_c (mm)	m_f / m_c	V_p
15 °C (± 5 °C)	7	8.37	17.3	5,978	2.06	0.483	0.065
35 °C (± 1 °C)	7	8.26	18.6	5,900	2.33	0.443	0.088

g/cm³), ρ_f^s is the surface density of carbon fiber fabric (0.02 g/cm²), n is the layer number of carbon fiber.

To observe the permeation degree of CFRP and epoxy resin, micrographs of CFRP panels were carried out with SEM under high vacuum conditions. The measured parameters, weight ratio of carbon fiber, and porosity of cured CFRP as shown in **Table 3-6**. There is a significant difference in the thickness and volume of CFRP cured at 15 °C and 35 °C. For CFRP cured at 15 °C, its weight proportion of carbon fiber is higher than that cured at 35 °C, while the porosity is less.

The SEM micro photos of CFRP cross-sections are shown in **Fig. 3-11**. Through the SEM photos with 60 times magnification, it shows the CFRP cured at 35 °C has more cavities compared with the CFRP cured at 15 °C. Under the condition of 35 °C curing, the cavity mostly appears in

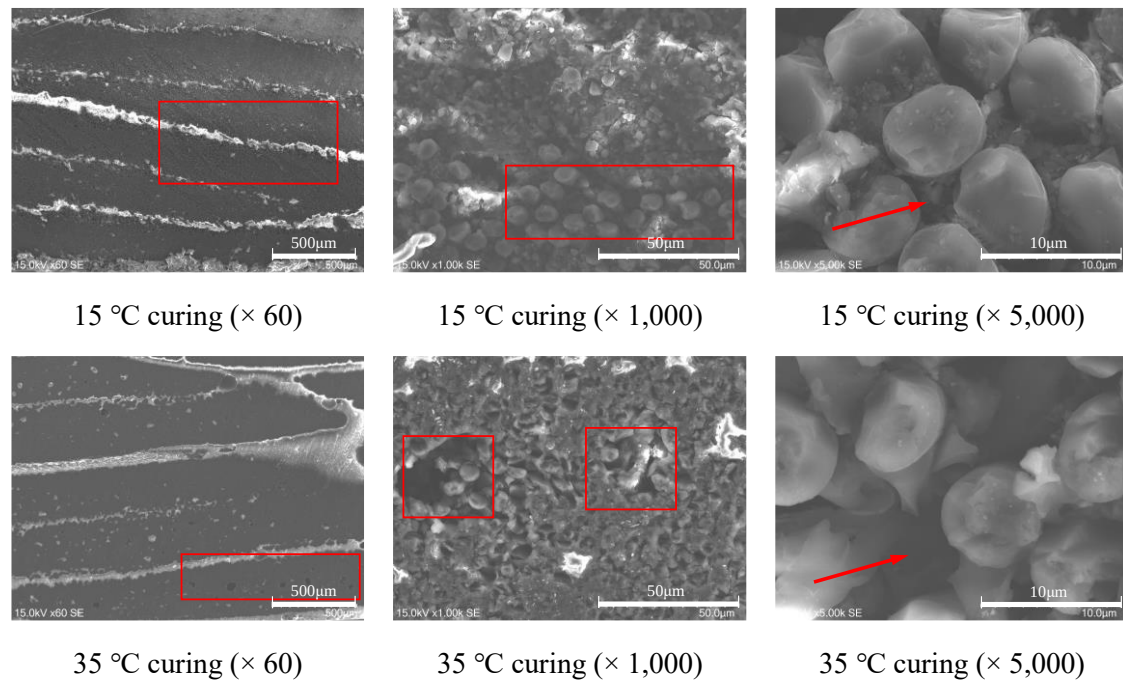


Fig. 3-11 SEM micro photos of CFRP cross-section

the interior of each layer of carbon fiber, which indicates that under the condition of high-temperature curing, the gel time of resin is relatively short, and the air inside of fibers cannot get out as the interlaminar resin harden quickly. In contrast, CFRP under 15 °C curing shows there are no obvious large bubbles whereas large numbers of the small pin-holing dispersed both at the boundary line among sheet layers and interior of carbon fiber layers. The microscopic view in **Fig. 3-11** shows there are gaps uniformly exist between each carbon fiber of CFRP-15, while fibers of CFRP-35 tend to be more tightly arranged except the pore zone.

3.3.2 Adhesive strength and glass transition temperature

In this section, the pull-off test is used to test the adhesive strength of CFRP–steel joint, and the specimen preparation method is the same as before, and the same DSC test as in section 3.2 was used to discuss the differences in their glass transition temperatures. In addition, the tensile strength of the XL-800 epoxy resin was tested by axial tensile test at two different curing temperatures using a tensile testing machine (Tokyo Koki Tester MSC-10/500-2) at a testing speed of 0.5 mm/min, The resin specimen is a dog bone made by filling resin in a silicon rubber

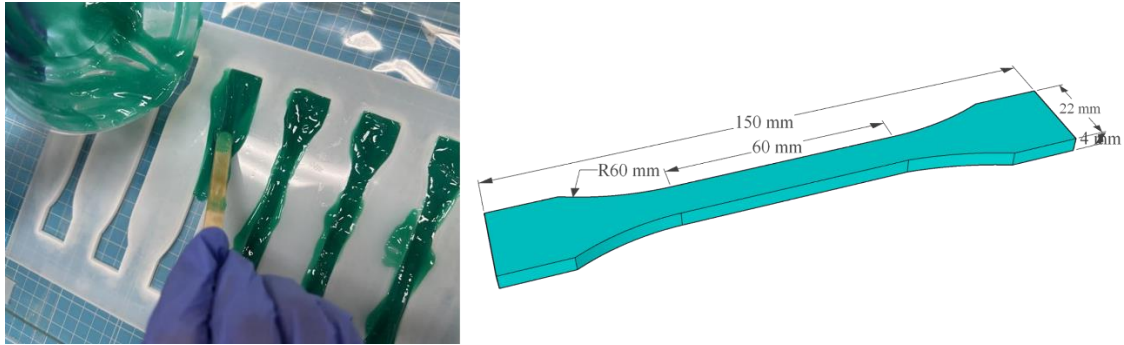


Fig. 3-12 Fabrication method and dimension of dog bone specimen

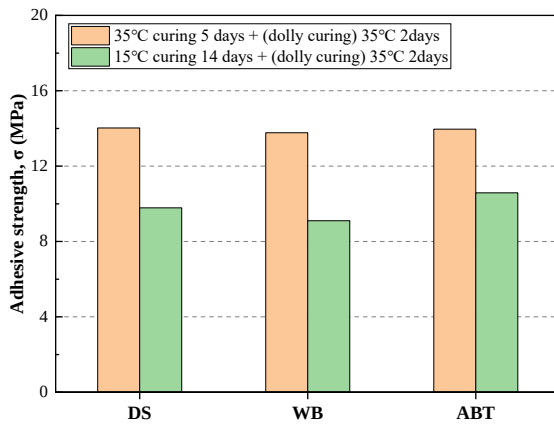


Fig. 3-13 Adhesive strength of composite specimens cured under different ambient environments

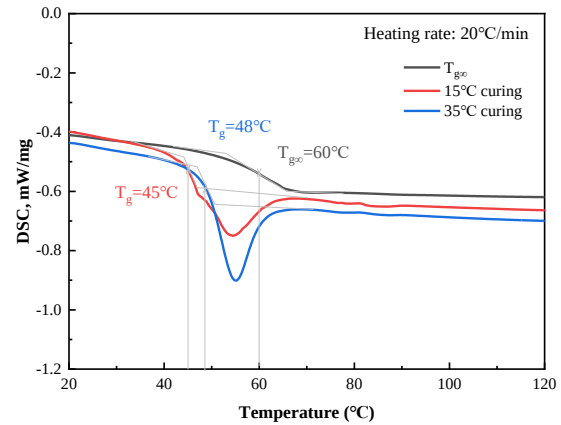


Fig. 3-14 DSC curves of the epoxy matrixes cured under 15 °C and 35 °C

mold. The dimensions of the specimen refer to ISO 527-2 and curing in an oven at 35 °C for 5 d, the method of fabrication and dimension are shown in **Fig. 3-12**.

Pull-off tests were performed on single-layer CFRP-steel joint that had been treated with DS, WB, and ABT surface treatments and cured at 15 °C and 35 °C to evaluate the adhesive strength. The bonding dolly required 2 d of curing at 35 °C. Combined with the curing time requirements in the product information, it can be determined that both specimens were fully cured. The adhesive strengths under both curing conditions are shown in **Fig. 3-13**. All failure modes were CFRP interlayer damage independent of the steel base surface treatment method. The fractured surfaces showed that most of the carbon fibers were flaked off in the specimen under the 35 °C curing condition, and the carbon fibers were scattered in the specimen under the 15 °C curing condition.

Overall, better adhesive strength was obtained when a higher initial curing temperature was used. Combined with the results above, the epoxy resin remains liquid for a long time at low temperatures during the early stage of curing, which facilitates the penetration of the resin into the interior of the fibers under pressure and reduces the porosity. However, the epoxy resin exhibits a lower annual at higher temperatures, which enhances the infiltration into the fibers and improves the interlaminar adhesive strength of the CFRP, with an overall improvement of about 20% compared to low-temperature curing.

The DSC curves of the resin matrix of the joints fully cured at 15 °C and 35 °C are shown in **Fig. 3-14**. The glass transition temperature (T_g) of the fully cured resin matrix obtained from the 2nd run was $T_g=60$ °C. The glass transition temperatures of the samples cured at 15 °C and 35 °C were much lower than 60 °C. This is due to the fact that the polymer network was not cross-linked and the polymerization reaction was not complete[132]. For epoxy resin adhesion used to reinforce steel structures, thermal deterioration results when the ambient temperature in use approaches T_g , so a safety redundancy of 15 °C above the maximum use temperature should be set[133]. Localized temperatures above 50 °C in summer steel structures pose a risk, but in general, materials with a T_g of around 60 °C are generally adequate for non-extreme conditions.

The load–displacement curve of axial tensile test results of the dog bone is shown in **Fig. 3-15**. From the curves, it can be seen that the specimen cured at 15 °C exhibited some ductility in

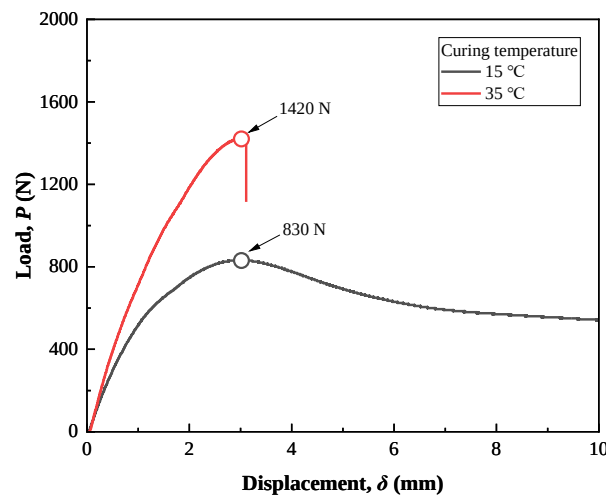


Fig. 3-15 Load–displacement curve of dog bone cured in 15 and 35 °C

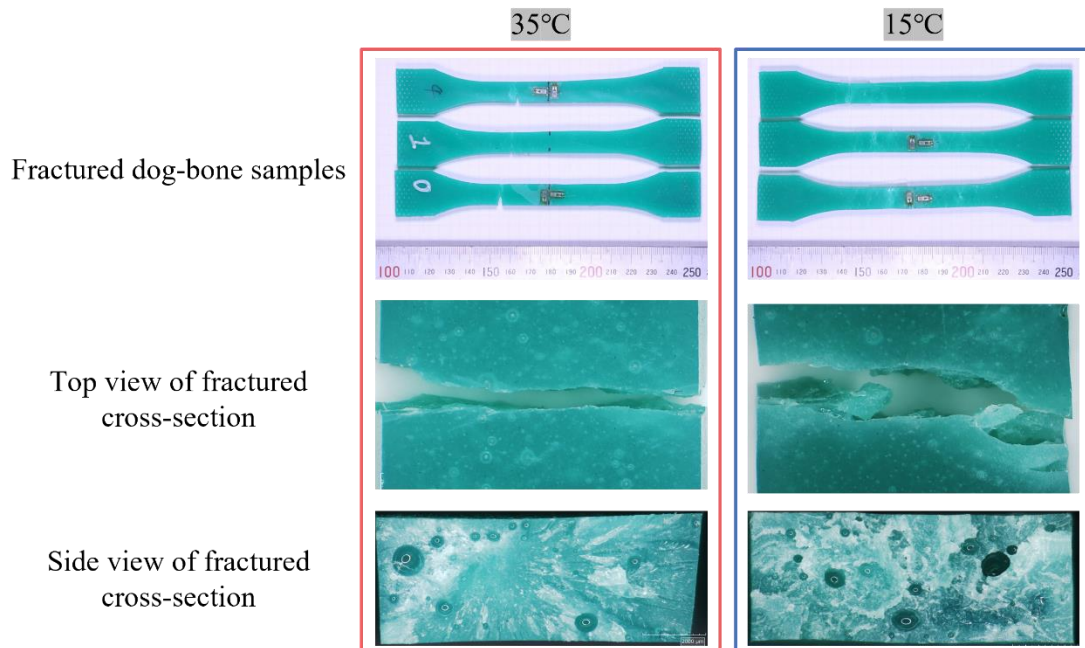


Fig. 3-16 Fracture part of resin dog bone

addition to lower tensile strength. 35 °C cured dog bone broke at 3 mm of stretching, while 15 °C cured dog bone remained unbroken at 10 mm of stretching. The breakage site of the specimen was observed using an optical microscope (**Fig. 3-16**). Comparing the fracture of the two kind specimens, the 35 °C cured specimen had a clear fracture with a relatively smooth and flat cross-section where a radioactive pattern spreading from the center to the surrounding area could be observed, indicating brittle damage, while the 15 °C cured specimen had a rough fracture with an irregular breakage pattern visible on the cross-section, indicating ductile damage.

3.4 Summary

In this chapter, effect of pre-coating process on bond strength of CFRP–steel joint was investigated. Moreover, summer and winter environmental curing temperatures were simulated to investigate the effect of curing temperature on the material properties of CFRP laminate manufactured by the wet layup method. The following conclusions were obtained from the test results:

- (1) The pre-coating process was effective in improving the adhesive strength of the CFRP–steel joint, but the enhancement varied for different surface treatment and was greater for steel surfaces with lower surface roughness. The pre-coating process improved the wettability of the epoxy resin to steel substrates by improving the adhesive strength over 20 MPa in all case. Adding SCA to the precoated primer can further improves the adhesive strength at the interface.
- (2) For CFRP–steel joint using the pre-coating process, compared to the immersion environment, the dry-wet cycle has a more significant negative impact on the adhesive strength. The dry-wet cycle rapidly decreases the glass transition temperature (T_g) of the epoxy resin. When the environmental temperature approaches T_g , it leads to thermal deterioration of the resin, plasticization by moisture uptake. This is probably the reason for the substantial decrease in adhesive strength of the joint.
- (3) At low curing temperatures, the porosity of composite laminates is lower than that of laminates cured at high curing temperatures. This is because under high temperature curing conditions, the gel time of resin is relatively short, the resin between layers hardens quickly, and the air inside the fibers cannot be discharged, while under low temperature curing conditions, the resin cures at a lower rate, which is more favorable for the discharge of internal air.
- (4) The CFRP–steel joint cured at 35 °C has a stronger adhesive strength compared to the composite joint head cured at 15 °C. Means increasing the initial curing temperature is favorable to the mechanical and thermal properties of composite joints. It is beneficial to carry out reinforcing repair operations in summer to obtain better repair results.

CHAPTER 4 EFFECT OF RESIDUAL RUST ON THE BOND BEHAVIOR BETWEEN CFRP AND STEEL PLATE

4.1 Introduction

Corroded steel constructions need to be reinforced with composites to improve structural strength and extend service life. Therefore, the problem of reinforcing corroded members is receiving more and more attention. Li and Xu investigated the bond behavior between CFRP plates and corroded steel plates, mainly considering the effects of corrosion duration and adhesive thickness[33,108], but did not consider de-rusting efficiency or rust residue problems[118]. The cleanliness of corroded surfaces is crucial for repair efficiency and bonding performance, Guo et al. reviewed current research on descaling techniques and analyzed their cleaning efficiency and environmental impacts[50], however, the quantitative characterization of corroded steel plates associated with different descaling methods is still inadequate.

Chapter 2 discusses the rust removal effectiveness of DS, WB, BNA, and ABT treatments. Building upon the results of Chapter 2, this chapter delves into the discussion of the adhesive strength on the steel surface after rust removal, comparing it with uncorroded steel. Additionally, CFRP-steel joint were fabricated using rust-removed steel to explore the influence of residual corrosion and the protective film formed after rust removal on interfacial bonding behavior. The experimental findings provide a novel perspective on understanding the interfacial bonding mechanisms between corroded steel structures and adhesives or CFRP composite materials, thereby enhancing their applicability in various fields, including aged steel structures.

4.2 Specimen manufacture and experimental parameters

Dimensions of 150 mm × 70 mm × 6 mm hot-rolled steel plates adhering to the Japanese Industrial Standards (JIS) G3106 SM490A were used in this part to make specimens. Prior to the

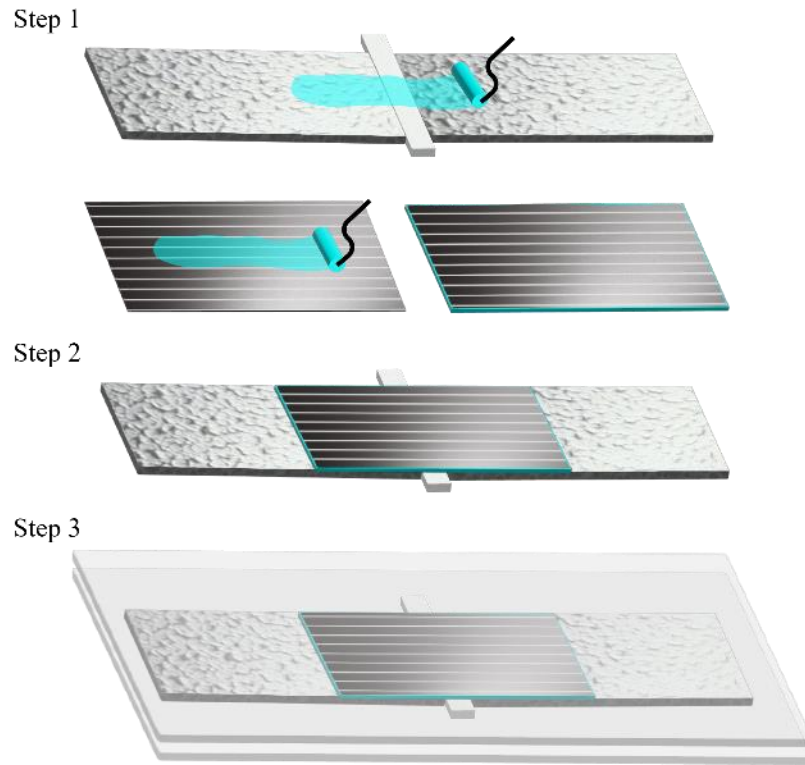


Fig. 4-1 The fabrication process of CFRP-steel single strap joints

fabrication of the CFRP–steel joint specimens, the cyclic corrosion test (CCT) of steel plates was carried out to prepare corroded steels. The corroded steel plates subjected to surface treatments for rust removal are called the corroded specimens. three types of surface treatment methods, 1) Disc sander + Wire brush (WB), 2) Bevel non-woven abrasive (BNA), 3) Abrasive blast treatment (ABT) which were mentioned in Chapter 2 were applied to the corroded steel plates.

In general, resin-impregnated carbon fiber sheet is wet layup laminated to structures and cured on-site, made of multi-layer carbon fiber sheets. Herein, two kinds of specimens 1) CFRP-steel joint, 2) CFRP-steel single strap joint were fabricated in the laboratory. The fabrication process is consistent with the actual situation, while the curing conditions are controlled to ensure stable mechanical properties. CFRP-steel joints are made in the same way as in Chapter 2. The fabrication process of CFRP-steel single strap joints is as follows in **Fig. 4-1**:

- (1) A roller soaked with an epoxy matrix (XL800) was used to wet the surface-treated steel plate and carbon fiber fabrics.

- (2) Hand-layup two materials together, aiding resin permeation using a hairbrush, exhausting bubbles, and laminating the CFRP sheet.
- (3) The specimens were covered by a transparent polytetrafluoroethylene (PTFE) film and glass plate and cured under a constant pressure of 1.736×10^{-3} MPa and temperature of 35 °C for at least 5 days in an oven. The mass fraction of the carbon fiber in the fully cured CFRP was approximately 60%.

Experiments on the pull-off and tensile-shear behaviors of corroded CFRP-steel joints were conducted to obtain essential data regarding 1) the influence of surface treatment methods on the surface substrate characteristics; 2) the influence of various parameters on the bond behavior of composite joints, and 3) the influence of the corroded surface conditions on the bond and fracture mechanisms of steel-CFRP-bonded interfaces under tensile and shear stress.

The specimens' fabrication and test procedures flowchart is shown in **Fig. 4-2**. For the uncorroded and CCT steel plates processed with WB, BNA and ABT three types surface treatments, all composite joint specimens made by three layers of wet-layup carbon fiber fabrics for the adhesive strength test and the tensile shear test. The specimen ID and experimental parameters are listed in **Table 4-1**.

Table 4-1 Mechanical test parameters and specimen ID

Initial surface condition	Specimen	Specimen ID			Test
Uncorroded	Composite joint	WB(M)-C	BNA(M)-C	ABT(M)-C	Pull-off test
	Single strap joint	WB(M)-S	BNA(M)-S	ABT(M)-S	Shear test
Corroded	Composite joint	WB(S)-C	BNA(S)-C	ABT(S)-C	Pull-off test
	Single strap joint	WB(S)-S	BNA(S)-S	ABT(S)-S	Shear test

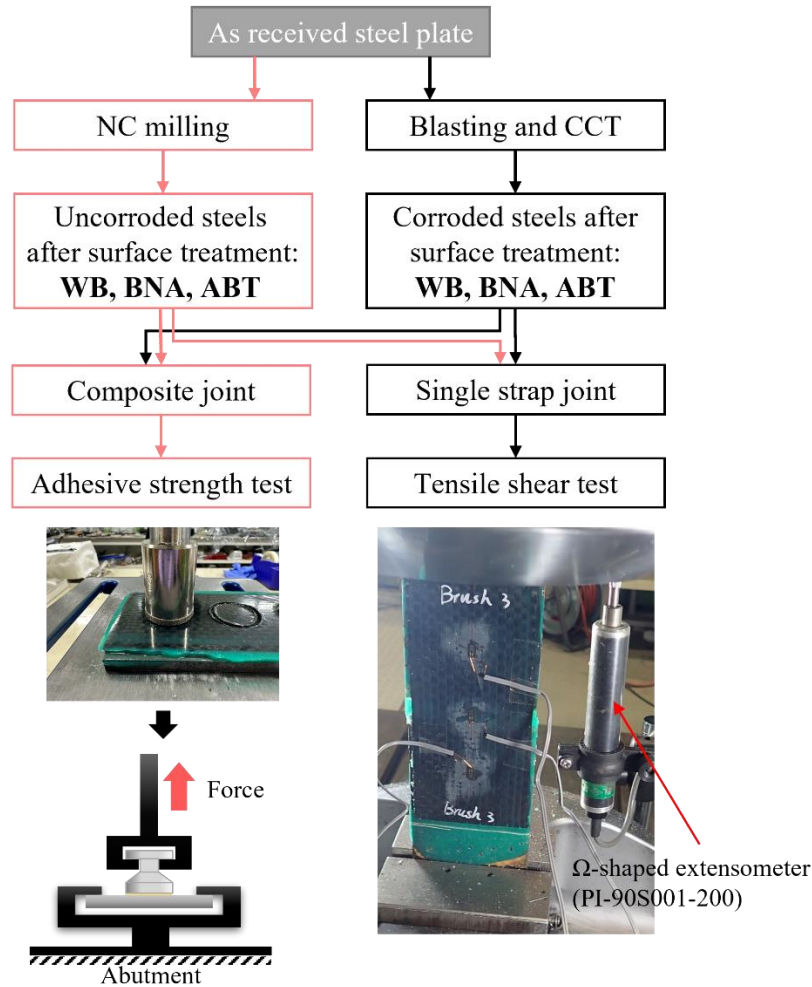


Fig. 4-2 Flowchart of specimen fabrication and test procedures

4.3 Adhesive strength of CFRP-steel joint

A desktop tension-compression testing machine (MSC-10/500-2, Tokyo Koki Testing Machine Co., Ltd.) was used for the pull-off test. The tensile speed was quasi-static at 0.5 mm/min. The test method and conditions as same as section 2.3.

A structural adhesive (Three Bond 2087) was used for dolly bonding. The adhesive surface of the dolly (JIS H 4000 Aluminum alloy A2017) was 20 mm in diameter, uniformly sanded, washed in an acetone solution, and then dried. The core area of the CFRP surface in the composite specimen was also removed using fine sandpaper to enhance adhesion. Moreover, the dolly was

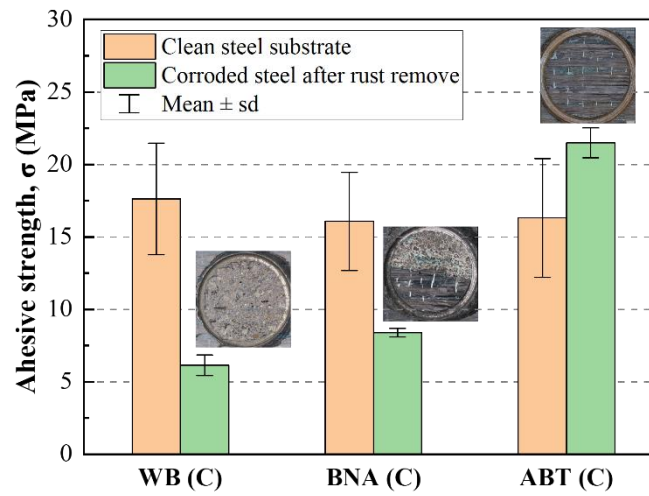


Fig. 4-3 Adhesive strength of uncorroded and corroded specimens

bonded to the core area of the specimen at room temperature under a uniform vertical compressive stress of 0.9 MPa for 30 min. Subsequently, the dolly specimen was cured at 35 °C for at least 48 hours and a circular groove was drilled around the core area before the test.

The adhesive strength results for the CFRP-steel joint specimens are shown in **Fig. 4-3**. For uncorroded steel substrates, regardless of the surface treatment, all failure modes are characterized by interlaminar CFRP delamination. As interlaminar strength depends solely on the adhesive's penetration and tensile strength within the CFRP, the bonding strength and standard deviation for the WB, BNA, and ABT specimens are approximately 14.2 to 17.5 MPa, with a standard deviation of around 3 to 4 MPa. This indicates that even exceptionally smooth steel surfaces can provide adhesive strength superior to interlaminar strength. The failure mode of the WB-C is a complete interfacial failure, which is a combination of interfacial failure and CFRP delamination, while ABT-C shows a typical delamination fracture. Accordingly, the tensile strength of the BNA-C and WB-C dropped to more than half of the corresponding value of the uncorroded specimens. In contrast, ABT treatment resulted in an increased adhesive strength of 31.7% for the corroded specimens.

It is assumed that the effective bonding area is altered due to residual rust or roughness. Treatment of corroded steel with power tools leaves residual rust that can create voids between the adhesive and the substrate, significantly reducing the effective bonding area and interfacial

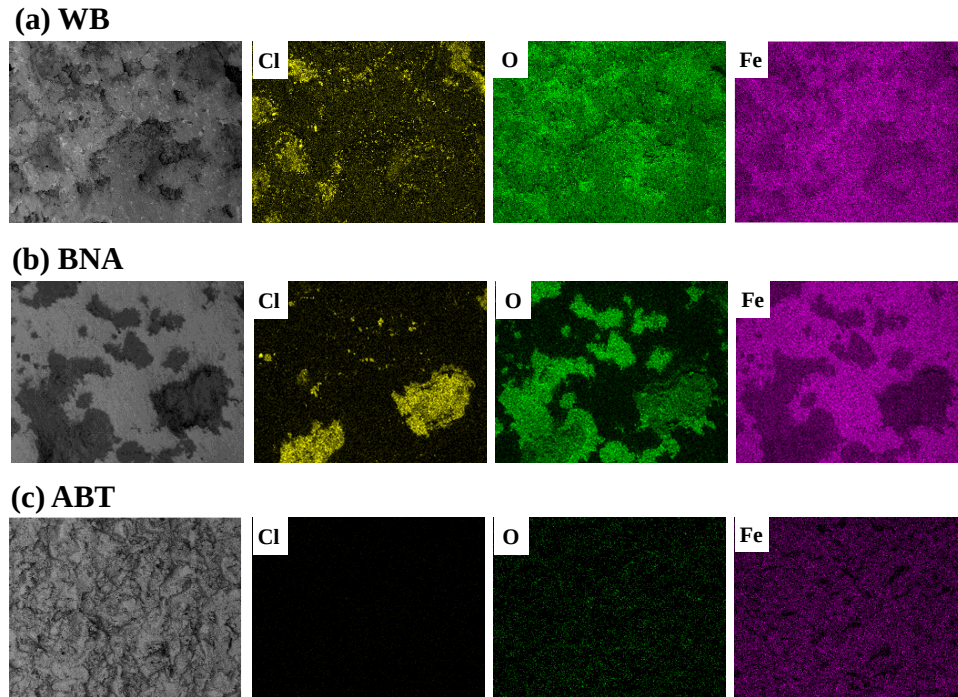


Fig. 4-4 SEM-EDX analysis on the de-rusting surfaces ($\times 50$ magnification)

adhesive strength. However, the ABT specimens exhibit an opposite trend. As shown in **Fig. 4-4 (c)**, there are few rust traces or oxide residues on the surface after ABT treatment. The actual attachment area for the same ABT treated uncorroded / corroded specimens differs by a factor of 1.58, as calculated based on the Wenzel roughness coefficient in **Table 2-7** mentioned above. Here, the surface fracture energy, G_f , is introduced and expressed by **Equation 4-1**:

$$G_f = G_0 + \psi \quad (4-1)$$

G_f is a combination of the energy dissipated at the interface G_0 and ψ , that ψ is the energy associated with the deformation of the bond substrate and adhesive materials (largely associated with viscoelastic loss). Packham proposed that G_0 may increase because of roughening of the surface, particularly for a moderately rough surface[134,135].

Therefore, can speculate that two aspects contribute to the increase in adhesive strength in ABT-C:

When adhesive failure occurs at the interface, G_0 equals the adhesive work W_a , which is closely related to the actual surface area (in cases of cohesive failure, G_0 equals W_c , which is also closely related to the actual surface area of the fracture). Hence, the larger Wenzel roughness factor is the

predominant factor leading to an increase in the apparent surface energy term G_a , resulting in greater fracture strength.

When the bonding surface is more irregular in shape (or rougher), a larger volume of epoxy resin is required to undergo plastic deformation during the fracture process[136], leading to a significant increase in ψ (the term for other energy absorption processes occurring during the fracture).

4.4 Tensile shear of CFRP-steel joint

Tensile shear tests were performed according to ASTM D5868-01(2014). The single-strap adhesively bonded joint was tested on a universal testing machine (MTS System Corporation, Eden Prairie, MN), and all specimens were loaded to failure under displacement control at a rate of 0.01 mm/sec. When loading, the out-of-plane stress and eccentric influence were ignored because the clamped area (clamping distance ≈ 50 mm) was relatively large.

Each specimen was fabricated using two pieces of corroded specimens after surface treatment, which were marked as the upper and lower parts for machine clamping. Next, three layers of carbon fiber fabric were bonded to the steel surfaces by wet layup process, and fully cured. The specimen dimensions are shown in **Fig. 4-5**; the width and length of the specimen were 70 mm

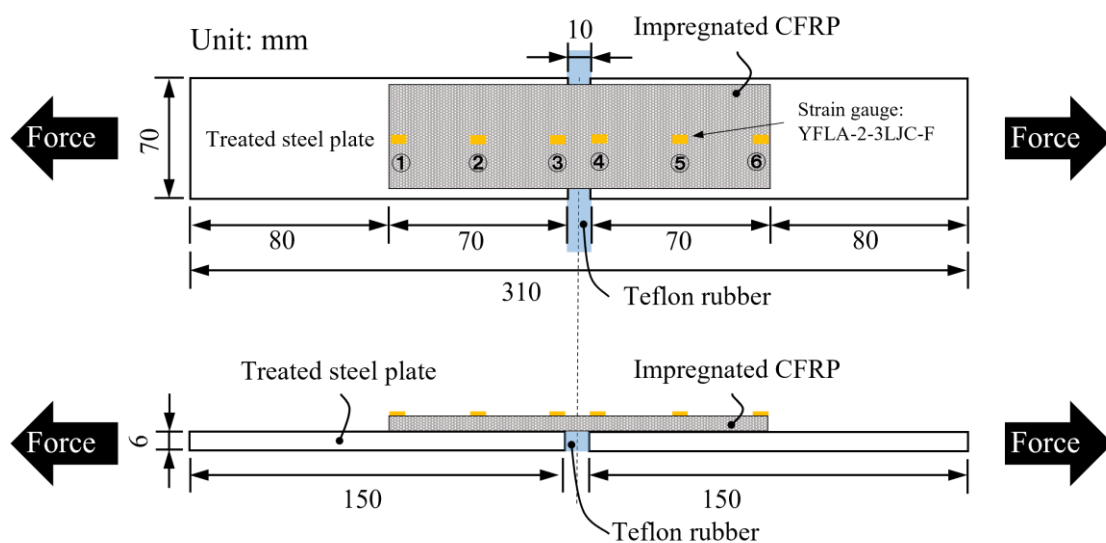


Fig. 4-5 Specimen configuration of CFRP-steel single strap joint for the tensile-shear test

and 310 mm, respectively, and the adhesive width was 60 mm. In addition, the overlap length of the impregnated CFRP and steel was approximately 70 mm on both sides, whereas the gap between the two steel plates was 10 mm, which was controlled using thick silicone rubber.

In addition, a Ω -shaped extensometer (PI-90S001-200) was set to record the corresponding displacement during the test, the plastic zone strain gauges of type YFLA-2-3LJC-F (gauge area $2 \text{ mm} \times 1.8 \text{ mm}$; base area $7.5 \text{ mm} \times 4 \text{ mm}$) were pasted to the central line of the CFRP top surface. For operational feasibility, the locations of strain gauge-1 and gauge-3 were set at 1 mm from the edges, whereas gauge-2 was set in the middle, between them. Strain gauges 4, 5, 6 are symmetrically placed on the other side.

The tensile properties of the epoxy matrix XL800 were determined using five resin dog bone specimens in their initial fully cured state, following ISO 527-1 (JIS K7161) standards. The average tensile strength was $36.25 \pm 7.47 \text{ MPa}$, exhibiting a typical brittle fracture mode. Due to the presence of bubbles at the fracture cross-section, this tensile strength value was significantly lower than the official data of 57.2 MPa. As the adhesive resin XL800 is relatively brittle, the shear strength is not influenced by the bonding length.

Severely corroded surfaces are more likely to exhibit non-uniform stress distribution. In this section, the adhesive area of the produced single test specimen exceeds the required area by the standards. After loading, the maximum shear stress (τ_{max}) was calculated using the **Equation 4-2**:

$$\tau = \frac{F}{L \cdot W} \quad (4-2)$$

Where F is the ultimate load measured by the testing machine, W is the bonding width (60 mm), and L is the bonding length at the fracture surface (70 mm).

The comparative results for the optimal shear stress and ultimate displacement of the three surface-treated specimens are presented in **Fig. 4-6**.

Fig. 4-7 provides an overview of the fracture surfaces on the steel side and CFRP side of the specimens. Observations from the results reveal the following:

WB (C): The shear strength is approximately one-third that of ABT and slightly lower than BNA. WB exhibits the highest standard deviation, and the CFRP surface peeled from the WB-treated steel surface shows brown residual rust spots.

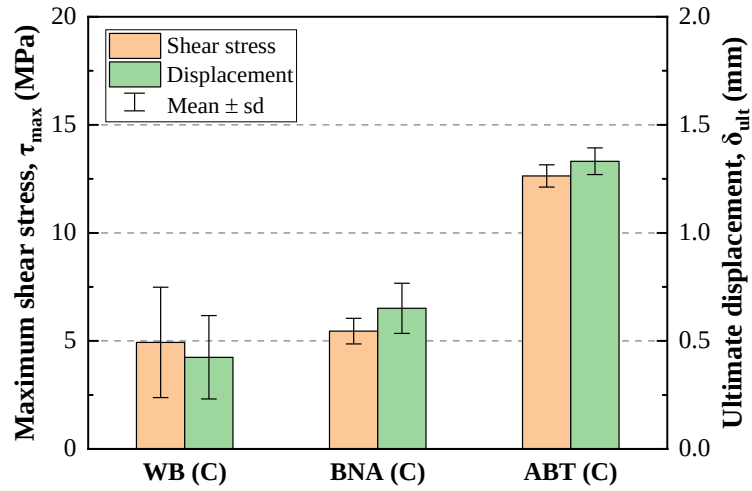


Fig. 4-6 Maximum shear stress and ultimate displacement of corroded specimens

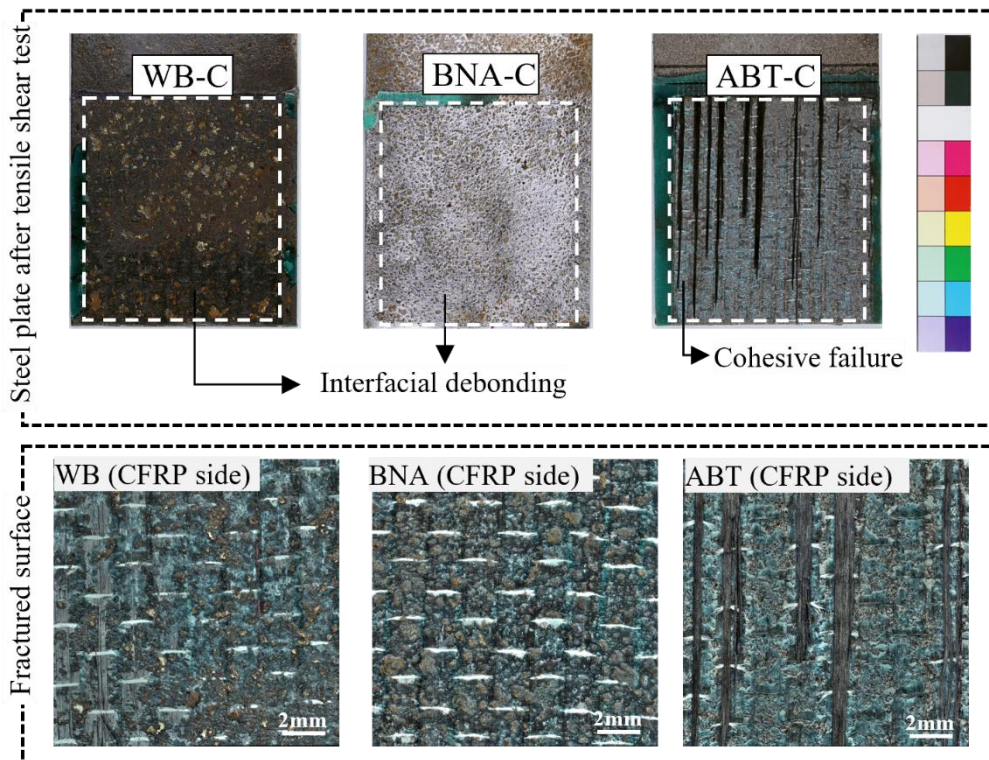


Fig. 4-7 Photos of shear failure interface of corroded specimens

BNA (C): Rust marks on the CFRP side correspond to the spotted pattern on the steel surface. Due to the more uniform surface created by BNA treatment and a cleaner steel substrate, the shear strength is lower but not random, and the bonding behavior is stable under different conditions.

ABT (C): Fracture surface observations indicate that primary cohesive failure occurs within the adhesive layer and is accompanied by delamination of the CFRP layers. Consequently, the shear strength of ABT depends on the strength of the resin and CFRP, representing the upper limit of shear resistance achievable in the tensile shear specimens.

In the load-displacement curve for steel-CFRP single-lap joints, as shown in **Fig. 4-8 (a)**, the joint stiffness was determined by extracting the slope in the elastic deformation region of the load-displacement curve for all three specimen types. Additionally, a complete load-displacement curve should include three stages: elastic, softening, and plateau[34]. These three stages are clearly observable in ABT-C. However, the curves for BNA and WB specimens lack the softening region.

Taking WB-No.1 as an example, **Fig. 4-8 (b)** illustrates the axial strain distribution on the CFRP surface during the loading process. As the rebound occurs, the strain values at Gauge-3 nonlinearly increase. This phenomenon is present in all specimens, regardless of surface conditions or fracture modes. By analyzing the equilibrium conditions, the average shear stress between two adjacent gauges is obtained, as expressed in **Equation 4-3** [122,126]:

$$\tau_i = (\varepsilon_{i+1} - \varepsilon_i)E_p t_p / \Delta l \quad (4-3)$$

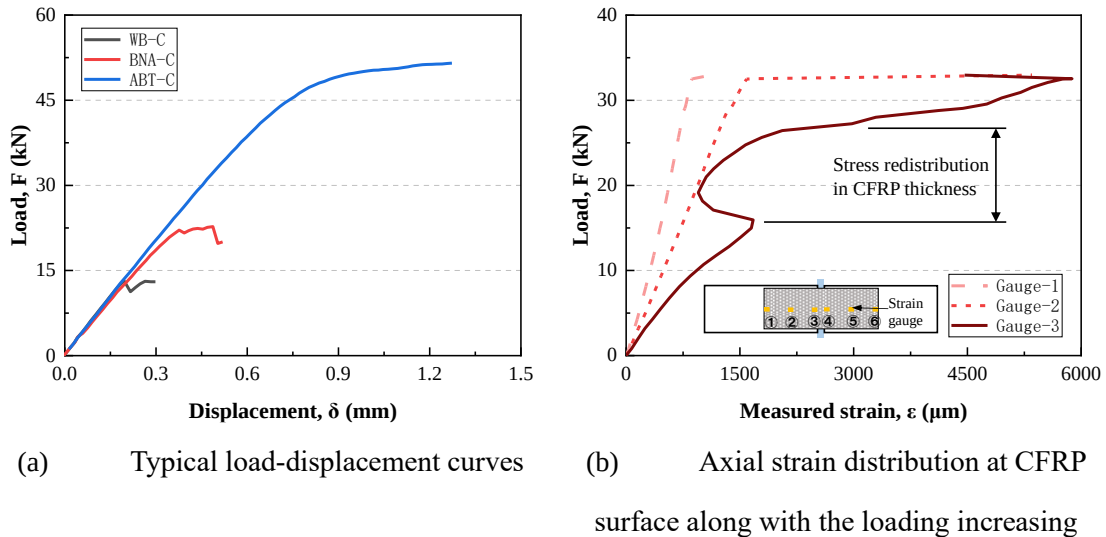


Fig. 4-8 Tensile shear test results

Where ε_i is the reading of the i th strain gauge ($i=1$ at the loaded end), E_p and t_p are the elastic modulus and thickness of the CFRP layer, respectively, and Δl is the distance between the adjacent strain gauges.

As $E_p t_p / \Delta l$ is approximately constant, the following three stages can be determined.

In the first loading stage, elastic deformation is primarily borne by the free part of the CFRP. The elastic deformation is maximum at Gauge-3, closest to the center (approximately equivalent to axial tensile stress). Due to the constraints imposed by adhesive deformation, the actual strain distribution across the thickness of the CFRP is non-uniform.

In the second loading stage, the bonding interface between the CFRP and steel begins to withstand greater shear forces. Stress redistribution occurs in the CFRP thickness direction, resulting in strain contraction at Gauge-3.

In the final stage, as shear deformation increases, debonding or resin brittle failure occurs starting from the free end. The average shear stress near the free end (Gauge-3) is significantly higher than that near the loading end (Gauge-1).

Fig. 4-9 compares the central gauge (gauge-2 or gauge-4) strain on the upside and downside surfaces of each specimen, which is located at the geometric center of the bonding area. The shear stress-strain curves on both sides are consistent, with random upward or downward fractures occurring. Since the CFRP experiences direct tension at the debonding site, the fracture-side strain

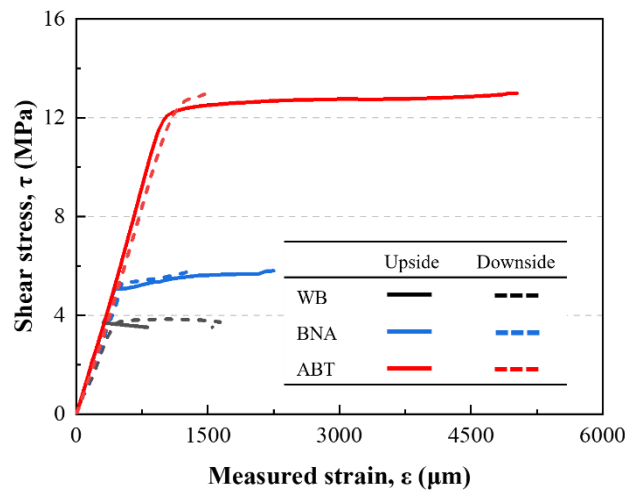


Fig. 4-9 Typical shear stress-strain curves of single strap joint

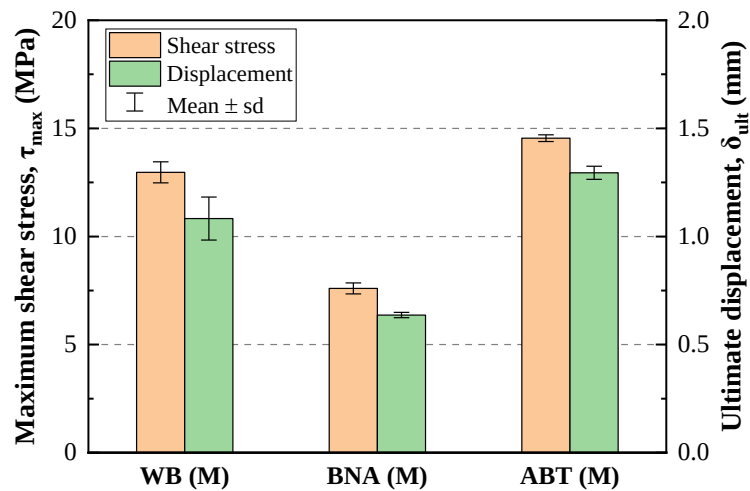


Fig. 4-10 Maximum shear stress and ultimate displacement of uncorroded specimens

covers a larger platform region. Therefore, the stress-strain curve of the ABT specimen that fails due to cohesive failure exhibits a longer platform. However, BNA and WB do not exhibit similar behavior. Hence, it is suggested that conventional bonding enhancement methods, such as using nonlinear adhesives or increasing bonding length, are only effective for ABT-treated surfaces.

Furthermore, the tensile shear test also performed on the specimens made by uncorroded steel, which were used as a comparison group. According to **Equation 4-4**, the shear stress and ultimate displacement of the three surface-treated uncorroded steel specimens are presented in **Fig. 4-10**. Compared with the corroded specimens, Rust had less of an effect on the blasted finish, and the surface adhesive strength of the blasted finish exceeded 12 MPa, regardless of the presence of rust on the steel surface. For the WB treatment, the impact from rust was larger, resulting in a significant reduction in the surface adhesive strength from about 12 MPa to about 55 MPa, which was caused by the relatively weak cleaning ability of WB treatment.

The photos of fracture surfaces on the steel side and CFRP side of the specimens are shown in **Fig. 4-11**. Observations from the test result and fracture surfaces reveal the following:

WB (M): The shear stress is slightly lower than that of ABT but higher than BNA, with a predominant failure mode being a combination of interfacial failure and cohesive failure. There is a small amount of carbon fiber residue on the surface, which is attributed to the interlayer failure of the wet-layer carbon fiber laminate.

BNA (M): The shear stress is the lowest in these three types of surface treatments and the fracture surface is mainly interfacial debonding. On the fracture surface of the CFRP side, many wave-like lines can be observed, which is produced by the local cohesion failure of the resin matrix.

ABT (M): Same with ABT (C), cohesive failure occurs mainly within the resin matrix and is accompanied by interlayer failure of the CFRP.

Compare the shear stress-strain curves of corroded and uncorroded single strap joint in **Fig. 4-12**. WB and ABT treatment methods showed a platform region caused by cohesion failure regardless of steel surface corrosion, while the BNA-treated uncorroded specimen did not. The bonding effect of the WB treatment was most affected by corrosion, and among the three treatments, the ABT treatment gave the best results and was least affected by the surface condition of the steel, while the BNA treatment method was the second best.

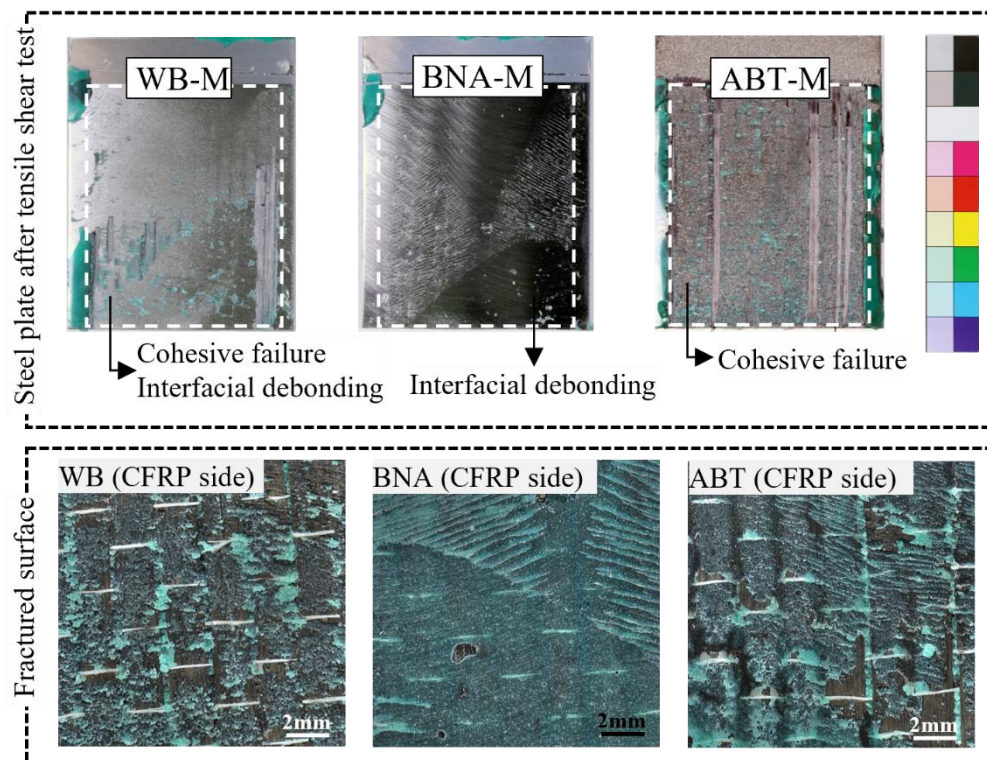


Fig. 4-11 Photos of shear failure interface of uncorroded specimens

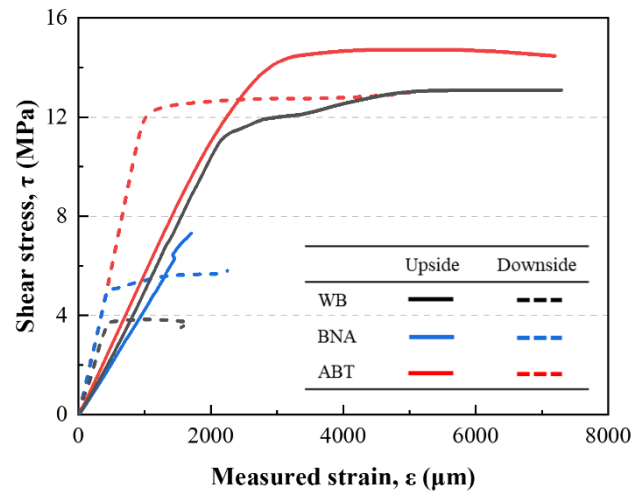


Fig. 4-12 Shear stress-strain curves of corroded and uncorroded single strap joint

4.5 Summary

Corroded and uncorroded steel were prepared and treated by three types of surface treatments (BNA, WB and ABT treatment) which commonly used in practice were applied. Systematic surface characterization and mechanical tests were performed to compared the tensile and shear strengths of the CFRP–steel joints under uncorroded and corroded surface conditions. The effect of residual corrosion on the interfacial bond behavior of the CFRP–steel joint was discussed and the following conclusions were drawn:

- (1) The interfacial adhesive strength of CFRP–steel joint is determined predominantly by the surface treatment methods. For the uncorroded and corroded steel, ABT-treated steel surface exhibited better bond behavior and tensile-shear strength than that processed with BNA and WB treatment because of its and large roughness.
- (2) Rust removal by ABT treatment can achieve the optimal surface condition for CFRP reinforcement. By comparing the fracture surfaces of the shear test specimens, rust adhesion can be observed in specimens treated with WB and BNA, while the ABT specimen does not show such adhesion. This is due to the lower rust removal efficiency of WB and BNA. Furthermore, the surface adhesion of rusted steel after WB treat is lower

than that of BNA. This is because epoxy resin directly bonds with the oxide film formed by heat friction rather than bonding with the steel substrate.

- (3) The factors influencing the bonding behavior of corroded steel, uncorroded steel, and CFRP are different. For uncorroded steel, the main factor affecting the adhesive strength is the surface roughness, greater roughness results in higher adhesive strength. However, for corroded steel, the impact of residual rust cannot be ignored. In addition to surface roughness, the rust removal efficiency also plays a crucial role. A lower rust removal efficiency can lead to more residual rust, reducing the effective bonding area of CFRP and subsequently lowering the adhesive strength.

CHAPTER 5 DETERIORATION MECHANISM OF CFRP– STEEL JOINT BASED ON THE HYDROTHERMAL AGING BEHAVIOR OF RESIN MATRIX

5.1 Introduction

Most studies conducted by researchers have focused on the hygroscopic properties of the polymers in extreme environments[137,138] and the effects of moisture and temperature on the mechanical properties of CFRP-steel joints. From their results, extreme environments have a significant effect on the mechanical properties of the CFRP-steel joints, with significant decreases in their tensile, compressive, and shear properties after hygrothermal aging[91–94]. However, the relationship between the moisture absorption rate and the degree of mechanical property deterioration in the actual use environment is unclear, and the recoverability of the mechanical properties of the material has not been assessed. The recoverability of CFRP material properties is crucial to ensuring the durability of the material and assessing the structural strength change in the reinforced parts. If CFRP can spontaneously recover owing to changes in ambient temperature and humidity or by manual methods, the service life of the material will be significantly extended. Therefore, assessing the recoverability of the mechanical properties of resin-impregnated carbon fiber fabrics is essential during different aging stages to predict the service life and maintenance intervals of reinforced structures.

This Chapter simulates the actual use environment of CFRP composite material, and comparatively studies the deterioration of CFRP–steel joint as well as resin dog bones under typical environmental conditions (e.g., high humidity, effect of salinity, etc.) from multiple perspectives. The relationship between moisture uptake and the decrease in mechanical properties was analyzed based on the total consideration of the deterioration of the material mechanical properties due to hygrothermal aging and the hydrolysis of the resin due to moisture absorption. Additionally, the recoverability of the mechanical properties of the resin materials after

hygrothermal aging was also investigated via physical heating desorption. Moisture absorption is examined in different temperatures and solution environments using resin sheet specimens, the chemical group content and thermophysical properties of the resin polymers during hygrothermal aging and after desorption were characterized using Fourier-transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC). The fracture surface morphology under moisture absorption and desorption state for the resin, as well as the fracture patterns of the CFRP–steel joint after hydrothermal aging were characterized using scanning electron microscopy (SEM).

5.2 Experimental materials and specimens

The materials used in this chapter are the same as in Chapter 2, using SM490A hot rolled steel with dimensions of 120 mm × 70 mm × 6 mm, unidirectional carbon fiber sheets MRK-M2-20 carbon fiber sheet, and XL-800 epoxy resin to make the CFRP–steel joint specimens. To obtain improved adhesive strength, the steel substrate was treated by ABT treatment (ISO 8501-1 Sa2.5, 30 cm projectile distance, 0.7 MPa projectile pressure, 60° projectile angle) with steel grit (10 Mosh hardness, 52.6 JIS particle size index, 7.4 specific gravity).

In this section of the experiment, two types of specimens were made. The first type is the CFRP–steel joint specimens for the hydrothermal aging test, which was made in the same way as in Chapter 3, with the only difference being that three layers of carbon fiber sheets were bonded on the surface of the steel. The second is two types of epoxy resin specimens, the epoxy resin dog bone specimen and the resin sheet, these two kinds of resin specimens were prepared for the hydrothermal aging test and moisture absorption test respectively. The dog bone specimens were made in the same way as in Chapter 3, the resin sheet specimens were made by filling a silicon rubber mold with epoxy resin, after which they were cured in an oven at 35 °C for 5 d. To minimize the individual variation of each resin sheet, a large resin sheet of 220 mm × 220 mm × 2 mm was first made using a 2.0 mm thick silicon rubber frame and then cut into equal parts to meet the design size requirements using an electric table saw with a blade width of 2 mm. Before curing, the mold was carefully checked to confirm that it was completely filled with resin to avoid the

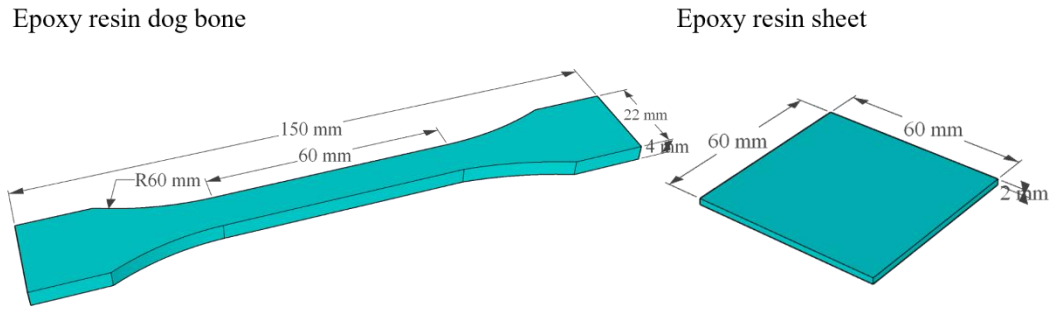


Fig. 5-1 Epoxy resin specimens dimension

formation of holes inside or on the surface of the specimens. The epoxy resin specimens dimension as shown in **Fig. 5-1**.

A total of 33 CFRP–steel joint specimens (for 99 times pull-off tests) and 125 resin dog bone specimens were prepared for this experiment, including the control specimens without aging. All specimens were initially adjusted (35 °C, 10% relative humidity (RH)) for 48 h. The experimental conditions and specimen IDs are listed in **Table 5-1**. Two test temperatures have been chosen, 25 °C for room temperature in the laboratory, which is the lowest temperature that can be effectively controlled in a thermostatic bath, and 40 °C, which is the temperature that can easily be reached in direct sunlight in the summer. Except for the control tests on the specimens unaged (denoted as UA), four aging conditions were performed: 25 °C distilled water (denoted as D25); 25 °C 3.5wt% NaCl aq (denoted as N25); 25 °C 95% RH (denoted as R25); and 40 °C distilled water (denoted as D40). The specimens for the distilled water and 3.5 wt% NaCl solution were placed in thermostat controlled water bath to obtain the 25 °C and 40 °C environmental temperatures, respectively, as shown in **Fig. 5-2**. For the 25 °C high humidity exposure conditions, the specimens were placed within a constant temperature humidity chamber. Different aging durations ($T=10$ d, 20 d, 40 d, 60 d) were set under each deterioration condition to assess the aging rates in various environments. Additionally, subsequent drying treatments were performed on specimens with different degrees of aging to remove absorbed moisture from the resin and CFRP–steel joint. This allowed for a quantitative comparison of the role of moisture in the irreversible deterioration of both the resin and joints. Half of the specimens under each deterioration condition underwent subsequent drying treatment.

Table 5-1 Experimental conditions for hydrothermal aging

Environmental condition	Adhesive joint (C)	Specimen type			
		Number	Epoxy resin (ER)	Number	
1) Control test of unaged	C-UA	1	ER-UA	5	
2) 25 °C distilled water	C-D25	8	ER-D25	40	
3) 25 °C 3.5wt% NaCl aq	C-N25	8	ER-N25	40	
4) 25 °C 95% RH	C-R25	8	—	—	
5) 40 °C distilled water	C-D40	8	ER-D40	40	

Note: D25, D40, N25 and R25 represent the exposure environment and temperature.

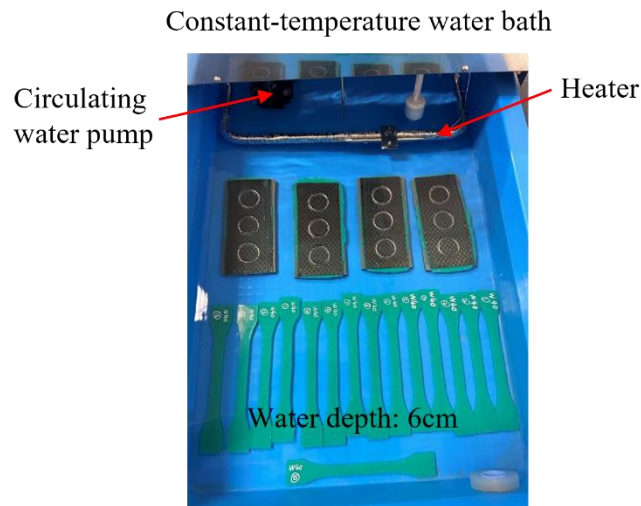


Fig. 5-2 Hydrothermal aging equipment

5.3 Moisture absorption and material characterization of resin matrix

5.3.1 Moisture absorption curve of resin matrix

To investigate the absorption rate of moisture in the epoxy resin in different environments, a moisture absorption test was designed referenced to JIS K7209. In addition to the moisture content of the environment, the ambient temperature and solution solute affect the water absorption rate of the resin. Therefore, five moisture absorption test environments were established based on the service environments of typical bridge applications. The tests were performed on the resin sheet

specimens for 1) 25 °C distilled water, 2) 25 °C 3.5wt% NaCl aq, 3) 25 °C 95% RH, 4) 40 °C distilled water and 5) 40 °C 3.5wt% NaCl aq. Three resin sheet specimens were prepared for each aging environment.

Before the test, all the specimens were cured in an oven at 35 °C and 10% RH for 24 h for full drying. All specimens were weighed using a scale with an accuracy of 0.01 mg to obtain their reference value dry stage weights (w_0). Thereafter, the specimens were immediately exposed to the experimental environment. To measure the weight change over time, the specimens were removed from the experimental environment after a fixed exposure period (t), wiped using a dry cloth, and weighed immediately (w_t). The specimens were subsequently returned to the experimental environment to continue exposure. The moisture uptake (M_t) of each specimen was calculated using **Equation 5-1**:

$$M_t = \frac{(w_t - w_0)}{w_0} \times 100\% \quad (5-1)$$

After the moisture absorption test, the specimens were put into an oven and dried at 3 °C for 10 d to desorb moisture. After drying, specimens were weighed one by one.

The intrusion of moisture causes the epoxy resin to swell[139], thereby reducing its structural strength. Discussing the moisture absorption rate in different environments can help predict the deterioration of resin-impregnated carbon fiber fabrics. According to the previous study, moisture is an important factor in resin deterioration, prolonged aging in a humid environment can lead to moisture infiltration. Therefore, discussing the moisture uptake of the resin matrix is essential. The moisture uptake (M_t) of each epoxy resin sheet was calculated using **Equation 5-1**. Several researchers have used the Fickian model to predict moisture diffusion in FRP composites and adhesives[140]. The thickness of the epoxy resin is small for the one-dimensional diffusion case; therefore, the solution to Fick's second law can be expressed by **Equation 5-2**[141]:

$$\frac{C(x, t)}{C_\infty} = 1 - \frac{\pi}{4} \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{(2n+1)} \right] \exp \left[-\frac{(2n+1)^2 \pi^2 D t}{h^2} \right] \cos \left(\frac{(2n+1) \pi x}{h} \right) \quad (5-2)$$

where h is the resin sheet thickness, D the diffusion coefficient, and C the concentration as a function of distance from the center of the plate x and time t . The total moisture content can be expressed by the time-dependent **Equation 5-3**:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2} \right] \exp \left[-\frac{(2n+1)^2 \pi^2 D t}{h^2} \right] \quad (5-3)$$

where M is the moisture content and the subscripts t and ∞ represent the conditions at the time of interest and saturation, respectively. The diffusion coefficient D can be obtained using the following **Equation 5-4**:

$$D = \frac{\pi h^2}{16 M_\infty^2} \left[\frac{M_2 - M_1}{t_2^{\frac{1}{2}} - t_1^{\frac{1}{2}}} \right]^2 \quad (5-4)$$

The moisture uptake and fitted curves are shown in **Fig. 5-5**. Although the epoxy resin sheet did not reach saturation during the test (120 d in a 25 °C environment, 60 d in a 40 °C environment), the results obtained during the moisture absorption period showed a high correlation with the nonlinear fitting curves. Therefore, it can conclude that the moisture absorption of the resin material used in this experiment was compounded by Fick's second law. The diffusion parameters were also calculated using the equations and are listed in **Table 5-2**. Initially, the increase in moisture uptake is rapid, and high temperature influences the moisture uptake speed. From **Table 5-2**, the resin sheets in the distilled water and 3.5wt% NaCl solution have higher diffusion rates of $7.51 \times 10^{-3} \text{ mm}^2/\text{s}$ and $7.56 \times 10^{-3} \text{ mm}^2/\text{s}$, respectively, at 40 °C, whereas the diffusion rates in the distilled water, 3.5wt % NaCl solution, and high humidity environment at room temperature (25 °C) are $2.17 \times 10^{-3} \text{ mm}^2/\text{s}$, $2.04 \times 10^{-3} \text{ mm}^2/\text{s}$, and $1.68 \times 10^{-3} \text{ mm}^2/\text{s}$, respectively.

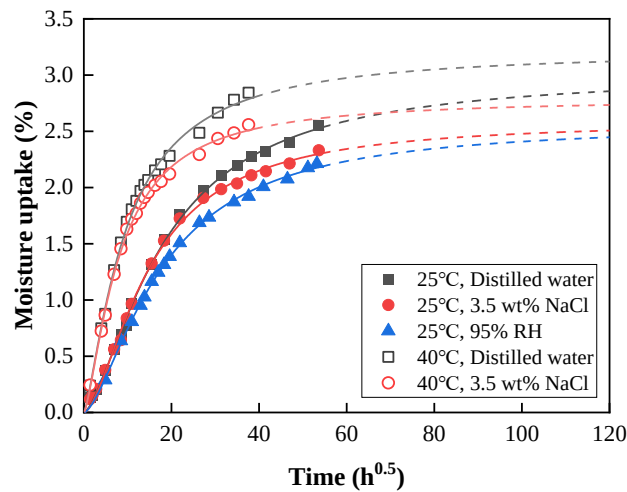


Fig. 5-3 Moisture uptake and fitted curves

Table 5-2 Diffusion coefficients for specimens in each aging environment

Aging environment	25 °C distilled water	25 °C 3.5wt% NaCl solution	25 °C 95% RH	40 °C distilled water	40 °C 3.5wt% NaCl solution
Diffusion coefficient ($\times 10^{-3} \text{ mm}^2/\text{s}$)	2.17	2.04	1.68	7.51	7.56

From **Fig. 5-3**, the fitted curves of the moisture absorption rate for the resin sheets at 25 °C and 40 °C, whether in the distilled water or 3.5wt% NaCl solution environment, eventually reach the same height for each environment. The maximum moisture absorption rate in the distilled water environment is higher than that of the 3.5wt% NaCl solution and high humidity environments, which indicates that the maximum moisture absorption rate is not affected by temperature but is only related to the electrolyte environment[142–144]. For the same period of moisture absorption, the temperature and moisture uptake are positively correlated, and high temperature will result in faster moisture absorption[145]. This is because the thermal movement of the molecules increases at high temperatures, and the number of voids formed between the resin molecules increases, enabling water molecules to enter the resin. In addition, the moisture absorption rate is influenced by the osmotic pressure inside and outside the resin sheet[139,146]. The osmotic pressures in the high-humidity environment and 3.5wt% NaCl solution were smaller than that in the distilled water environment; therefore, the maximum moisture absorption rates in the high-humidity environment and 3.5wt% NaCl solution were also smaller than that of the distilled water environment.

5.3.2 FT-IR analysis results

Fourier-transform infrared spectroscopy–attenuated total reflectance (FTIR-ATR) was used to analyze the resin sheet specimens in the moisture absorption and desorption test. The test was conducted for wavenumbers (cm^{-1}) between 400 cm^{-1} and 4000 cm^{-1} , which correspond to the O–H stretching band, C–O–C (ether bond), hydroxyl group, and $\text{C}\equiv\text{C}$ (carbon triple bond). The

analysis was repeated 32 times under atmospheric conditions and resolution is 4 cm^{-1} . The center of each test resin sheet was analyzed, and moisture was wiped from the surface of the test sheet before analysis to avoid affecting the results. After the FT-IR analysis, the specimens were immediately returned to the test environment to continue exposure.

In contrast to high-temperature aging environments, aging environments close to room temperature are more common. To investigate the change in the chemical structure of the epoxy resin as affected by different aging environments, the epoxy resin sheets subjected to varying aging periods at room temperature ($25\text{ }^{\circ}\text{C}$) were analyzed using FTIR-ATR. The measurement results in **Fig. 5-4** show the peaks of the O–H stretching band in $3600\text{--}3300\text{ cm}^{-1}$ range, the C–H stretching band in $3000\text{--}2800\text{ cm}^{-1}$ range and C≡C bond in $2400\text{--}2000\text{ cm}^{-1}$ range change with immersion time. Similar trends were observed in the three aging environments. In all three aging

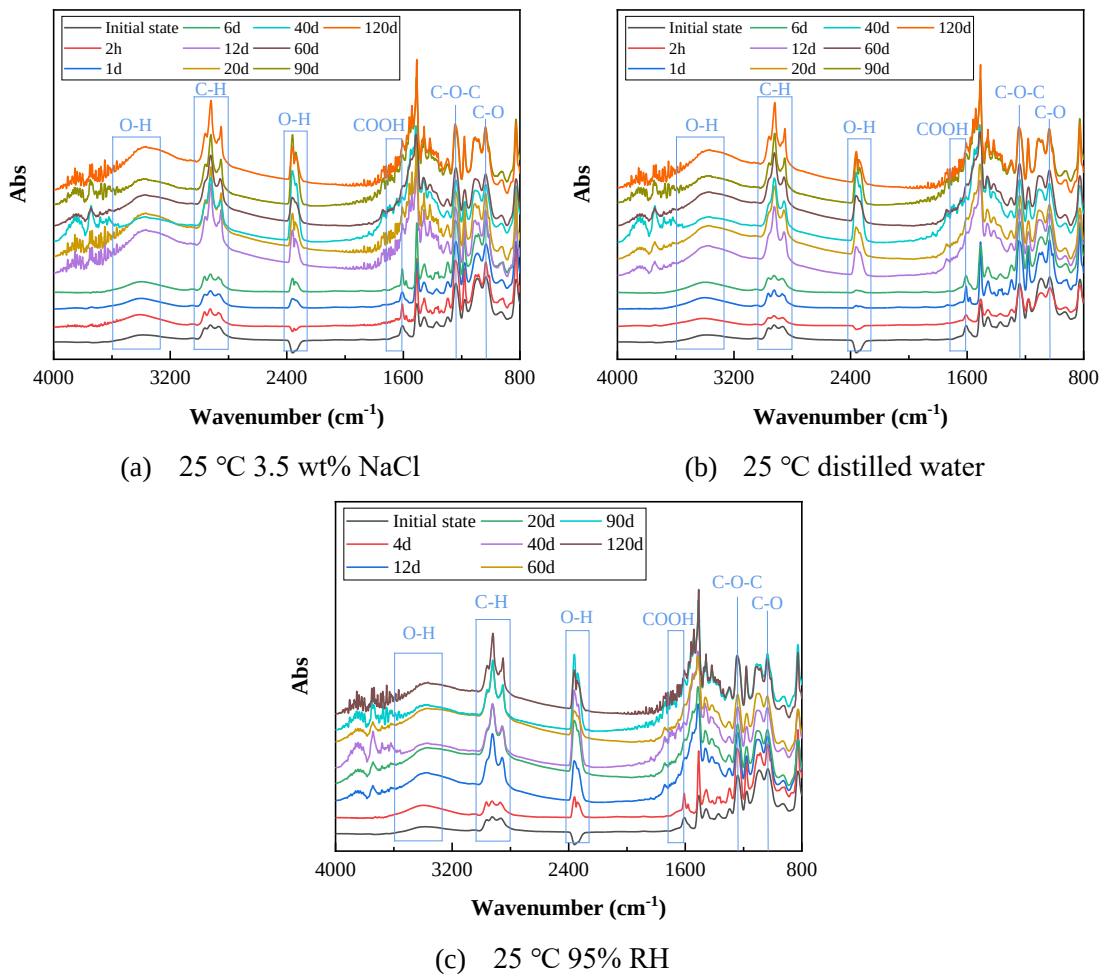


Fig. 5-4 FTIR-ATR curves of resin sheets after moisture absorption test

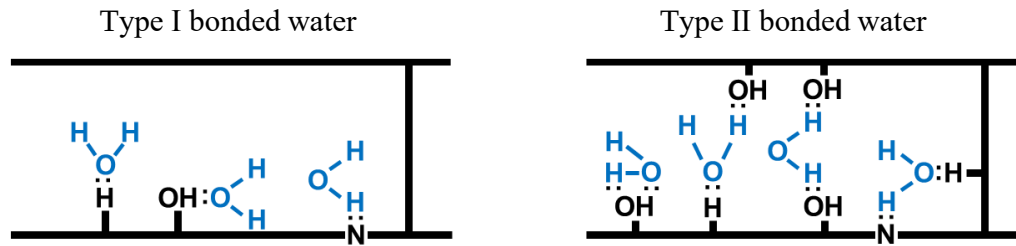


Fig. 5-5 Types of bonded water in epoxy resin[142]

environments, a significant increase in the peak of the O–H and C–H stretching band as well as C≡C bond was found at the beginning of 12 h. Compared Fig. 5-4 (a) to Fig. 5-4 (b), there is no significant difference in stretching band of the peaks, indicating that the solution solute does not significantly affect the peak change of each stretching band at the same temperature. From Fig. 5-4 (a) and Fig. 5-4 (c), the stretching band in the immersion and high humidity environments is also the same, while there is a difference in the magnitude of change of the peak. The magnitude of change in the high humidity environment is lower than that in the immersion environment, indicating that the diffusion rate of moisture is lower than that in the immersion environment, which is consistent with the conclusion in section 5.3.1.

According to Zhou[142], after the resin has absorbed water over a long period, two types of bonded water are produced inside the resin: 1) type I and 2) type II bonded water, as shown in Fig. 5-5. The peak curve of the O–H stretching band shows that the type I bonded water content in the resin gradually increases with increasing immersion time. The hydrolysis reaction leads to the decomposition of the ester group (C=O) in the epoxy resin into the carboxylic acid group (COOH) by water, and an increase in the carboxylic acid group (COOH) peak can be clearly observed from the results in the range of 1700-1750 cm⁻¹. The changes in the peak curves for the C≡C bond, C–H stretching band also show that the resin is hydrolyzed during immersion[147], and the degree of hydrolysis increases with time.

By comparing the peaks of the O–H stretching band at different aging times, the peaks did not always increase with time and dynamic changes were exhibited. In Fig. 5-6, the peak intensity of the type I bonded water increased rapidly after the first 2 h of aging and then decreased after 1 d,

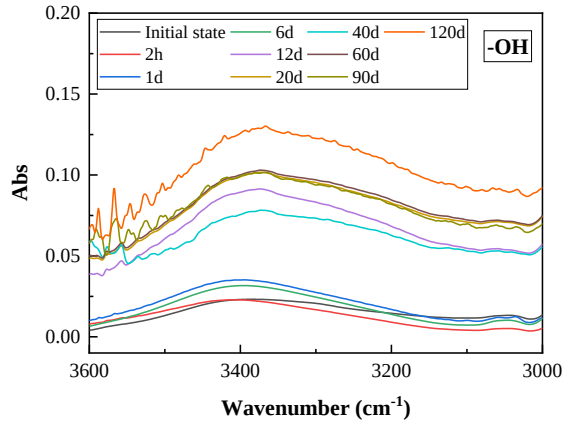


Fig. 5-6 Infrared spectra of the O–H stretching band

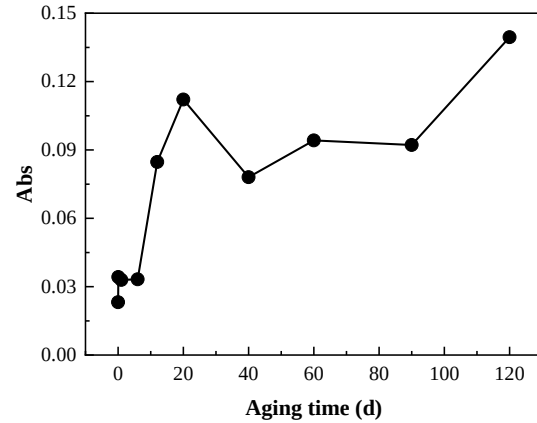


Fig. 5-7 Relationship between curve peak and aging time

which may be attributed to the conversion of type I into type II bonded water. Thereafter, the peak intensity continued to increase, and after 20 d of immersion, the peak intensity decreased again, indicating another conversion of the type II bonded water. The relationship between the peak value and aging time is shown in **Fig. 5-7**; similar changes were observed in Galvez's experiments[148].

5.3.3 Thermal characteristics after moisture absorption

To analyze the thermal characteristics of the epoxy resins as affected by moisture, temperature, and chloride presence, the specimens in the water absorption tests and hydrothermal aging test were analyzed using a high-sensitivity differential scanning calorimeter (DSC 7000, Hitachi High-Tech). The glass transition temperature (T_g) was measured at temperatures between 0 °C and 200 °C with a heating rate of 10 °C/min and cooling rate of 20 °C/min. Nitrogen was used as a protective gas. The weight of the specimen was maintained at approximately 10 mg to ensure the accuracy of the results.

A thermodynamic analysis of the resin sheets subjected to moisture absorption tests at room temperature (25 °C) was performed (1st run), and the results are shown in **Table 5-3** and **Fig. 5-8**, the first and second run curves of the unaged resin were also given. From the results, after 20 d of moisture absorption deterioration, the glass transition temperature (T_g) of the resin sheet in the

Table 5-3 Increased weight percentage compared to the initial dry state

Temperature	25 °C			40 °C	
Environment	Distilled	3.5 wt% NaCl	95%	Distilled	3.5 wt% NaCl
	water	aq	RH	water	aq
Wg (%)	0.759	0.600	0.591	0.472	0.408

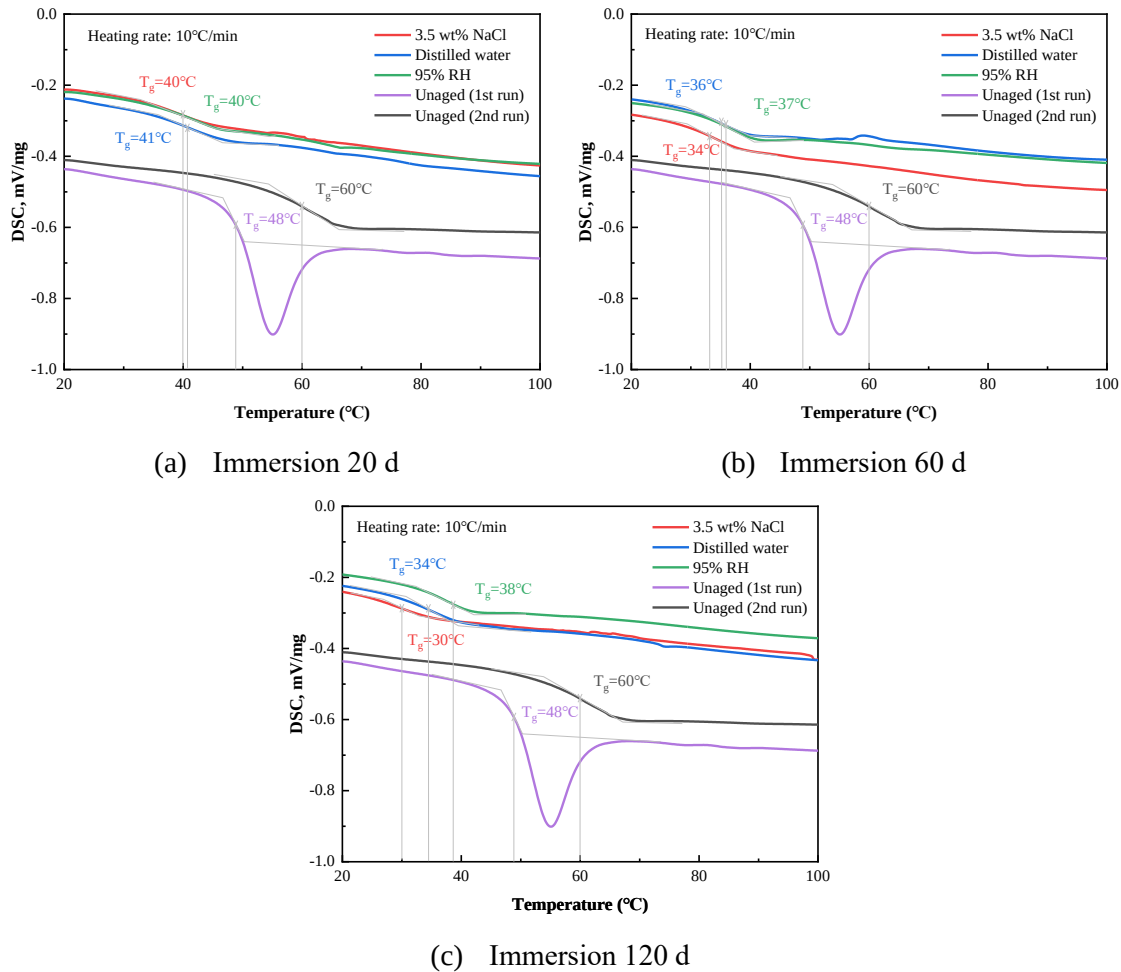


Fig. 5-8 DSC curves of resin sheets during moisture absorption test

3.5wt% NaCl solution and high-humidity environments decreased from 48 °C to 40 °C. The T_g of the resin sheet in the distilled water environment decreased to 41 °C. After 60 d, the T_g decreased to 37 °C, 36 °C and 34 °C. After 120 d, the T_g of the resin sheet in the 3.5 wt% NaCl solution environment decreased to 30 °C, which was approximately two-thirds the T_g before aging (Unaged 1st run). The T_g of the resin sheet in the distilled water environment decreased to 34 °C.

However, the T_g of the resin sheet exposed to the high humidity environment was 38 °C, an increase of 1 °C compared to that after 60 d of moisture absorption.

This change occurred because type I bonded water caused the resin to swell, resulting in a significant decrease in the T_g at the beginning of the deterioration[149]. From the results of previous studies, both type I and type II bonded water affect the T_g of the resin. Type II bonded water promotes secondary cross-linking of the hydroxyl and hydrophilic groups in the epoxy resin network, and this reaction inhibits the decrease in T_g [149,150]. As the moisture uptake increased and the amount of type II bonded water contained within the resin increased, this inhibitory effect became increasingly significant. Therefore, the T_g at 120 d was slightly higher than that at 60 d, which may be caused by the inhibitory effect of the type II bonded water. However, in general, an increase in moisture uptake promotes a decrease in T_g .

5.3.4 Irreversibility of moisture absorption

The epoxy resin sheets with moisture absorption test were put into an oven and dried at 35 °C (10%RH) for 10 d to desorb moisture. The weight of the specimens after drying was measured and the rate of weight gain (W_g) relative to the unaged state was calculated. Calculated results are shown in **Table 5-4**. From the results, it can be observed that the weight of the specimens after drying remains higher than their initial, non-absorbed state. This indicates that at 35 °C, the absorbed moisture cannot be completely removed, and this residual moisture is irreversible. When comparing specimens exposed to humidification at 25 °C and 40 °C, the residual weight of the specimens in the 3.5wt% NaCl environment is consistently lower than that in the distilled water environment. This aligns with the results of the moisture absorption test, where the moisture absorption rate in the saltwater conditions is lower than that in the distilled water environment. Under the same distilled water environment, the W_g of the resin sheet absorbing moisture at 40 °C is less than that of the resin sheet absorbing moisture at 25 °C. This may be attributed to the longer absorption exposure time (25 °C 120 d, 40 °C 60 d), resulting in more irreversible bonding behavior and would lead to more residual moisture in the specimen.

Table 5-4 Glass transition temperature of resin sheets in different environments

	25 °C 3.5wt% NaCl	25 °C distilled water	25 °C 95% RH
20 d	40 °C	41 °C	40 °C
60 d	34 °C	36 °C	37 °C
120 d	30 °C	34 °C	38 °C

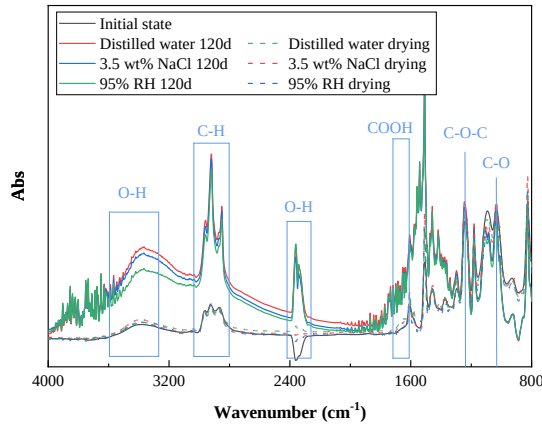


Fig. 5-9 FTIR-ATR curves of resin sheets after moisture desorption

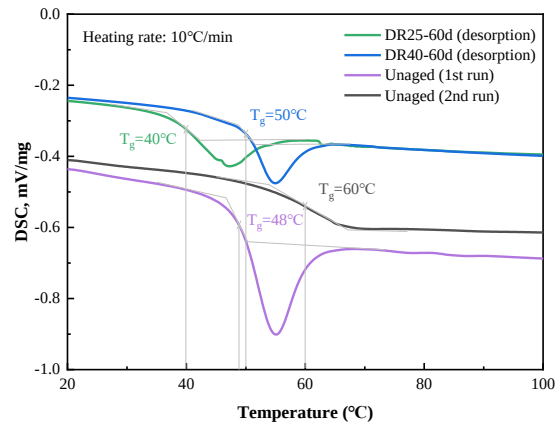


Fig. 5-10 DSC curves of resin sheets after moisture desorption

The FTIR curves of epoxy resin sheets after desorption moisture were also measured, result as shown in **Fig. 5-9**. By comparing the FT-IR curves of the specimens absorbed moisture for 120 d and desorption. It is clearly observed that the intensity of the hydroxyl stretching vibrations located between the 3200-3600 cm^{-1} range is substantially reduced, this indicates that type I bonded water is removed during the drying and desorption process. On the other hand, comparing the FTIR curves of the specimen after moisture desorption and initial states, it was found that there was still a difference, the peaks corresponding to hydroxyl group stretching vibrations remain slightly elevated compared to the unexposed specimens, and the peaks associated with the carbon-carbon triple bonds formed during hydrolysis still maintain higher levels than those in the unexposed specimens. This indicates that residual moisture (type II bound water), continues to exist within the desiccated specimens, and the effects resulting from hydrolysis are irreversible.

To investigate the reversibility of the effects of different environments on the thermal properties of resins, the dog bone specimens at different hydrothermal aging conditions were dried in oven

at 35 °C for 10 d. A sample of approximately 10 mg was cut from each specimen for DSC analysis and the results are shown in **Fig. 5-10**. Compared to the moisture absorption specimens in **Fig. 5-8 (b)**, the glass transition temperature of the dry specimens (DR25-60d) was increased from 34 to 40 °C, this suggests that the aging effects induced by the environment include a partially reversible component, which can be restored to some extent through physical dehumidification, thus improving a portion of the material's thermal performance. However, for the specimens (DR40-60d) aged at 40 °C, the T_g after drying is slightly higher than that of the unaged samples (1st run) but lower than the fully cured T_g (2nd run). This can be attributed to post-curing occurring in the specimens in the 40 °C aging environment, with further cross-linking reactions happening within the resin. Consequently, the specimens aged at 40 °C exhibit a higher T_g compared to those aged at 25 °C after drying. However, on the whole, these effects are irreversible, as the thermal performance does not fully recover.

5.4 Hydrothermal aging of epoxy resin

5.4.1 Mechanical properties of aged epoxy resin

To investigate the effects of moisture and temperature on the mechanical properties of the epoxy resin and its recoverability. All specimens were subjected to a tensile test after hydrothermal aging and dehumidification recovery using a tensile testing machine (Tokyo Koki Tester MSC-10/500-2) at a testing speed of 0.5 mm/min. Strain gauges were attached to the centers of the dog bone specimens to measure their strains under different conditions during the test, as shown in **Fig. 5-11**. Epoxy resin dog bone specimens under all working conditions were tested 5 times in parallel to obtain reliable tensile strength.



Fig. 5-11 Tensile test setup

Table 5-5 Tensile test results for unaged specimens

Load, P_{ER} (N)	Tensile strength, σ_{ER} (MPa)	Young's modulus, E_{ER} (MPa)
1420	33.2	2500

Table 5-6 Tensile test results for aged epoxy resin dog bone

		25 °C distilled water		25 °C 3.5wt% NaCl solution		40 °C distilled water	
		Aging	Drying	Aging	Drying	Aging	Drying
20 d	Load, P_{ER} (N)	1,200	1,433	1,263	1,332	870	1,359
	Tensile strength σ_{ER} (MPa)	28.9	32.9	29.6	305	18.9	31.4
40 d	Load, P_{ER} (N)	918	1,417	1,087	1,591	793	1,242
	Tensile strength σ_{ER} (MPa)	21.3	31.5	25.8	37.0	18.4	28.7
60 d	Load, P_{ER} (N)	910	1,338	1,108	1,351	622	1,099
	Tensile strength σ_{ER} (MPa)	20.9	32.3	25.8	31	14.1	25.4

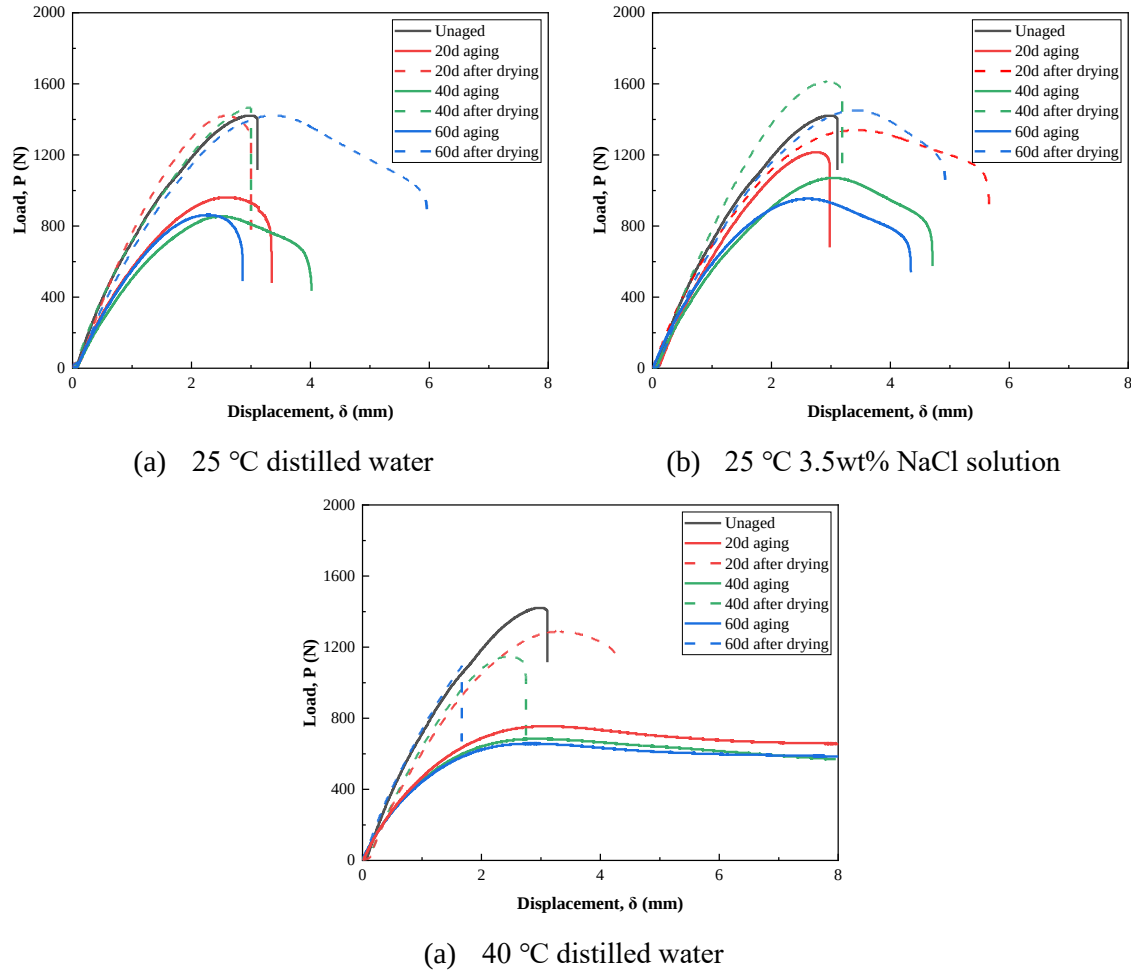


Fig. 5-12 Load–displacement curves

Tensile tests were performed on dog bone specimens that were unaged, subjected to 60 d hydrothermal aging and aging followed by drying, the experimental results are presented in **Table 5-5** and **Table 5-6**, respectively. The load–displacement curves for the aged specimens are shown in **Fig. 5-12**. Because of the large number of specimens, the results of only one specimen from each environment are shown in the **Fig. 5-12**. Compared with the unaged dog bone specimens, the maximum loads of the dog bone specimens immersed in distilled water at 40 °C decreased the most, followed by those immersed in distilled water at 25 °C. The decrease for the specimens immersed in the 3.5wt% NaCl solution at 25 °C was the smallest, indicating that chloride ions are not significant to the process of resin deterioration and that the main factor leading to a reduction in the resin mechanical properties is the immersion environment. A significant portion of the dried specimens did not recover to their undeteriorated strength, indicating that the damage caused by

moisture to the resin polymer is irreversible and that physical dehumidification can reduce the damage to some extent but cannot completely remove it. This can be explained by the formation of bonded water resulting from the resin's water absorption.

As mentioned in section 5.3.2, the ingress of moisture into the resin results in the formation of two types bonded water. Type II bonded water is more difficult to physically remove than type I bonded water because it is linked to the resin by multiple hydrogen bonds and has a high activation energy[142]. When type I bonded water diffuses into the epoxy resin network and breaks the initial interchain van der Waals forces, the epoxy resin swells[149]. The increase in the amount of type I bonded water changes significantly during the early stage of moisture absorption, which leads to plasticization of the resin[151]. The infrared spectroscopic analysis of the specimens shows that the type I bonded water dominates the epoxy resin during hygrothermal aging and, as the aging proceeds, a portion of the type I bonded water transforms into type II bonded water, contributing to the overall effect. Therefore, the reduction in material properties is the result of the joint action of the two types of bonded water. However, due to the difficulty in removing type II bound water, the mechanical properties of the material cannot be fully restored through physical drying methods.

By comparing the load–displacement curves of dog bone specimens under three different conditions in **Fig. 5-12**, it was also found that, unlike the elastic-plastic material characteristics exhibited by dog bone specimens in distilled water (**Fig. 5-12 (a)**) and 3.5wt% NaCl solution (**Fig. 5-12 (b)**) at 25 °C, the specimens under the condition of immersion in distilled water at 40 °C (**Fig. 5-12 (c)**) exhibited plastic deformation characteristics, the deformation continued to increase within the measurement range without any occurrence of fracture, The experimental results from Sections 5.3.1 and 5.3.3 provide an explanation that moisture causes a decrease in the glass transition temperature of the resin, while elevated temperatures significantly increase the resin's moisture absorption rate. When the glass transition temperature is lower than the ambient temperature, the resin transitions from a glassy state to a rubbery state, leading to a loss of its original mechanical strength. This effectively explains the continuous elongation of the resin within the measurement range shown in **Fig. 5-12(c)**, without experiencing fracture.

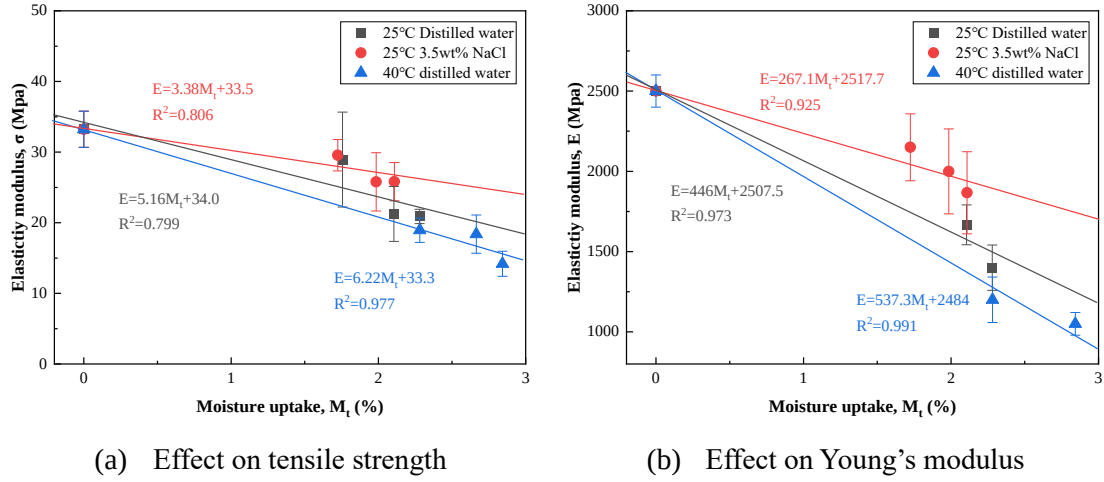


Fig. 5-13 Effect of moisture uptake on mechanical properties of the resin

In addition, the relationship between the moisture uptake and mechanical properties of the epoxy resin is discussed, and the results are shown in **Fig. 5-13**. Both the tensile strength and Young's modulus of the epoxy resin decreased linearly with increasing moisture uptake. For the same temperature, the decreased rate of the strength and Young's modulus in the 3.5wt% NaCl solution is lower than that of the distilled water environment. In addition, the temperature influences the rate of decrease within the same aging environment, the higher the temperature, the faster the decrease. These data enable the evaluation of the stress redistribution caused by moisture uptake in the resin-impregnated carbon fiber fabric during exposure.

5.4.2 Fracture surface analysis

To investigate the effect of moisture on the fracture mechanism, fracture analysis of the fracture surfaces was carried out by scanning electron microscopy (SEM, SU3500) with backscattered electron (BSE) imaging under 15 kV low-vacuum conditions on dog bone specimens that were unaged, hydrothermal aging for 60 d, and dried after 60 d of hydrothermal aging as shown in **Fig. 5-14**.

From **Fig. 5-14 (a)**, the fracture surface of the unaged specimen was quite smooth, and even at magnification of 500 times, no obvious fracture cracks were observed, only a few longitudinal conical cracks.

In **Fig. 5-14 (b) and (c)**, the fracture surfaces of the specimens subjected to 60 d of hydrothermal aging at 25 °C and 40 °C showed distinct radial striations, as well as narrow shear bands, which were very uneven. The fracture surfaces of the crack extension zones of ER-D25 were relatively smooth, with regular spacing “ribs” perpendicular to the direction of crack extension. Compared with ER-D25, ER-D40 has more dense radial stripes and parabolic cracks, indicating that during continuous loading, the cracks expand slowly due to the decrease in plasticity of the resin caused by the higher aging temperature, and their preambles cross each other to form parabolic cracks.

Fig. 5-14 (d) shows the fracture surfaces of ER-40 after drying. Different from ER-D25 and ER-D40, the fracture surface has a dense fracture crack, is generally flat, and does not show high or low relief. No distinct narrow shear bands or parabolic grain patterns were observed. The cracks on the fracture surfaces are irregular, showing elliptical cracks with short cracks. This is supposed to be due to the fact that the test body is more brittle after dehydration from ductile to plastic as compared to the aged test body, the cracks expand at a very block rate and the cracks initiated near the crack front do not have enough time to expand. As a result, a large number of fine oval patterns were left on the fracture surface.

Fractographic analysis results of resin dog bone specimens show that there is a transition from brittle to ductile between the unaged and hydrothermal aged specimens and a transition from ductile to brittle between the moisture-absorbed specimens and desorbed specimens. This is because water as a low molecular weight molecular client, penetrates the polymer and acts as a plasticizer, affecting the overall properties of the material, especially at higher temperatures. Due to moisture induced plasticization, the ductility mechanism is more pronounced than in unaged test specimens thus affecting the fracture mechanism of the resin. Moisture cannot be completely removed by physical dehumidification and therefore the deterioration effects are irreversible.

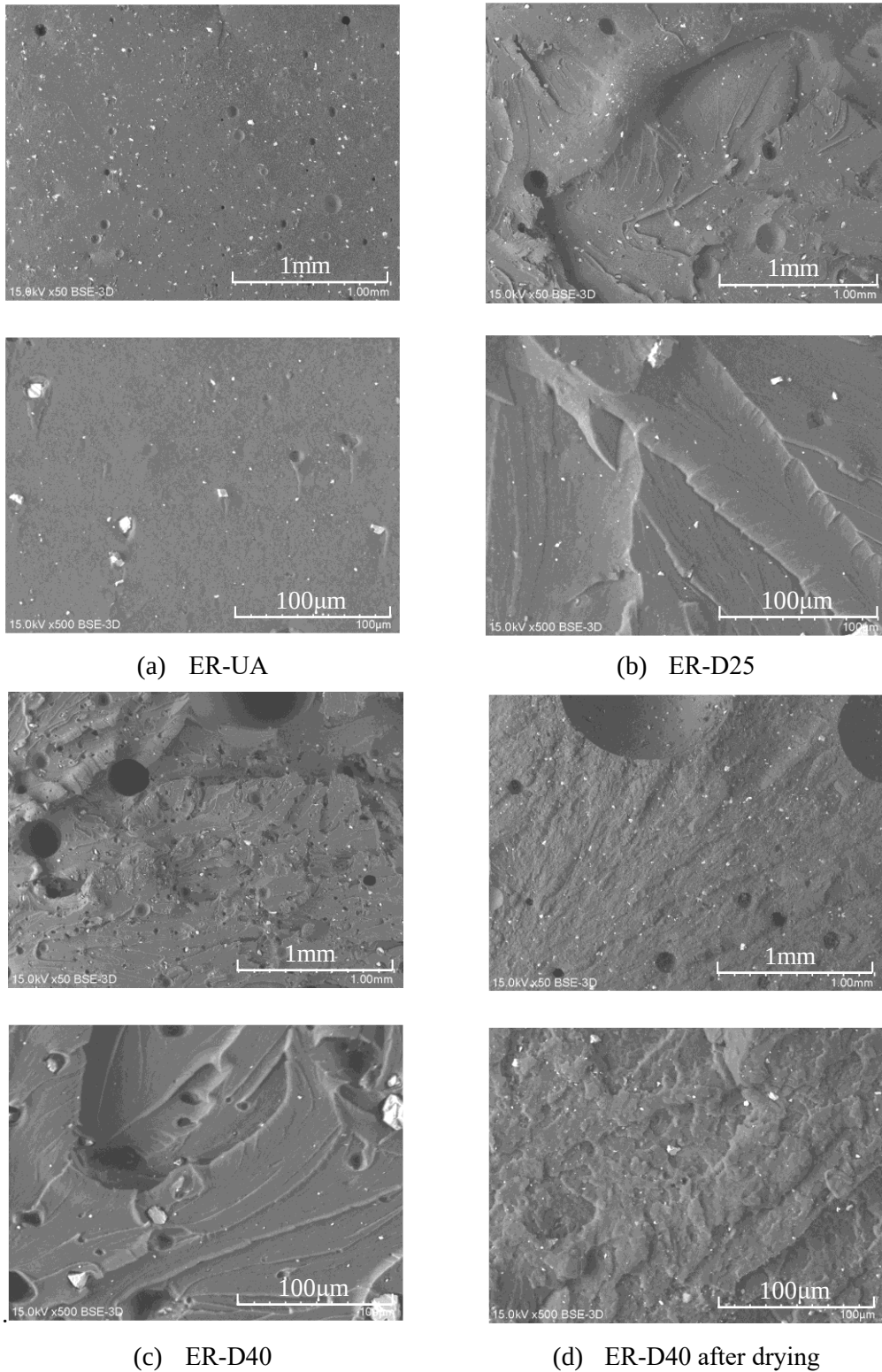


Fig. 5-14 Surface morphology of fracture patterns of dog bone specimens

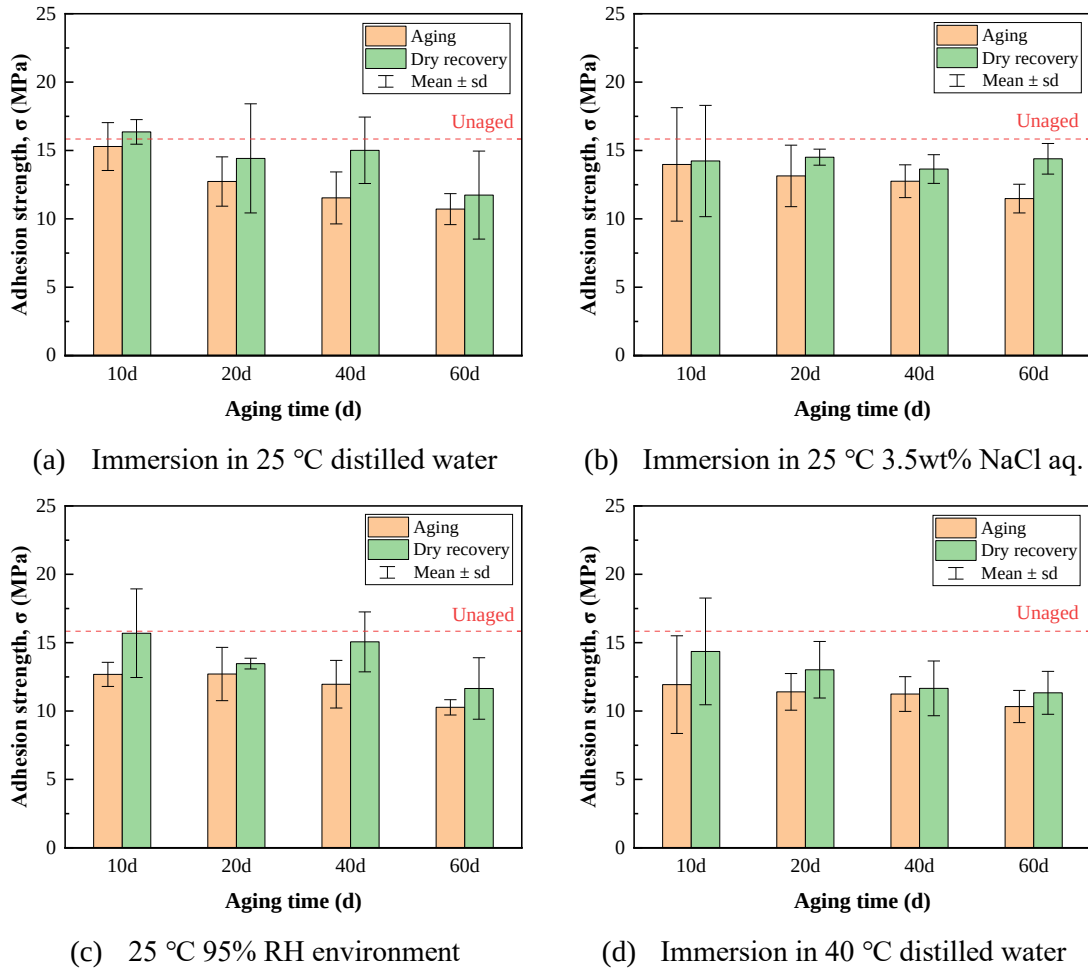


Fig. 5-16 Adhesion strength from pull-off test

By comparing the pull-off test results of the joint specimens exposed to the four aging environments as shown in **Fig. 5-16**, the adhesive strength decreases with increasing time in the same environment. In comparison between **Fig. 5-16 (a)** and **(b)**, it can be observed that at the same temperature, the distilled water environment exhibits a greater decrease in adhesive strength after 10 d of aging compared to the 3.5wt% NaCl solution environment. Additionally, after 60 d of aging, the adhesive strength in the distilled water environment is significantly lower than that in the 3.5wt% NaCl solution environment. The recovery of adhesive strength after drying for the specimens subjected to 60 d of aging in the distilled water environment is much lower than that in the 3.5wt% NaCl solution environment. These findings indicate that distilled water environment induces more severe damage to the CFRP–steel joint compared to the 3.5wt% NaCl solution environment. From **Fig. 5-16 (a)** and **(c)**, it is evident that immersion environments at

the same temperature result in more significant adhesive strength loss. Even after 40 d of aging in the high-humidity environment, the specimens exhibit a higher adhesive strength after drying, indicating that the adhesive strength reduction caused by high humidity can be easily recovered through the drying process compared to the immersion environment. By comparing the results from **Fig. 5-16 (a) and (d)**, it is apparent that elevated temperature has a greater negative impact on the adhesive strength of the joint under the same immersion environment. Although the decrease in adhesive strength is not significant with increased aging time after 10 d, the adhesive strength has already reduced to a lower level during the first 10 d of aging. Moreover, the specimens subjected to high-temperature aging exhibit a lower recovery of adhesive strength after physical drying compared to those subjected to ambient temperature aging, and the recovery is lower than that observed for the other three aging conditions.

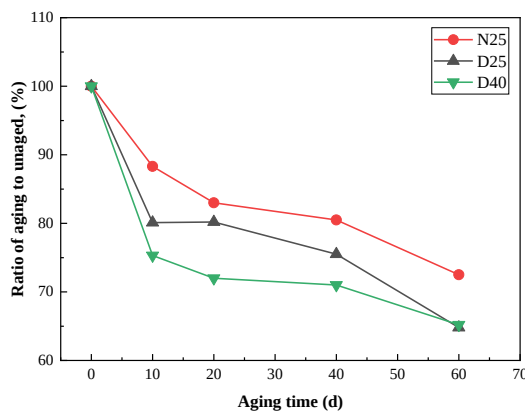
The rates of decrease and recovery for each specimen compared to the undeteriorated strength are recorded in **Table 5-7**. After the 60 d aging, the adhesion strength of the specimens immersed in the 25 °C distilled water decreased by 35.2% from 15.8 MPa to 10.27 MPa; those in the 25 °C 3.5wt% NaCl solution decreased by 27.5% to 11.48 MPa; those in the 25 °C 95% RH environment decreased by approximately 32.5% to 10.7 MPa, and those in the 40 °C distilled water decreased by 34.8% to 10.33 MPa. Except the 3.5wt% NaCl solution environment, the decreased ratio of adhesion strength all over 30% in the other environments. The rate of decrease in the adhesion strength can vary in different environments, indicating that exposure conditions can influence the

Table 5-7 Average ratio of adhesion strength to unaged after aging and drying recovery

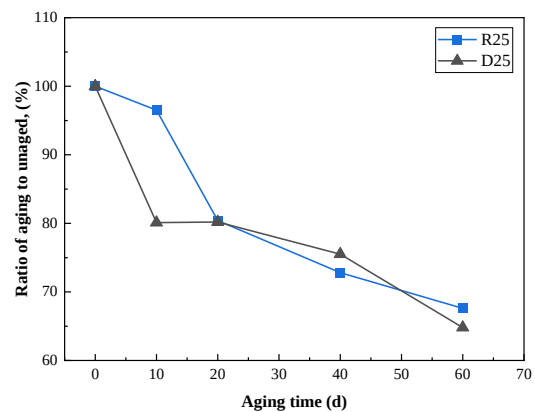
Aging time (d)	25 °C distilled water		25 °C 3.5wt% NaCl		25 °C 95% RH		40 °C distilled water	
	Decrease (%)	Drying recover (%)	Decrease (%)	Drying recover (%)	Decrease (%)	Drying recover (%)	Decrease (%)	Drying recover (%)
10	19.9	99.1	11.7	89.8	3.5	103.3	24.7	90.7
20	19.8	85.0	17.0	91.6	19.6	91.0	28.0	82.2
40	24.5	95.1	19.5	86.1	27.2	94.8	29.0	73.6
60	35.2	73.5	27.5	90.8	32.4	74.1	34.8	71.5

adhesion strength. The experiment also found that the average adhesion strength of the specimens did not fully recover to the undeteriorated level after drying, except for the specimen immersed in distilled water at 25 °C and 95% RH for 10 d. The recovery rate of 95% RH high humidity environment in 10 d is over 100%, this may be due to the cross-linking reaction of the resin during the drying process, leading to secondary curing and an increase in strength. The aging time has a significant effect on the recoverability of the adhesion strength of the specimens. For example, the specimens that were immersed in distilled water at 40 °C for 60 d only retained 71.5% of the undeteriorated adhesion strength after drying. This indicated that the longer the specimens were exposed to the high-temperature aging environment, the more difficult the recovery of their adhesion strength. However, although the specimens immersed in the 3.5wt% NaCl solution did not fully recover to their unaged state after drying, they recovered approximately 90% of their strength.

Based on the results shown in **Fig. 5-17 (a)**, a comparison of the decrease ratio in adhesion strength in an immersion environment. The smallest rate of decrease was observed in the 25 °C 3.5wt% NaCl solution environment, which suggests that this environment is less aggressive toward the adhesive strength of the specimens. On the other hand, the largest rate of decrease was observed in the 40 °C distilled water and high humidity environments, indicating that these



(a) Decrease ratio of adhesion strength with time in the immersion environment



(b) Comparison of adhesion strength decrease ratio under immersion and high-humidity environment

Fig. 5-17 Ratio of adhesion strength to unaged after aging joint

environments are more detrimental to the adhesive strength of the specimens. Compared to the other three test environments, the specimens exposed to a distilled water environment at 40 °C experienced the fastest decrease in adhesion strength during the initial aging period (0 d - 10 d). This indicates that higher temperatures have a more severe impact on the aging of resin-impregnated carbon fiber fabrics. Additionally, the distilled water environments at 25 °C and 40 °C exhibited similar rates of adhesion strength decline after 60 d of aging, suggesting a similar level of ultimate aging in the same liquid environment, with the temperature only affecting the aging rate.

Fig. 5-17 (b) compares the decreased ratio of adhesion strength between the immersion environment and the high-humidity environment at the same temperature. The decreasing trends in both environments are similar. In the initial 10 d of aging, the decreased ratio of adhesion strength in the high-humidity environment is much lower than that in the immersion environment. It took 20 d of aging for the adhesive strength in the high-humidity environment to decrease to the same level as in the immersion environment. This indicates that the final decrease ratio in the immersion environment is greater than that in the high-humidity environment where it takes more time for moisture to invade the CFRP–steel joint. After 60 d of aging, the ratio of adhesive strength decrease is higher in the immersion environment than in the high-humidity environment.

The trend observed in **Fig. 5-7** indicates that as the duration of degradation increases, the adhesive strength gradually decreases. Due to limitations in the experimental duration, the lowest strength was not measured in this study. Combining the results obtained in section 5.4, during the moisture absorption process, Type I bonded water converts to Type II bonded water, which is difficult to remove. Therefore, with the progression of degradation, the amount of Type II bonding water in CFRP increases over time, leading to a decrease in bond strength and eventual failure. The degradation tests in this chapter simulate various environmental conditions that may occur during atmospheric exposure. However, due to the short duration of the experiments, accurate predictions of structural strength after long-term degradation cannot be made based solely on the experimental results. Nevertheless, it can be inferred from the results that structures undergoing prolonged degradation in atmospheric environments exhibit a continuous trend of decreasing strength until structural failure occurs.

5.5.2 Fracture pattern

Photographs of the fracture surfaces and cross-sections of the specimens were taken by SEM with backscattered electron (BSE) imaging under 15 kV low-vacuum conditions. Energy-dispersive X-ray spectroscopy (EDX) was also performed on the fractures of CFRP–steel joint specimens to semi-quantitatively determine the elemental composition (Fe, C, O, and Cl). **Fig. 5-18** shows the delamination failure surfaces of the unaged and the CD25, CN25, CH25, and CD40 specimens after 60 d aging. Compared to the unaged specimen (**Fig. 5-18 (a)**), peeling between the carbon fiber and the resin was evident in the specimens aged for 60 d (**Fig. 5-18 (b–e)**). The carbon fibers were completely peeled from the epoxy resin, and the peeled surface was smooth, indicating that the bond between the resin and carbon fiber was weakened by hydrolysis. Therefore, the carbon fibers were easily removed during the pull-off test. In addition, cohesive fractures were observed in all aged specimens. The aged specimens had the same failure modes: 1) cohesive fracture of the epoxy resin matrix and 2) resin and carbon fiber bonding failure. The cross-sectional morphologies of the fracture patterns are shown in **Fig. 5-19**. As shown in the

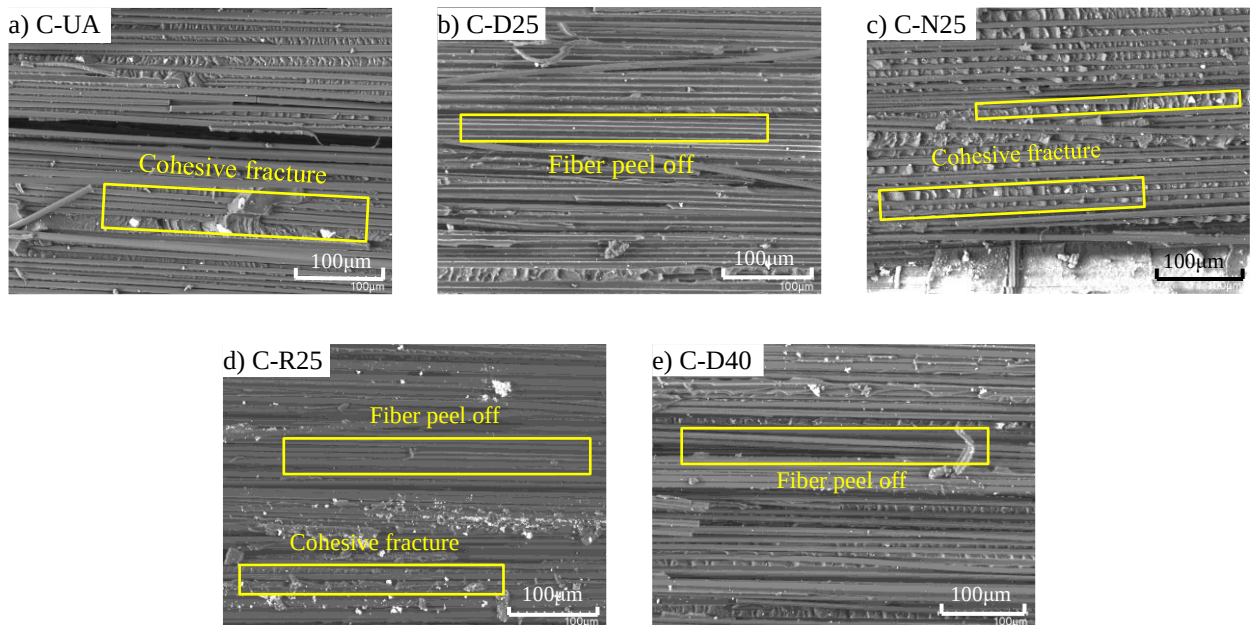


Fig. 5-18 Surface morphology of fracture patterns in composite specimens after 60 d aging
(×500 magnification)

figure, holes appeared within each bundle and between each layer of carbon fibers, which contributed to the diffusion of moisture and caused the interlayer damage observed in the composite specimens.

The fracture of the composite specimen aged in the 25 °C 3.5wt% NaCl solution for 60 d was analyzed using EDX. **Fig. 5-20**, obtained from the EDX analysis, shows the presence of Cl, indicating that chloride ions penetrated the carbon fiber laminate interior from the outside during the prolonged immersion period. Chloride ions cause metal corrosion. In this case, they can potentially penetrate the bonded surfaces of the CFRP and steel, leading to interfacial corrosion. However, in this study, the blasted steel surfaces had high adhesion strength and were less prone to interfacial damage[152] and no interfacial damage was observed; thus, this could not be confirmed conclusively. Further research is required to investigate the extent of the damage caused by the penetration of chloride ions into the CFRP–steel interface.

Overall, this experiment suggests that environmental conditions can significantly affect the adhesion strength of composite specimens and that the recoverability of adhesion strength after drying may vary depending on the aging period and environmental conditions. The adhesion strength is likely to be reduced by moisture, with temperature contributing to this phenomenon, this has the same trend as the experiment results for the resin matrix in section 3.2. Therefore, it can be inferred that the aging behavior of the CFRP–steel joint is primarily governed by the aging behavior of the resin matrix. If the aging resistance of the resin matrix can be improved, the durability of the joint will also experience a significant enhancement.

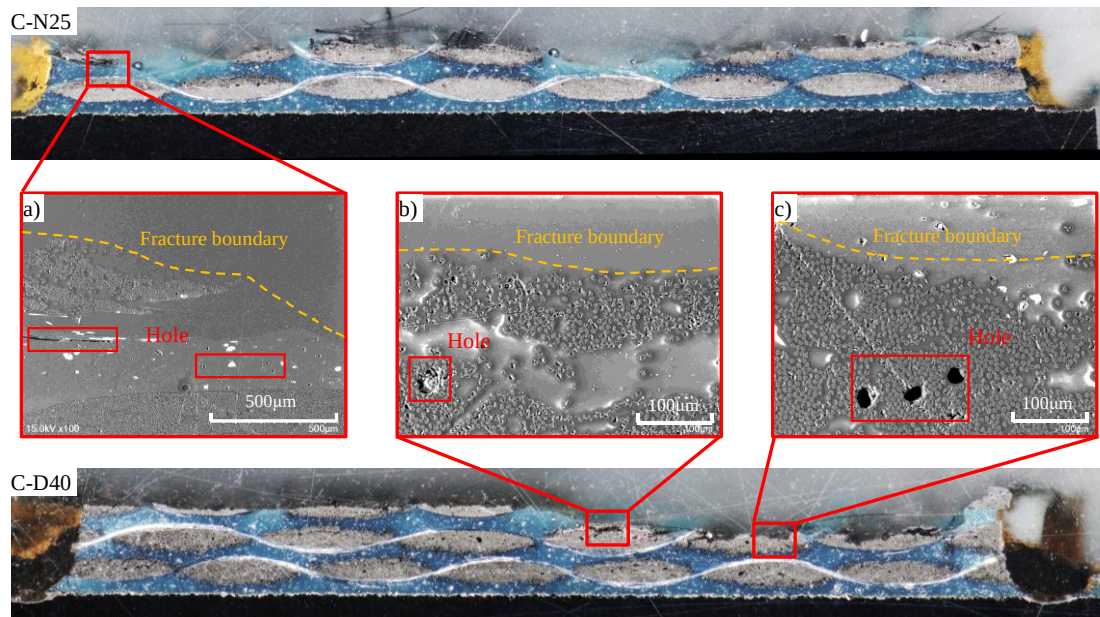


Fig. 5-19 Cross-sectional morphology of fracture patterns in C-N25 and C-D40 composite specimens after 60 d aging

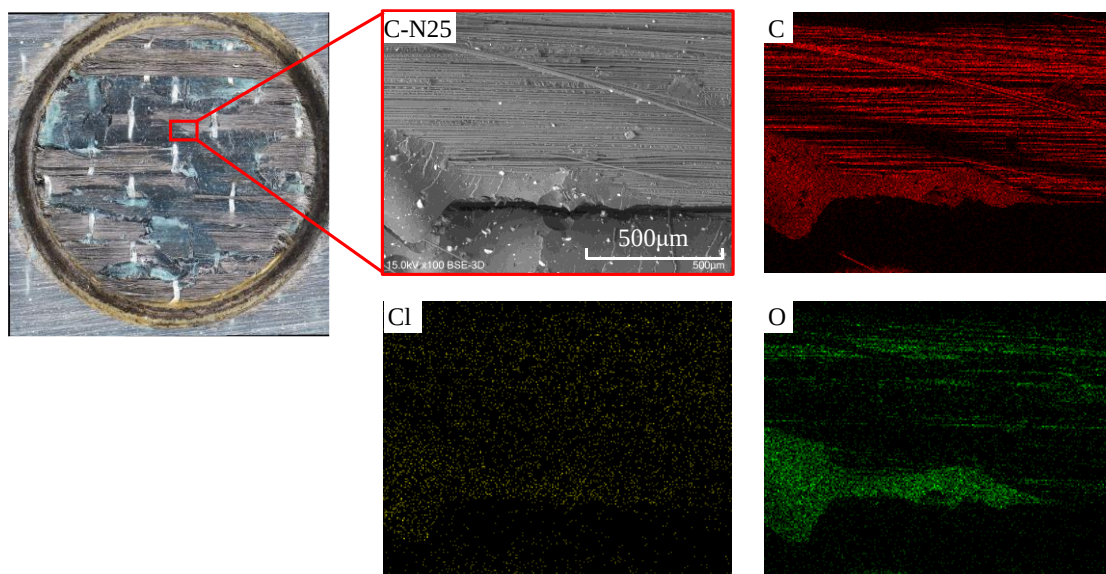


Fig. 5-20 EDX analysis results of fracture patterns in C-N25 composite specimens after 60 d aging

5.6 Summary

In this study, the irreversible deterioration mechanism of CFRP–steel joint based on the hydrothermal aging behavior of resin matrix was investigated. Physical dehumidification was employed to assess specimen recoverability. The main conclusions are as follows.

- (1) Moisture diffusion in the resin matrix of resin-infused carbon fiber fabric follows Fick's first law, with the maximum moisture uptake unaffected by temperature but dependent on the electrolyte environment, distilled water environments result in higher maximum moisture absorption rates. Temperature and moisture uptake are positively correlated. The hygroscopic behavior is partially reversible but hydrolysis due to moisture is irreversible.
- (2) Moisture-induced bonded water has a notable impact on degrading the mechanical properties of the resin matrix, particularly at elevated temperatures. Chloride ions do not exhibit a significant promoting effect on resin aging. Moisture absorption exhibits a linear, negative correlation with both the tensile strength and Young's modulus of the resin. Drying eliminates Type I bonded water, partially restoring mechanical strength and thermal properties. However, residual Type II bonded water leads to irrecoverable reductions in mechanical strength and thermal properties despite physical drying.
- (3) SEM shows microcracks and resin matrix deterioration in composite joints during aging. Moisture causes cohesive failure within the resin and weakened adhesive strength between the resin and carbon fibers, resulting in delamination and interlayer failure under external forces. Mechanical properties of the CFRP–steel joint cannot be fully recovered after moisture absorption by drying. CFRP–steel joint aging is influenced by the resin matrix's aging behavior.

CHAPTER 6 EVALUATION OF GALVANIC CORROSION BEHAVIOR BETWEEN CARBON FIBER SHEET AND STEEL

6.1 Introduction

The mechanical properties of the CFRP-steel joint and the thermal properties of the resin-impregnated carbon fiber sheet have been discussed in **Chapters 2, 3, 4, and 5**, and the electrochemical properties of the resin-impregnated carbon fiber sheet as well as the composite joints will be discussed in this chapter. In the field of civil engineering, CFRP reinforcement of steel structures is susceptible to electrochemical corrosion, especially when used in high-humidity and moist cyclic environments for steel structures[153]. High-humidity conditions can introduce electrolytes into the joints of composite materials used for reinforcement. While electrical insulating materials like epoxy resin adhesives can prevent electrochemical corrosion between the two materials, completely blocking electrical contact in practical applications is challenging[154]. Pinholes in CFRP and the presence of bubbles in the adhesive layer may result in electrical contact between CF fibers and the steel, both during the reinforcement process and after curing. This phenomenon is particularly common in on-site applications, such as the localized reinforcement of continuous CF fabric using epoxy resin wet layup. However, the results from current studies on the electrochemical corrosion mechanism between steel and CF have limited direct implications for engineering applications. Hence, it is necessary to investigate the mechanisms and influencing factors of electrochemical corrosion occurring between CFRP and steel structures in real-world applications.

Carbon fiber-reinforced plastic (CFRP) strengthened steel structures are susceptible to galvanic corrosion, especially in high-humidity and marine environments. The object of this chapter primarily involves steel components reinforced with carbon fiber cloth used in atmospheric and marine environments. Based on the actual application conditions, this part focused on the influence of the conductive properties of carbon fiber material and environmental factors on

galvanic corrosion. The electrical resistance behavior of various forms of carbon fiber materials was accurately evaluated using electrochemical measurement techniques. Meanwhile, the difference in the temperature accelerating effect on the corrosion of the steel and carbon fiber-affected steel systems was clarified.

6.2 Experimental materials

The materials used in this chapter are the same as in above Chapter, using SM490A hot rolled steel and unidirectional carbon fiber sheets MRK-M2-20 carbon fiber sheet with an areal weight of 200 g/m^2 . As shown in **Fig. 6-1** Photo depict various carbon fiber materials, the carbon fiber tow is the basic unit of the carbon fiber cloth, with a line width of 4 mm and line density of 0.8 g/m . Approximately 12,000 single carbon fibers constituted a fiber tow; the carbon fiber has a diameter of $7 \mu\text{m}$ (manufacturer's data) and density of 1.82 g/cm^3 .

Individual carbon fibers were separated from the CF sheet manually and confirmed as single undamaged fibers by means of optical microscopy (VHX-1000). In addition, the diameter of a single carbon fiber sample was measured using scanning electron microscope (SEM, SU3500) in the secondary electron mode under low accelerating voltage and low-vacuum conditions. Prior to SEM observation, the samples were mounted directly onto adhesive stub mounts in an indoor environment.

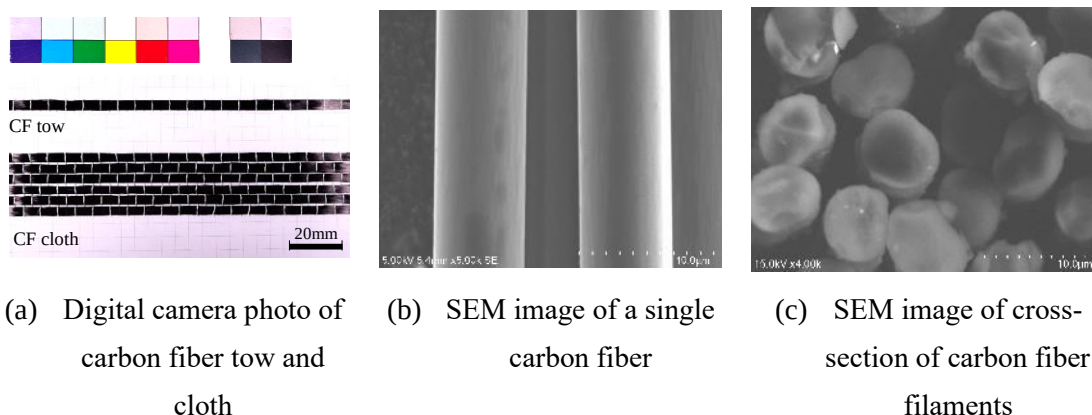


Fig. 6-1 Photo depict various carbon fiber materials

All the electrochemical tests were conducted at room temperature (about 25 ± 2 °C, 50% RH) using a potentiostat (Versa STAT 4, Princeton Applied Research). Electrical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used to evaluate the resistance properties of single carbon fiber and carbon fiber tows, respectively.

6.3 Volume resistivity and anisotropic electrochemical behavior

6.3.1 Anisotropic electrochemical behavior of single carbon fiber

The test method for the volume resistivity measurement of a single carbon fiber is based on JIS R 7609. First, five individual carbon fibers approximately 40-50 mm long were picked out using tweezers under the microscope. A test hole bench was cut with a mat mount, the set method and dimensions of the bench are shown in **Fig. 6-2**. Subsequently, each single carbon fiber was straightened along the central line, and the ends were fixed with conductive paste to control a test length of 20 mm between the electrical contact points. EIS measurements were then conducted to evaluate the capacitive, resistive, and inductive elements of a single carbon fiber in the fiber direction. The EIS frequencies ranged from 10 to 1 Hz, with an amplitude of 25 mV vs. DC potential. One sweep cycle from high to low frequencies was repeated nine times for each sample.

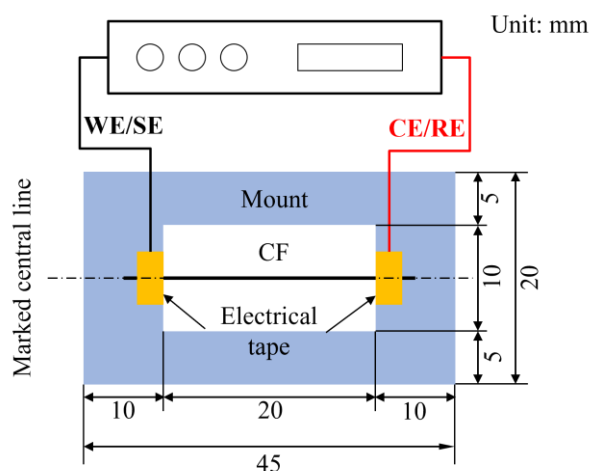


Fig. 6-2 Schematic diagram for the volume resistivity measurement of single carbon fiber

EIS tests were performed on five single carbon fibers, and nine sweep cycles were repeated from high-frequency 10000 Hz to low-frequency 1 Hz. The EIS results indicate that the impedance value is independent of the frequency for each cycle. The Bode plot shows that the phase is close to zero ($^{\circ}$) regardless of the frequency changes. This implies that a single carbon fiber behaves as a resistor in the fiber direction. The volume resistivity of carbon fiber can be obtained using **Equation 6-1**:

$$\rho_v = \frac{RA}{L} \quad (6-1)$$

Where ρ_v is the volume resistivity ($\Omega \cdot \text{mm}$), R is the resistance (Ω) equal to the impedance measured using EIS, A is the cross-sectional area of a single carbon fiber measured using SEM, and L is the length of the sample (mm) measured using an optical microscope.

On the one hand, for impedance under the same frequency, the measured $|Z|$ of nine sweep cycles is approximate ($\text{COV} < 1.5\%$). On the other hand, in all specimens, $|Z|$ at 10 kHz was less sensitive to the sweep cycles, even though the $|Z|$ value should be frequency-independent. Therefore, the resistance of a single CF was determined to be equivalent to the $|Z_{\text{mean}}|$ of nine sweep cycles at 10 kHz; the corresponding results are presented in **Table 6-1**.

For the target five single carbon fibers with a test length of 20 mm, the obtained impedance was $12.2 \text{ k}\Omega \pm 5.66\%$. After EIS measurements, the diameter of the same carbon fiber specimen was confirmed by SEM. Nine random positions were selected for diameter measurements so that the actual cylindrical cross-section area A of the carbon fibers can be calculated from d_{mean} . An inversely proportional relationship existed between the measured values of A and R . The negative correlation between carbon fiber length and resistance was also verified by Dandy et al[155].

Based on the measured diameter and impedance of the carbon fibers, the mean volume resistivity of the five samples was calculated as $0.0256 \pm 2.91\%$ ($\Omega \cdot \text{mm}$), as shown in **Table 6-1**. This deviation is acceptable because of the unavoidable error during microscopic length measurements. Therefore, carbon fiber filaments can be considered physically homogeneous materials. The electrical conduction in the fiber direction was stable, with the volume resistivity approximately equal to a constant value of 0.026 ($\Omega \cdot \text{mm}$).

Table 6-1 Measured results of single CF by EIS and SEM

Specimen ID	Resistance $R= Z_{\text{mean}} (\Omega)$	Diameter $d_{\text{mean}} (\mu\text{m})$	Volume resistivity $\rho_v (\times 10^{-3} \Omega \cdot \text{mm})$
No.1	11,660	7.53	25.9
No.2	12,522	7.03	24.3
No.3	13,158	7.09	26.0
No.4	12,260	7.34	26.0
No.5	11,431	7.60	25.9
Mean	12,206	7.32	25.6
SD	691	0.254	0.7
COV	5.66%	3.47%	2.91%

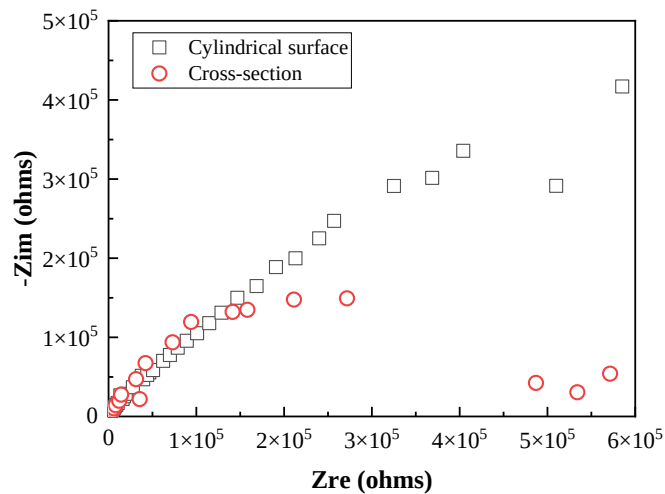


Fig. 6-3 EIS of the cross-section and cylindrical surfaces in 3.5% NaCl solution

The EIS results of the cross-sectional and cylindrical surfaces are presented in **Fig. 6-3**. At the low frequency, cylindrical surfaces of CF show large values in both Z_{im} and Z_{re} , while the EIS of the cross-sectional surface is a semicircle on the Nyquist plot. Besides, the impedance of the cross-section is much smaller than that of the cylindrical surface in CF.

The electrochemical behavior of cross-sectional and cylindrical surfaces of a CF shows a large difference. Two different equivalent circuits can be employed, as shown in **Fig. 6-4**, to fit the measured EIS results. EIS in a cross-sectional surface was simulated by a simple single-time constant equivalent circuit. Particularly, the discontinuous passive layer on the cylindrical surface

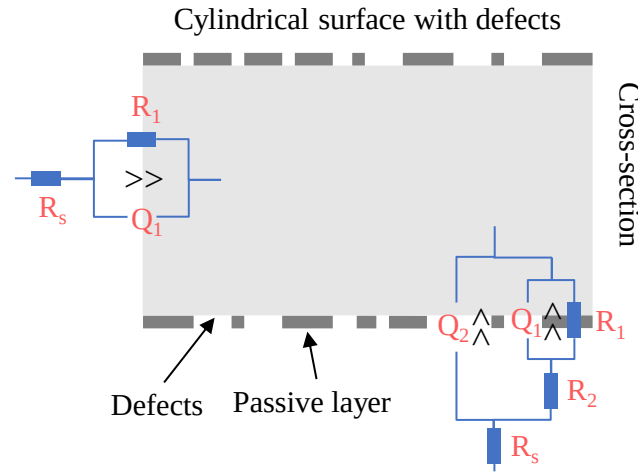


Fig. 6-4 Equivalent circuits of the cross-section and cylindrical surfaces in a CF

caused its EIS behavior to act like a damaged coating. For both cross-section and cylindrical surfaces, R_s , R_1 , and Q_1 are represented the solution resistance, the resistance of the carbon substrate, and the capacitance of the interface between CF and solution, respectively. Besides, R_2 is the resistance of the active defects while Q_2 represents the capacitance of the passive layer.

When the wet layup CFRP was used for reinforcing steel structure, the galvanic corrosion between carbon fiber and steel would occur after the protective coating and resin matrix deteriorated. So the anisotropic electrochemical behavior of carbon fiber cannot be ignored, as it would largely affect the risk level of corrosion. In practice, coating and adhesive deterioration occur at the edge of the CFRP, causing a large amount of cross-sectional surface of CF exposed in the atmosphere or short-connected to the steel substrate. This case was considered as the most adverse situation for galvanic corrosion occurring when carbon fiber is used for the steel structural strengthening.

6.3.2 Volume resistance of carbon fiber tow

After confirming the impedance behavior of the individual carbon fibers, the resistance of the CF tow was measured using the CV technique with the same method shown in **Fig. 6-2**. The CV loop was performed at a scan rate of 1 V/s between -1 and $+1$ V (vs. open circle potential (OCP)). Furthermore, each carbon fiber tow sample was cut to approximately 60 mm in length, and the

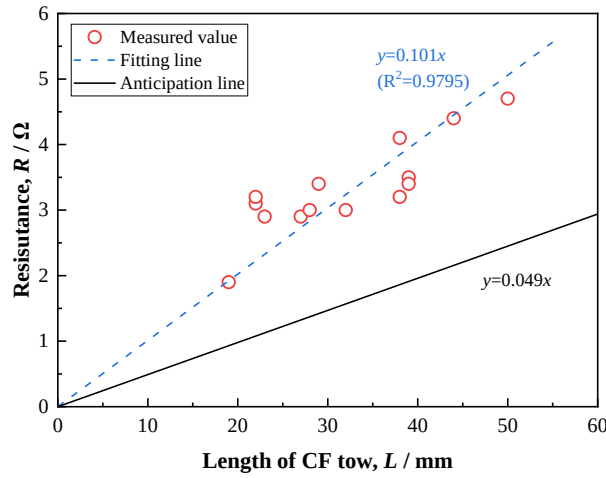


Fig. 6-5 Resistance as a function of length for carbon fiber tows

test length was varied from 20 to 50 mm by changing the positions of the electrical contact points. The resistance of each tow was shown in **Fig. 6-5**. A positive proportional relationship was found between the length L and resistance R of the carbon fiber tows; the fitted line of the measured resistance data is given by **Equation 6-2**:

$$R = 0.101L \quad (6-2)$$

The actual resistance can be expressed as a function of L with a relatively large fluctuation, which reveals that the conductivity of a carbon fiber tow in the fiber direction primarily depends on L . Furthermore, the coefficient of determination (R-squared) of this fitting line has a small value, indicating that the fluctuation of the measured resistance value is large. This shows that the actual tow resistance is also determined by the electric conduction among the carbon fibers, according to the gap and arrangement of filaments in thickness.

Assuming that the carbon fiber tow material is quasi-uniform in the cross-section, its sheet resistivity ρ_s can be calculated using **Equation 6-3**:

$$\rho_s = \frac{\rho_v}{t} \quad (6-3)$$

Where t is the mean thickness of the carbon fiber tow (0.13 mm), measured using the caliper Vernier scale.

When considering the actual area of the cross section, the ideal resistance of a carbon fiber tow should conform to **Equation 6-4**:

$$R = \rho_s L / W = 0.049L \quad (6-4)$$

Where the W is the width (4mm), and L is the measured length of the carbon fiber tow, which ranges from 20 mm to 50 mm.

By comparing the fitted curve to the theoretical value curve of R with respect to L , the measured R is found to be approximately twice the theoretical value. There are two main reasons for the increase in measured resistance R . Firstly, the true area available for electric conduction is smaller than the macroscopic cross-section of a carbon fiber tow, because the fiber body is cylindrical. Secondly, incomplete contact between carbon fiber cylindrical surfaces significantly increases the measured R by reducing the effective conduction area of the cross-section.

The calculated volume resistivity of carbon fiber in this study is approximately 179 times greater than that of carbon steel ($1.43 \times 10^{-4} \Omega \cdot \text{mm}$) at 20 °C, and the carbon fiber material has much lower conductivity than common steel. Meanwhile, the gaps between the filaments further reduced the effective conductivity of the tow. Therefore, galvanic corrosion can only occur on the carbon fiber that is within a certain distance from the electrical contact surface was estimated. The corrosion acceleration effects caused by the galvanic cell between the carbon fiber and steel are significantly diminished with the increase in distance between the cathode and anode area (the larger the distance, the greater the resistance of the carbon fiber and solution).

6.4 Water film condition effect on galvanic corrosion between CFRP and steel

The electrochemical tests were conducted in a 3.5 wt% NaCl solution at 25 °C. Two kinds of water film thicknesses (0.5 mm and 10 mm) were set for this experiment. The electrode is made of SM490A steel and the electrode area is 1 mm². Two electrodes are buried in epoxy resin, and cured at room temperature (25 °C) for 24h, the distance between the two electrodes is 10 mm. The surfaces of the electrodes are sanded with sandpaper from # 400 to # 1000, then wiping the surface of the electrodes with acetone solution to remove impurities and grease. The aqueous film thickness was controlled using the apparatus as shown in **Fig. 6-6**. The electrode and the measuring terminal of the electronic micrometer were connected by a multimeter. The multimeter detected a weak resistance when the terminal contacts the electrode surface. Currently, return the

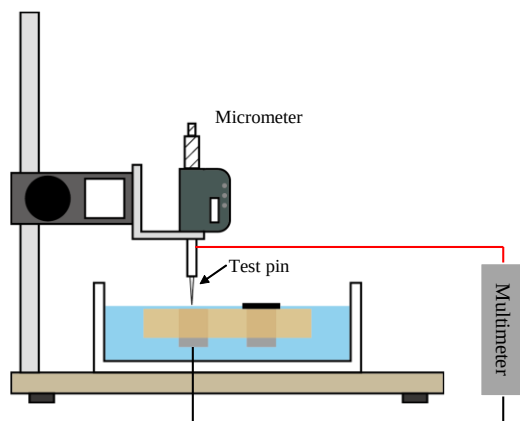


Fig. 6-6 Measurement system for water film thickness

indication of the electronic micrometer to zero, slowly rotate the measuring terminal to 0.5 mm or 10 mm for fixation, and then slowly add salt water to the water tank. When the surface of the saltwater touches the measuring terminal of the electronic micrometer, the multimeter detects the resistance again. At this time, the water film setting is completed.

ZRA (Zero Resistance Ammeter) method was used to measure the corrosion current for 48 h while Ag/AgCl/sat. KCl was used as the reference electrode. As shown in **Fig. 6-7 (a)**, the reference electrode is placed near the working electrode (WE). During the test, to prevent the CFRP from detaching from the electrode surface due to buoyancy, the four corners of the CFRP board were fixed on the resin around the electrode with transparent tape. After the test, uncover the CFRP from the electrode surface, remove the corrosion products, wash with acetone, and photograph the electrode surface state with an optical microscope. For each water film thickness, two tests were carried out in different contact methods between the CFRP and the electrode: 1) flat surface of CFRP in contact with the electrode, 2) cross-section of CFRP in contact with the electrode, the surface properties of CFRP as shown in **Fig. 6-7 (b)**. For the section contact, several carbon fiber plates are made into cubes with adhesive and then one side of the section is cut into a 15 mm × 15 mm × 2 mm plate. In addition to this, the open circuit potential of the electrodes was measured under different contact conditions.

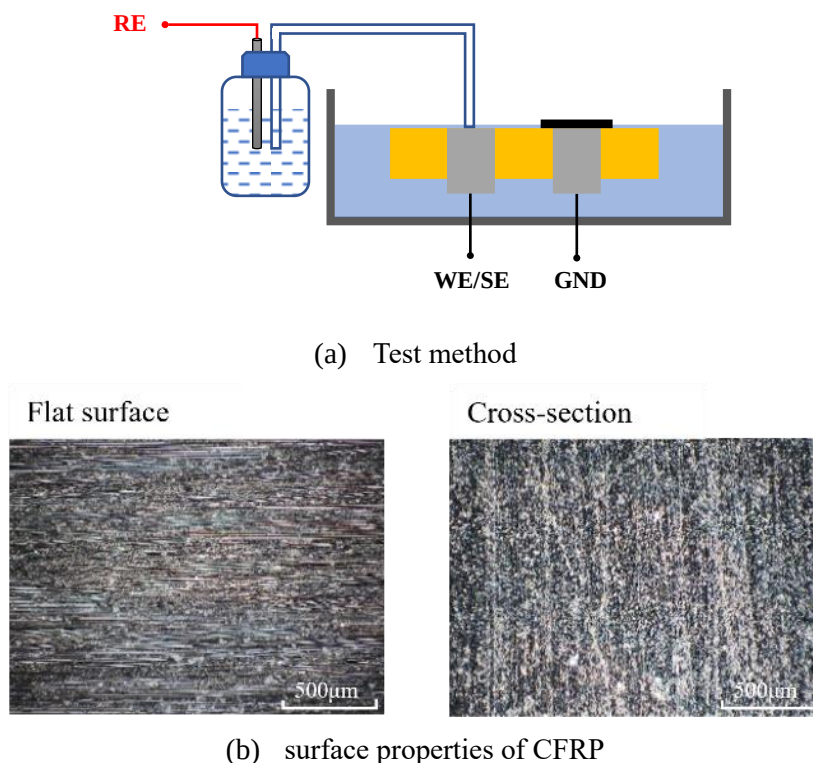


Fig. 6-7 Test method and surface properties of CFRP

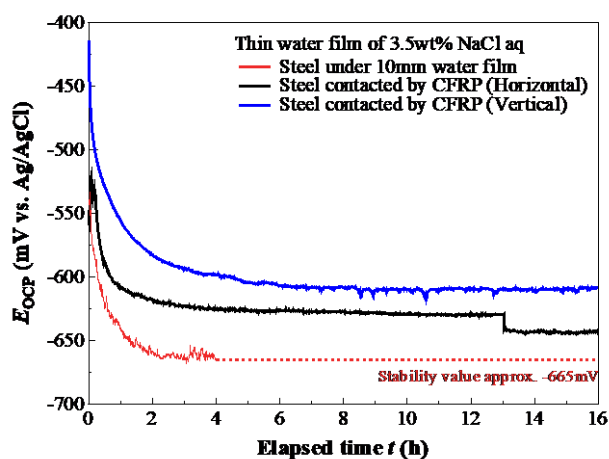


Fig. 6-8 Test result of OCP

Fig. 6-8 shows steel electrodes' open circuit potential with and without CFRP contact. The result shows the open circuit potential of steel tends to increase by the influence of the CFRP. Of these, the CFRP cross-sectional contact has the greatest effect, it increases the open circuit

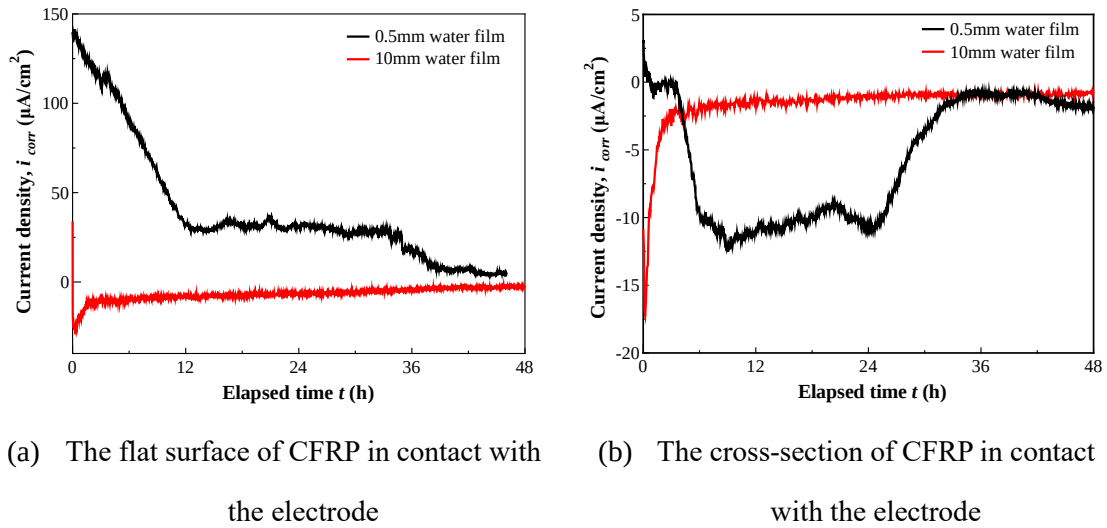


Fig. 6-9 Current density result of different contact methods

potential by approximately 50 mV compared to the case of steel immersed in a 10 mm thick electrolyte.

Fig. 6-9 (a) shows the current density result when the CFRP flat surface is in contact with the electrode, and it can be seen from the current results that current density is positive when the water film thickness is 0.5 mm, but it is negative when the water film thickness is 10 mm. When the thickness of the water film is 0.5 mm, the oxygen in the air is dissolved in the water film, and the working electrode is subjected to oxygen absorption corrosion. Therefore, the initial corrosion current density is very large in the first 12 h and then decreases rapidly. This is due to the rapid consumption of oxygen at the interface between CFRP and steel. The change of corrosion current density is relatively stable between 12 and 36 h, the corrosion formed on the electrode surface hinders the oxygen absorption corrosion of the electrode to a certain extent, and the corrosion reaction reaches the equilibrium state. At 36 h, due to the natural evaporation of water and the increase of corrosive substances on the electrode surface, the water film thickness decreases and the corrosion current density gradually tends to zero. Under the condition that the water film thickness is 10mm, the corrosion current density is large within the first 3 h of the test. However, due to the thick water film, the oxygen consumed in the water cannot be supplemented in time, and then the current density gradually decreases. **Fig. 6-9 (b)** shows the current density results when the cross-section of CFRP is in contact with the electrode. It has the same trend as the test

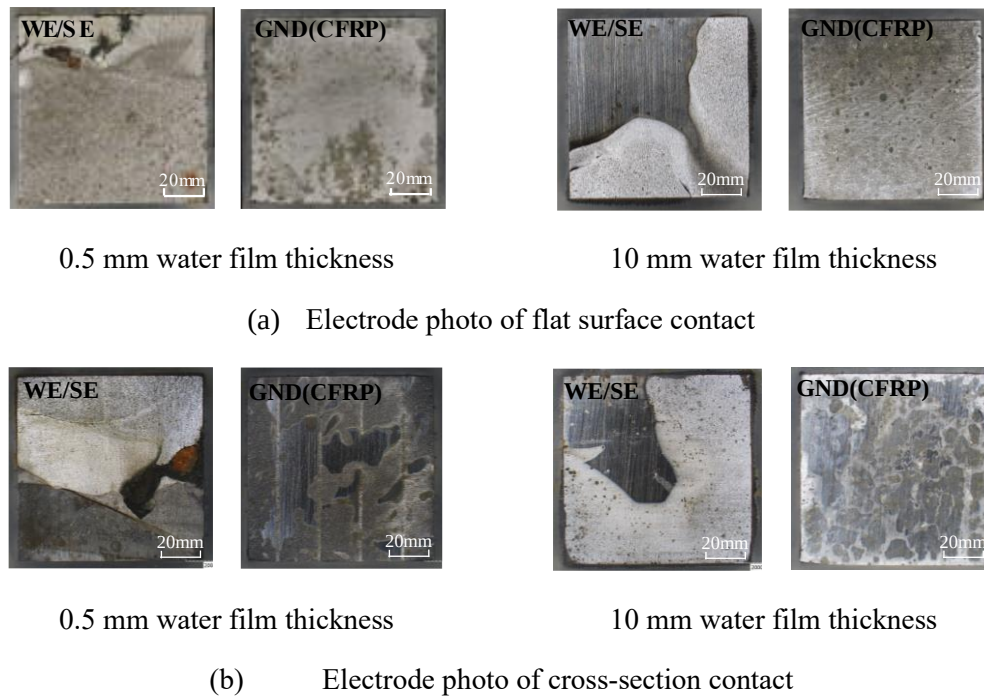


Fig. 6-10 Electrode photo of different contact types

results of plane contact under 10 mm water film. A larger corrosion current will be generated in the water film environment of 0.5 mm.

The surface states of the steel electrodes after the test are shown in **Fig. 6-10**. The surface states of the two working electrodes with different water film thicknesses and contact methods are different. As shown in **Fig. 6-10 (a)**, in the condition of flat surface contact, the working electrode with the water film thickness of 0.5 mm has more than 70% of the area corroded, while the working electrode with the water film thickness of 10 mm has less than 40% of the area was corroded. Both water film thicknesses showed the same spot-like corrosion on the GND electrode surface due to the CFRP plate's contact between steel and exposed carbon fiber. As shown in **Fig. 6-10 (b)**, in the condition of cross-section contact, the whole surface of the working electrode under 0.5 mm water film was corroded, but the corrosion area of the 10 mm water film was about 75%. Comparing the corrosion area ratio of the flat surface contact and cross-section contact, the larger corrosion area shows a higher corrosion tendency, it is because the cross-section of carbon fiber has stronger electrochemical activity than the cylinder surface[156].

6.5 Effect of carbon fiber on corrosion behavior at degraded joint

A nine-electrode array (shown in **Fig. 6-11**) was fabricated to simulate the progression of corrosion in the composite joint when carbon fiber is not in direct contact with the steel substrate. The electrodes are made of SM490A steel, machined into 10 mm × 10 mm × 20 mm rectangles using a CNC machine, with hole (Φ 3 mm) at the bottom to allow for the connection of wires. Nine electrodes were mounted on the mold at 1 mm intervals to form a 3 × 3 array and filled with epoxy resin for encapsulation. After the resin hardened, the surface of the electrode array was cur flat using a CNC machine to remove excess resin, and then the surface of the electrodes was polished using a wet grinding method (from #400 to #2000).

Two group experiments were conducted to verify the corrosion-promoting effect of the contrasting carbon fibers:

- (1) As shown in **Fig. 6-12 (a)**, the experiment set up two electrode arrays, one with only electrodes and the other with a carbon fiber bundle (effective length of 3.5 mm) placed 2 mm away from the edge of the electrode array. The electrode array was placed in a 3.5wt% NaCl solution environment with a depth of 10mm, and the measurement was performed using the ZRA method with a zero-resistance ammeter. The electrode array and the carbon fiber bundle were connected in sequence with the anode of the zero-resistance ammeter, and the cathode was short-circuited.
- (2) Apply a thin layer of XL-800 resin to the electrode surface, approximately 0.1 mm thick, and a cross-shaped groove is carved into the surface of the finished resin with a carving knife to expose the lower steel substrate, as shown in **Fig. 6-12 (b)**. Measuring method and wiring are the same as 1). In addition, 0.6 ml of phenolphthalein and 1.0 ml of potassium ferricyanide indicator were added to 3.5 wt% NaCl solution.

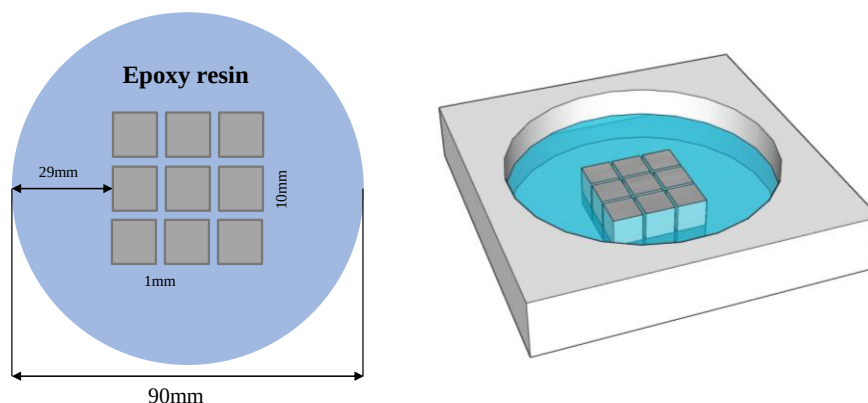
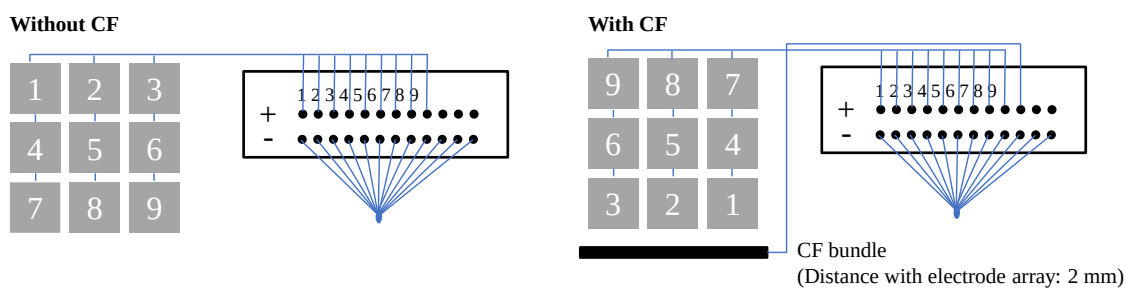
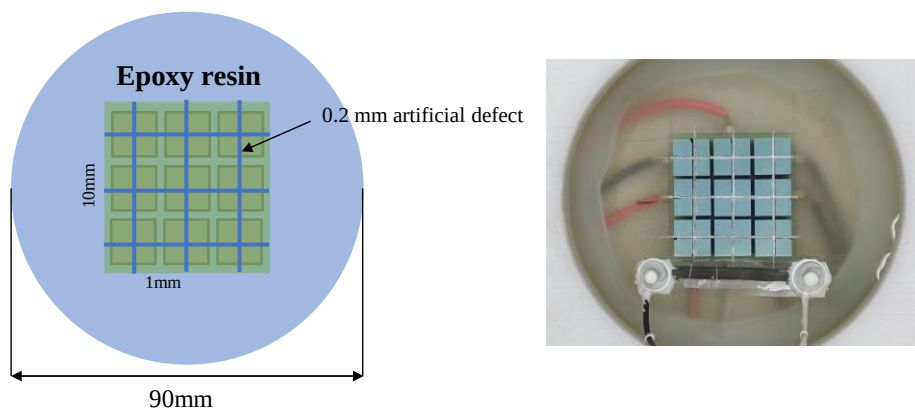


Fig. 6-11 Schematic diagram of nine-electrode array



(a) Nine-electrode test with and without CF



(b) Nine-electrode test with resin and artificial defect

Fig. 6-12 Schematic diagram of the nine-electrode test

Both groups of experiments were conducted in a constant temperature environment of 25 °C, and the measurement time was 24 h. In order to avoid the change of solution concentration caused

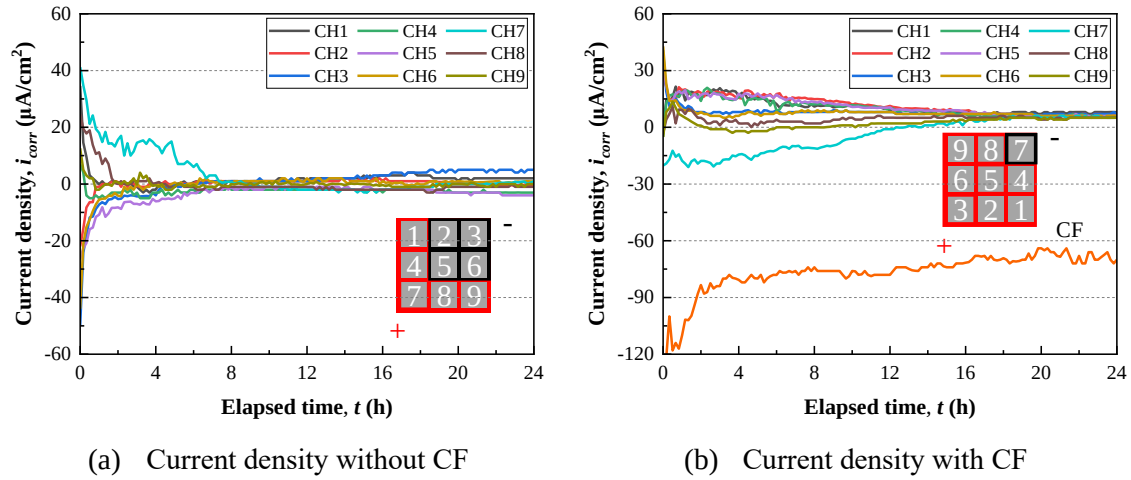
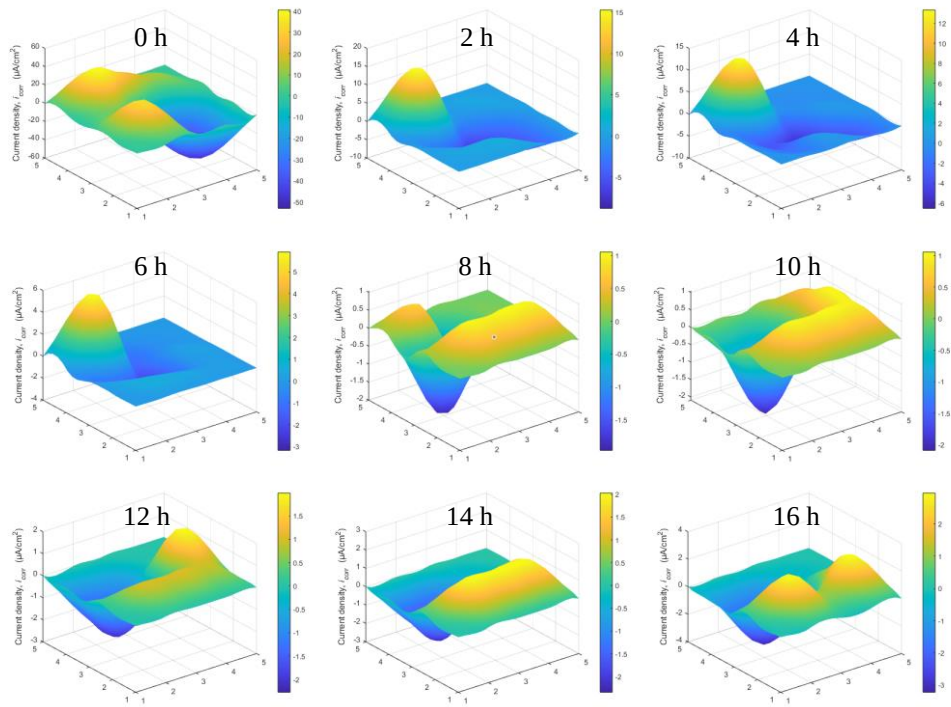


Fig. 6-13 Current density of electrode array with and without CF

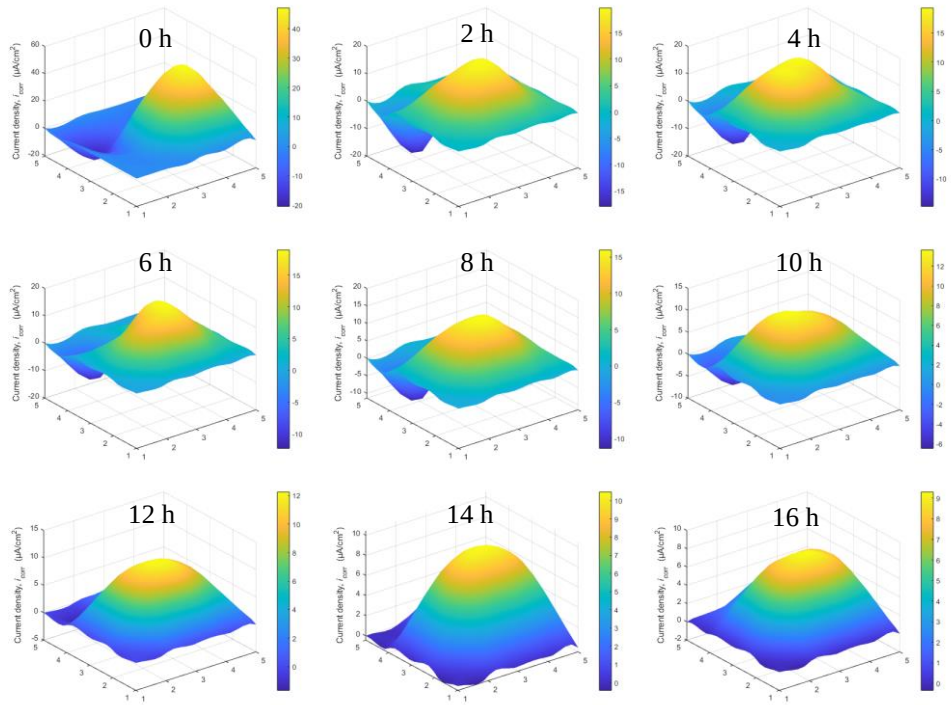
by water evaporation, which would affect the experimental results, a timed water replenishment device was set up to maintain the constant water level.

The measure result as shown in **Fig. 6-13**, As shown in **Fig. 6-13 (a)**, in the electrode array without carbon fibers, half of the electrodes function as cathodes, and the other half as anodes, with the maximum current density of cathodes and anodes being approximately equal. After 7 hours from the start of the experiment, the change in current density gradually stabilized, approaching 0, indicating a uniform corrosion state. At this point, the corrosion products gradually covered the electrode surface as the corrosion reaction progressed, hindering the continuation of the corrosion reaction and resulting in a gradual decrease in corrosion current density. In **Fig. 6-13 (b)**, influenced by carbon fibers, the overall electrode array behaves as an anode, and the corrosion current density is positive. After 16 h, the anodic current density gradually stabilizes.

Visual representation of the current density was conducted using MATLAB, as depicted in **Fig. 6-14**. In **Fig. 6-14 (a)**, in the case of the pure electrode array, as the corrosion process advances, the positions of the anode and cathode change. This implies that, with the progression of the reaction, the locations at both ends surpass the critical threshold, leading to alterations in the sites of oxidation and reduction reactions within the electrode array. In **Fig. 6-14 (b)**, influenced by carbon fibers, at the beginning of the experiment, the proximal end near the carbon fibers serves as the anode, and the distal end serves as the cathode. After 10 h, the entire electrode array uniformly behaves as the anode. The change in current density indicates that the corrosion process



(a) Visualization of current density distribution without CF



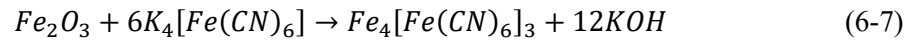
(b) Visualization of current density distribution with CF

Fig. 6-14 Visualization of current density distribution

of the electrode array is accelerated, reaching its peak at 14 h, and a decreasing trend has started at 16 h. The Current density of the electrode array with an artificial defect is shown in **Fig. 6-15**. The current density was recorded over 24 h, and the trend of current density change was the same as that of the experimental group without resin artificial defect, and there was no change in cathode position. In the test electrode array went through three stages: 1) In the first stage at the beginning of the test 0-6h, the artificial defect site gradually showed a red color, in this stage the electrode began to corrode, producing divalent iron ions, phenolphthalein and the reaction of hydroxide in the solution showed a red color, as shown in **Equation. 6-6**:



As the reaction continued, the corrosion of ferrous iron oxide produced by the corrosion and ferrous iron indicator reacted to produce a cyan product, as shown in **Equation 6-7**:



As shown in **Equation 6-8**, as the reaction intensifies, the cyan product is more and more, the solution of oxygen is consumed in large quantities, and ferrous iron is gradually transformed into trivalent iron, at this time phenolphthalein indicator shown by the red color begins to fade.

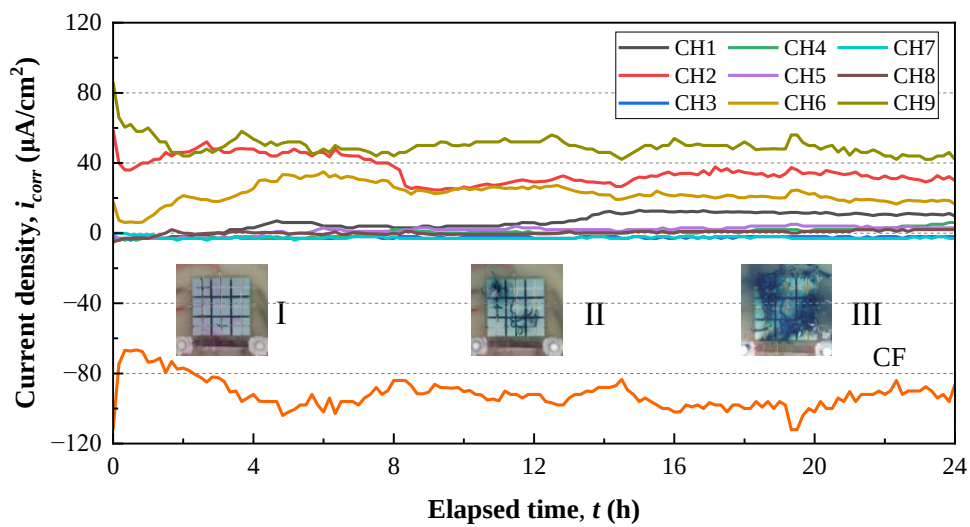
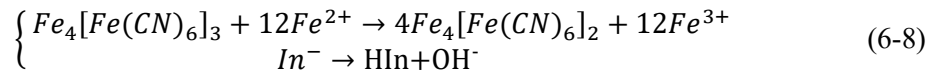


Fig. 6-15 Current density of electrode array with artificial defect

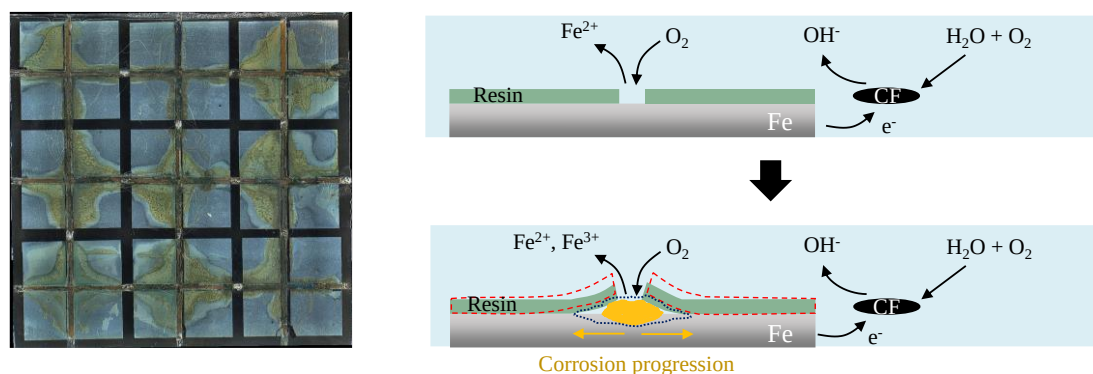


Fig. 6-16 Progress mechanism of resin stripping

After the test, remove the corrosion products and observe the surface of the electrode array. It can be clearly seen that the corrosion spreads in all directions centered on the cross-artifact defects, and the corrosion products lead to the failure of the bond between the resin and the electrode. The resin gradually expands and peels away from the electrode as the corrosion process progresses. The corrosion progress as well as the resin stripping mechanism is shown in **Fig. 6-16**.

6.6 Discussion on galvanic corrosion mechanism

The galvanic corrosion behavior between carbon fiber fabric and steel is influenced by the effective cathode reaction area in the circuit, and the immersion environment. Different environments play varying roles in promoting galvanic corrosion. In addition to these factors, the deterioration of the adhesive also affects the galvanic corrosion behavior between carbon fiber fabric and steel. The electrochemical corrosion mechanism of carbon fiber cloth and steel in the immersion environment is illustrated in **Fig. 6-17**. Due to the distinct electrochemical characteristics of the cross-section and cylindrical surface of carbon fibers, the cross-section facilitates charge flow. As carbon fiber fabric is continuous in the fiber direction, in practical situations, the cathode surface involved in the reaction might be much larger than the contact area when the resin matrix or adhesive of CFRP deteriorates. Research results indicate that more severe galvanic corrosion occurs when the cross-section of carbon fibers contacts steel. Moreover, because a bundle of carbon fibers has a smaller resistance than a single carbon fiber, the corrosion area often extends to a location farther from the point of contact between carbon fibers and steel.

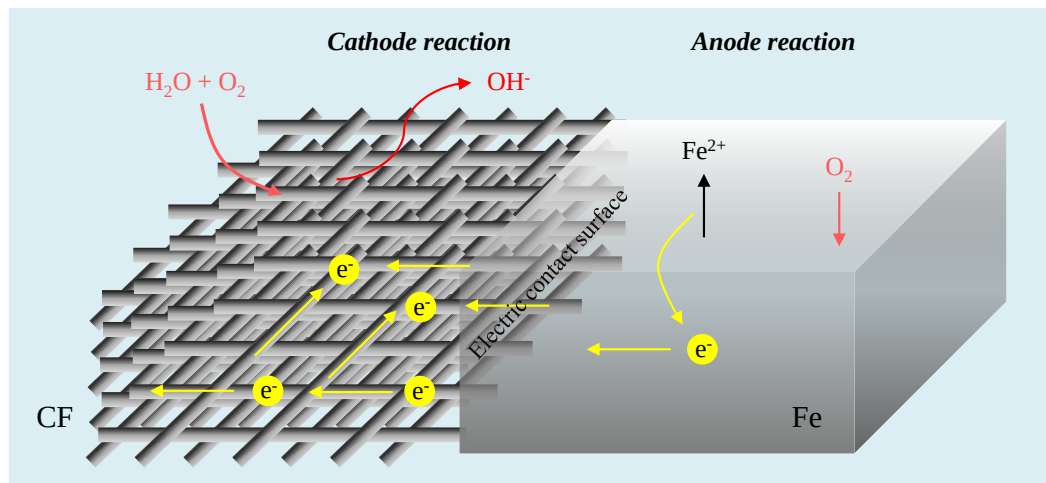


Fig. 6-17 Mechanism diagram of galvanic corrosion between carbon fiber fabric and steel in an immersion environment

With the occurrence of galvanic corrosion, corrosion at bonding defects expands, leading to more serious corrosion beneath the resin, causing resin delamination, and further enlarging the reaction area.

Among the various factors affecting carbon fiber-steel corrosion, in addition to the thickness of the water film in the service environment. Due to the deterioration of the resin matrix of the binder or CFRP laminate, direct or indirect contact between the carbon fiber and the steel will have a significant impact on the corrosion rate, and sectional contact will lead to more serious corrosion, therefore, when carrying out structural reinforcement maintenance of the steel structure should be avoided as much as possible to avoid sectional contact of this kind of situation occurs. On the other hand, compared with the impregnation environment, the thin water film environment is more conducive to the oxygen in the air to participate in the corrosion reaction, leading to more serious corrosion conditions. Therefore, in the repair construction, the repair surface should be made as flat as possible to reduce the number of areas prone to waterlogging.

6.7 Summary

This chapter evaluated the electrical resistance behaviors of carbon fiber materials in the form of single carbon fiber and carbon fiber tows. Moreover, the effect of the contact form between

carbon fibers and steel on galvanic corrosion behavior was clarified. The following conclusions were drawn.

- (1) A single carbon fiber demonstrates stable conductivity along the fiber's length and can be considered as a resistor with extremely low resistance. The measured resistance is directly proportional to the length of the carbon fiber. A bundle of carbon fibers, consisting of thousands of individual fibers, can be regarded as a parallel arrangement of resistors. Experimental results indicate that the volume resistance of the carbon fiber bundle is significantly lower than that of a single carbon fiber.
- (2) The experimental results indicate that carbon fiber exhibits anisotropic electrochemical characteristics. The cross-section of carbon fiber has stronger electrochemical properties compared to the cylindrical surface of the fiber. A passive layer influencing charge movement is present on the cylindrical surface of carbon fiber, and these passive layers may be a result of the manufacturing process.
- (3) In the environment of thin water film, oxygen is more likely to enter the water and participate in the corrosion reaction, so it is more likely to cause serious corrosion behavior compared to thick water film. Under the condition of the same thickness of water film, the electrode in contact with the CFRP cross-section has a larger corrosion area than the electrode in contact with the CFRP flat surface. Therefore, to mitigate the galvanic coupling corrosion between CFRP and steel structure, the section contact between carbon fiber and steel structure should be reduced.
- (4) After the deterioration of the resin matrix in the CFRP-steel joint, the exposed carbon fibers, when subjected to a humid environment, intensify the corrosion of the adjacent steel in the same environment. Additionally, corrosion tends to propagate inward along the deteriorated resin gaps, leading to the resin peel off from the steel.

CHAPTER 7 CONCLUSION

7.1 Summary of works

As lightweight materials such as CFRP are increasingly used for structural reinforcement in steel constructions, adhesive technology provides an effective solution to the bonding challenges between dissimilar materials. However, during prolonged service, the performance of bonded joints is susceptible to factors such as environmental temperature, moisture, and corrosion. Therefore, it is essential to study the adhesive strength, aging patterns, and failure mechanisms of joints under different conditions. This paper investigates the impact of various surface treatment methods on the adhesive strength of CFRP–steel joints, the aging mechanisms of these joints under hydrothermal conditions, and the galvanic corrosion behavior of the joints. The main research content and conclusions are summarized as follows:

In Chapter 2, five typical surface treatment methods, named disc sander (DS), belt sander (BS), wire brush (WB), bevel non-woven abrasive (BNA), and abrasive blast treatment (ABT), were used to treat uncorroded steel surfaces. The surface roughness was measured and analyzed, and the relationship between surface roughness and adhesive strength of the joints was studied through pull-off tests. In addition, BS, WB, BNA, and ABT was applied to remove rust from corroded steel surfaces. The rust removal effectiveness was compared using SEM, EDX, and XRD analyses. Research findings indicate that the surface roughness of steel increases after treatment with the five surface methods, with ABT treatment producing the highest roughness and BS treatment the lowest. In terms of adhesive strength, the order is $ABT > BNA > WB > DS > BS$. ABT has the best rust removal effectiveness. Compared to individual use, combining DS and WB yielded better rust removal effectiveness.

In Chapter 3, the effect of pre-coating process on adhesive strength was discussed. The environmental durability of the pre-coating process was examined by comparing adhesive strengths under dry-wet cycle and immersion conditions, along with DSC and SEM analyses. Results show apart from enhancing adhesive strength by increasing surface roughness, the

application of primer coating also proves effective. Low-viscosity primers increase the wettability of the adhesive to the treated steel surface, thereby increasing adhesive strength, with an average improvement exceeding 20 MPa. Dry-wet cycle test suggest that moisture infiltration and thermal deformation mismatch at the adhesive interface are the primary causes of interface delamination. In practical applications, chloride ion penetration can lead to corrosion at the steel interface, exacerbating the decline in the mechanical performance of composite joints. Moreover, simulating summer and winter environmental temperatures, the adhesive strength of CFRP under curing conditions of 35 °C and 15 °C was investigated through static tensile tests and DSC analysis. The changes in glass transition temperature were also calculated, along with the internal porosity. The results indicate that raising the initial curing temperature is beneficial for both the mechanical and thermal performance of composite material joints. However, the internal porosity of CFRP cured at high temperatures is higher than that cured at low temperatures.

In Chapter 4, the surface adhesive strength and shear strength of uncorroded steel and corroded steel under the same treatment methods was analyzed through static pull-off and shear tests. The results show that ABT provides greater surface roughness and better rust removal compared to hand-held power tools (WB, BNA). The steel surface treated with ABT exhibits superior bonding performance and shear strength. In contrast to WB, BNA does not form an oxide film on the steel surface due to frictional heat during processing, thereby preserving adhesive strength. The bonding mechanism and influencing factors at the steel-adhesive interface after corrosion differ from uncorroded conditions. For corroded steel, geometric features of the surface become crucial in determining strength, with additional residual substances on the corroded surface further affecting bonding performance.

In Chapter 5, aging tests were conducted on CFRP-steel joints and epoxy resin matrix under five environmental conditions: 1) 25 °C distilled water immersion, 2) 25 °C 3.5wt% NaCl aq. immersion, 3) 25 °C 95% RH high humidity, 4) 40 °C distilled water immersion, and 5) 40 °C 3.5wt% NaCl aq. immersion. The effect of different aging environments on mechanical performance was discussed through tensile tests. Resin specimens were used to analyze water absorption under the five test environments. FT-IR analysis was employed to study the trends in functional groups like -OH and C-O-C within the resin matrix. DSC analysis was conducted to

examine the influence of moisture and salt on the glass transition temperature of the resin matrix. Additionally, specimens were dehydrated through physical drying, and changes in adhesive strength, group content, and glass transition temperature before and after water absorption were compared. The fracture modes of non-aged, aged, and physically dried specimens were analyzed using SEM.

Results indicate that moisture diffusion in the resin matrix follows Fick's first law, with the maximum water absorption rate unaffected by temperature but dependent on the electrolyte environment. Distilled water shows a higher maximum absorption rate than in a humid environment. Temperature and water absorption are positively correlated. Moisture absorption is partially reversible, but water-induced hydrolysis is irreversible. Chloride ions do not significantly accelerate resin aging. Moisture absorption is linearly inversely proportional to the tensile strength and Young's modulus of the resin. Physical drying can eliminate type I bonding water, partially restoring mechanical strength and thermal performance. However, despite physical drying, residual type II bonding water still causes irrecoverable decreases in mechanical strength and thermal performance. SEM analysis reveals that moisture leads to cohesive failure within the resin and weakened adhesive strength between the resin and carbon fibers, resulting in delamination and interlayer failure under external forces. Mechanical properties of CFRP-steel joint cannot be fully recovered after drying following moisture absorption. Aging of CFRP-steel joints is influenced by the aging behavior of the resin matrix.

In Chapter 6, electrochemical impedance spectroscopy (EIS) analysis was performed on the cross-section and cylindrical surface of carbon fibers using a potentiostat, volume impedance of the carbon fiber fabric was measured. The corrosion behavior of carbon fibers and steel under conditions of room temperature (25 °C), a 0.5 mm water film, and 10 mm immersion was analyzed. The differences in corrosion behavior between cross-section surface contact and flat surface contact of carbon fiber were discussed. Additionally, an electrode array experiment was designed to analyze the impact of carbon fibers on corrosion at multiple damage sites and the progression of resin-damaged area corrosion.

Research results indicate that carbon fibers exhibit anisotropic electrochemical behavior, with significantly higher electrochemical activity on the cross-sectional surface compared to the

cylindrical surface. Testing resistance of carbon fiber bundles suggests incomplete electrical conductivity due to the passive layer on the cylindrical surface hindering electrical conduction. The actual surface resistivity of the carbon fiber fabric is significantly higher than that of the carbon fiber material. However, when it makes direct contact with a rough conductive metal surface, the surface resistivity decreases significantly due to optimized conductive paths and increased contact area. In a thin water film environment, oxygen is more likely to participate in corrosion reactions, making it more prone to severe corrosion compared to a thick water film. The cross-section of carbon fibers has more active electrochemical characteristics, making electrochemical corrosion more likely when the electrode contacts the cross-section of CFRP. Therefore, to mitigate galvanic corrosion between CFRP and steel structures, it is advisable to reduce cross-sectional contact between carbon fibers and steel structures.

7.2 Recommendations for future works

Due to the limited expertise of the author, this paper has some shortcomings, and there are still some issues that need further investigation in the future:

- (1) The surface rust removal methods involved in the current experiments are all traditional methods. Newly developed methods, such as water jet treatment and laser treatment rust removal, have not been discussed or compared. A supplementary comparison will be conducted in the subsequent research.
- (2) The current study focuses on a relatively narrow range of experimental subjects, considering only one type of epoxy resin, specific CFRP, and steel substrates. Future research will involve a broader range of material combinations (such as aluminum magnesium alloy, etc.) for comparative studies to explore the effects of different material combinations on the aging patterns and failure mechanisms of bonded structures.
- (3) This paper primarily investigates the static mechanical properties of bonded joints under hydrothermal aging conditions. Reinforced steel structures in actual service are subjected to dynamic loads. Therefore, subsequent research needs to explore their failure or fatigue behavior under dynamic loads.

- (4) The study of aging mechanisms in this paper was mainly conducted under hydrothermal conditions. The subsequent research plan is to investigate the deterioration behavior of the joint under freeze-thaw conditions. Combining practical engineering applications, a predictive model with a broad range of applicability will be developed.

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