Durability of CFRP Sheets and Epoxy Resin Exposed to Natural Hygrothermal or Cyclic Wet-Dry Environment

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Fiber reinforced polymer (FRP) composites are used in harsh environments, resulting in degradation of their mechanical properties. Such degradation is critical in terms of the reliable design and application of FRP composites. In this study, a set of CFRP flat coupons and epoxy resin matrix flat coupons were prepared and subjected to alternating conditions of 10 h immersion in a 40°C NaCl solution with a concentration of 3.5%, and 14 h drying at 25°C and 60% relative humidity (RH). They were divided into five series, subjected to 0, 60, 120, 240, and 360 wet-dry cycles, respectively. For a comparison with the acceleration simulation tests, the same numbers of specimens were exposed to a natural hygrothermal environment for 0, 6, 12, 18, and 30 months, respectively. After removal from the environment at the designated time, a series of tension tests were carried out. Based on the experimental results, the relationship regarding the tensile strength degradation of the CFRP sheets between the natural hygrothermal environment and the cyclic wet-dry environment was determined. It was found that the tensile modulus of the CFRP sheets increased by 1.4%, and the tensile strength and ultimate strain decreased by 8.1% and 8.0% after 360 wet-dry cycles, respectively. After a 30-month natural exposure period, the tensile strength, tensile modulus, and ultimate strain of the CFRP sheets decreased by 9.9%, 3.4%, and 7.2%, respectively. The tensile property of the epoxy resin matrix appeared to be more sensitive to these two types of exposure environments than that of the CFRP sheets, and the tensile strength decreased by 59.4% at the end of 30-month exposure. POLYM. COMPOS., 00:000–000, 2017. © 2017 Society of Plastics Engineers

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INTRODUCTION

Carbon fiber reinforced polymers (CFRPs) are widely used materials for the repair and rehabilitation of existing structures. The increasing use of CFRPs for strengthening and retrofitting can be attributed to their excellent material properties, including a high stiffness-to-weight ratio, high strength-to-weight ratio, and ease of field application [1]. These structural members typically encounter high humidity environments [2] or are exposed to aggressive elements such as ions [3] (a chloride-containing environment), which can often accelerate their degradation and decrease their structural integrity [4]. Because long service lives are required for civil engineering structures under various harsh environmental conditions, the long-term mechanical behavior of CFRP composites or CFRP-strengthened structures is always a concern [5].

Many previous studies have been conducted on the durability of a CFRP-concrete interface [6–8]. Shrestha et al. [8, 9] studied the effects of water immersion on the bond behavior of the interface between CFRP plates and a concrete substrate immersed in water at 20°C for 24 months. It was found that the adhesive was susceptible to moisture ingress resulting in a 12% decrease in bond strength, and the water immersion altered the debonding mode from a cohesive concrete fracture to adhesive separation from the concrete substrate, whereas the tensile strength and tensile modulus of the adhesive remained nearly constant. As reported by Al-Tamimi [6], the combination of temperature and moisture accelerated the degradation of the bonded systems through a gradual transformation of the matrix status between glassy and rubbery conditions. Sen [10] also concluded that the deterioration of the interface is primarily dependent on the performance of the epoxy resin owing to the changes in the physical and mechanical properties resulting from the exposure. Pan et al. [7] found that an 8-week water immersion at 50°C did not change the failure mode of the bonding system of a CFRP-concrete interface, although the tensile modulus and tensile strength of the adhesive were reduced by 14.4% and 8.5%, respectively. Naderi and Hajinasri [11] studied the interface degradation of CFRP-concrete exposed at wet-dry condition, the shear bond strength reduced to 30% after 180 cycles.

For hygrothermal conditions, numerous studies have been carried out based on acceleration simulations. Shrestha et al. [8] studied the effect of the wet-dry cycles on the interface behavior of CFRP and concrete for an 18 months period by designing a wet-dry cycle process that includes 7 days of immersion in water and 4 days of drying at 20°C. The bond strength decreased up to 5%, and there was no reduction in tensile strength until 18 months, although a slight reduction in tensile modulus did occur. Dai et al. [12] also studied the durability of a CFRP-concrete interface under a wet-dry cycle for 2 years, which consisted of a 4-day immersion in 60°C seawater and a 3-day exposure to dry conditions. The interfacial bond strength degraded asymptotically with the exposure time, and a bond failure of the FRP-to-concrete interfaces consistently occurred at the primer-to concrete interface, and not within the concrete substrate.

In addition to the concrete members, the durability of the interface between steel and CFRP has also been studied. Borrie et al. studied [4] the durability of CFRP-steel immersed in a 5% NaCl solution (by weight) at 20, 40, and 50°C for a 6 month period. The bond strengths were seen to deteriorate more significantly with longer exposure durations. Moisture was identified as the primary factor, along with the expansion of salt crystals in the micro-cracks [13]. Heshmati et al. [14] studied the durability of the interface under wet-dry condition (5% NaCl saltwater at 45°C). The results indicated that moisture can enter the resin matrix and adhesive bonds through bulk adhesive diffusion, and transport along the interface through capillary action. The moisture can change the resin matrix through swelling, plasticization, hydrolysis, and cracking, thereby leading to degradation in the interface property [3, 7, 15]. Batuwitage et al. [16] studied the durability of a CFRP-strengthened steel plate with double-strap joints using an electrochemical accelerated method. It was found that the degradation of the CFRP becomes dominant when exposed to an accelerated corrosive. Karbhari claimed that the deterioration of a fiber-matrix interface and consequent fiber de-bonding is the main failure mechanism for the tensile behavior of FRP composites [17].

As indicated above, understanding the performance degradation of CFRPs under harsh environments is necessary for application of this material to civil engineering projects. Moisture attacks the composites through the fibers, matrix, and fiber-matrix interface, and all types of adhesives are susceptible to deterioration [13, 17]. Cromwell et al. [18] studied the durability of a CFRP plate and CFRP fabric under 38°C water immersion conditions, and found that the performance of the CFRP plate was relatively unaffected by the environment, whereas the tensile properties of the CFRP fabric were slightly increased, which was explained by the post-curing, and found that no damage to the carbon fiber occurred [17]. At low temperature, the CFRP sheet was more susceptible to longer exposures; however, at elevated temperatures, degradation occurred faster with comparable losses in strength after both 1- and 6-months durations [4]. Moisture usually increases the ductility of resins and adhesives, but reduces their elastic modulus and tensile strength [4, 7, 13].

Many researchers have conducted extensive studies on the short-term mechanical behavior of CFRP. However, as mentioned previously, existing studies have provided only a limited understanding of the durability of CFRP composites and their constituents, particularly in chloride-containing hygrothermal environments. Owing to the variation in material parameters and the different exposure conditions, it is difficult to compare these different test results and draw general conclusions. In addition, it should be mentioned that most studies reported have been based on acceleration simulation tests, with a very limited number conducted under a natural exposure environment. Moreover, the relationship between the simulated and natural environments is not yet clear. In this study, the durability of CFRP sheets and an epoxy resin matrix exposed to a cyclic wet-dry environment or a natural hygrothermal environment was investigated. First, the test program is presented, which is aimed at introducing the specimen design, material properties, implementation of the environmental exposure, and the instrumentation. Following this, the experimental results are described and analyzed. Finally, the relationship regarding the tensile strength degradation between a cyclic wet-dry chloride-containing environment and a natural environment is discussed.

EXPERIMENTAL

Raw Materials

A high-performance carbon fiber sheet, UT70-30 (Toray Industries, Tokyo, Japan), was used in this study. The nominal thickness of the CFRP was 0.167 mm for each ply, and the areal weight of the fiber was 300 g/cm^2. The tensile strength, tensile modulus, and ultimate strain were 4,200 MPa, 245 GPa, and 1.76%, respectively. The parameters were provided by the manufacturer.

The epoxy resin (HM-E8) used in this study was provided by Heroman Ltd., which is a two-component resin with a thixotropic epoxy adhesive and an epoxy resin binder mixed at a ratio of 2:1 by weight.

Preparation of the Specimens

The CFRP sheets were prepared in accordance with the ASTM D 3039/D 3039 M-00 guidelines [19]. The manufacturing process of the specimens used comprised three steps: First, cutting the CFRP sheet into a size of 250 mm × 200 mm. The second step was to impregnate the epoxy resin matrix on a piece of glass board, where a roller was used to remove any trapped air from within the

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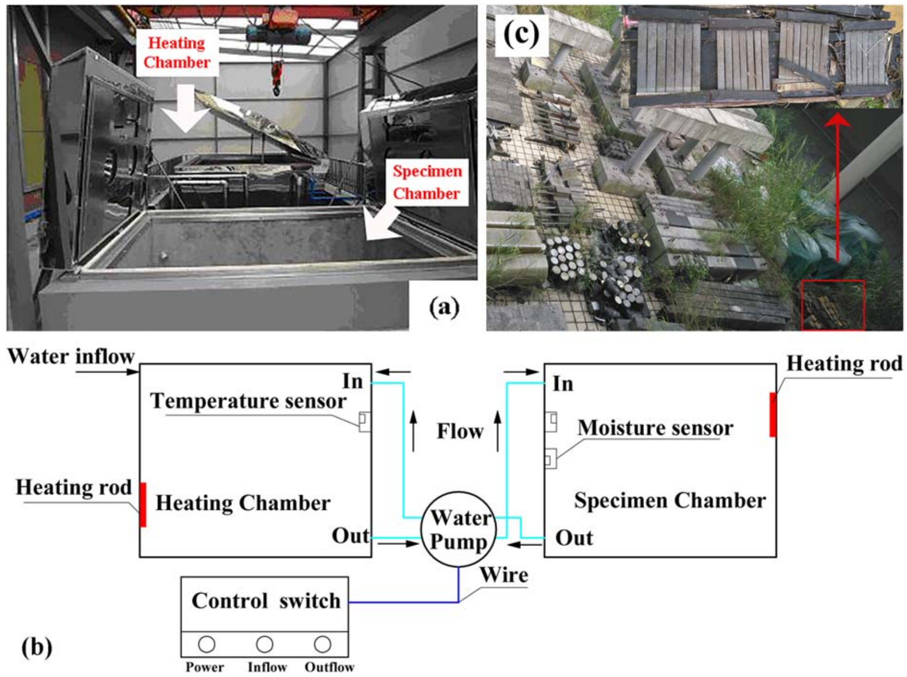

FIG. 1. Exposure conditions: (a) physical map of the wet-dry cycle system, (b) sketch map of the wet-dry cycle system, and (c) natural environment. [Color figure can be viewed at wileyonlinelibrary.com]

specimens. The specimens were covered by another piece of glass board with a heavy object, and cured at ambient room temperature for at least 7 days. The last step was cutting the specimens into dimensions of 250 mm × 25 mm.

Dog-bone shaped resin specimens for the uniaxial tensile testing were prepared following ASTM D 638-99 [20]. The epoxy resin matrix was mixed at the recommended proportion, and transferred into an ultrasonic cleaning machine for 10 min in a 40°C water environment. The epoxy resin matrix was then poured into the mould and tapped several times to remove any bubbles from the specimens, which were 3 mm in thickness. The specimens were cured at ambient room temperature for more than 7 days before being subjected to the exposure environment.

Exposure Conditions

Accelerated aging through wet-dry cycling was conducted in a structural laboratory at Guangdong University of Technology in Guangzhou, China, as shown in Fig. 1a, and sketch map of the wet-dry cycle system is shown in Fig. 1b. The concentration of chloride ions (Cl^-) was set to 3.5%. The process of a single wet-dry cycle was as follows: the specimens were immersed in a 40°C NaCl solution for 10 h, followed by drying at 25°C and 60% RH for 14 h. The temperature control precision was ± 2°C. The numbers of exposure cycles were set to 60, 120, 240, and 360.

For the natural environment, the outdoor conditions at Guangdong University of Technology were selected, as shown in Fig. 1c. In the test area, the average annual temperature is 21.5–22.2°C, the extreme high temperature is approximately 39.3°C, the extreme low temperature is approximately 0°C, and the duration of difference in temperature between day and night for up to 10°C is about 1 month. The average annual precipitation is about 1,800 mm. In addition, the test area has an average annual relative humidity of 78%. The exposure durations were set as 6, 12, 18, and 30 months.

Tensile Property Tests

The CFRP specimens were prepared according to ASTM D 3039/D 3039 M-00 [19]. Aluminum sheets were used to anchor both sides of the specimens, as shown in Fig. 2a. Tensile tests were carried out at a loading rate of 1.5 mm/min. The load was controlled using an electronic universal testing machine (DDL-100 model, Changchun Research Institute for Mechanical Science Co. Ltd., Changchun, China) equipped with a 100 kN load cell. The longitudinal strain of the CFRP sheets was measured to determine the elastic modulus, and three strain gauges were used for one specimen (see Fig. 2a). The strain gauges (measurement type BHF 350-3AA) were provided by Zhejiang Huangyan Testing Apparatus Factory (Taizhou, China), and α-cyanoacrylate adhesive super glue (502 glue, purchased from a supermarket in Guangzhou, China) was used. A TDS-530 high-speed static data logger (Tokyo Sokki Kenkyujo Co., Ltd., Tokyo, Japan) was utilized to record the strain data.

The tensile tests of the epoxy resin matrix were conducted following ASTM D 638-99 [20]. The test

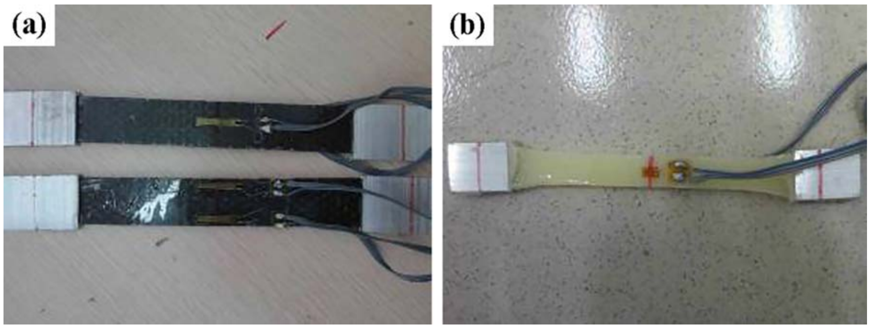

FIG. 2. Tensile specimens: (a) CFRP sheet and (b) epoxy resin matrix. [Color figure can be viewed at wileyonlinelibrary.com]

instruments and parameters were the same as with the CFRP sheets, the differences being the distribution of the strain gauges and the test rate (0.8 mm/min was used for the epoxy resin matrix). Two strain gauges were used during the test (see Fig. 2b), and the stain was reported as the average value between the two.

A summary of all parameters, along with the number of specimens tested, is presented in Table 1. Seven specimens were prepared for each series, five test results were selected, and the average value was reported.

RESULTS AND DISCUSSION

Tensile Properties of the Control Specimens

Table 2 shows the tensile test results of the CFRP sheet and epoxy resin matrix at room temperature. For the CFRP sheet, the variation in tensile strength, elastic modulus, and fracture strain are all lower than 5%, indicating a good stability of the CFRP specimens. Regarding the epoxy resin matrix, the tensile strength and tensile modulus showed good stability as well, but the variation in ultimate strain increased to 8% for an unknown reason. This showed no effect on the durability described herein, however.

The relationship between the stress and strain of the CFRP sheets and epoxy resin matrix is shown in Fig. 3. As shown in Fig. 3a, the stress–strain curves of the CFRP sheets showed a linear relationship. The stress–strain relationship of the epoxy resin matrix showed only a slight difference, and an inflection point near the failure load is shown in the test results. This can be attributed to the micro-cracks that developed at the fracture location, and the stress concentration occurring in the specimen [17].

The failure modes of the specimens are shown in Fig. 4. As Fig. 4a indicate, the CFRP sheets showed a brittle failure mode, and the epoxy resin also showed a brittle failure (Fig. 4b), which occurred within the middle region of the specimens.

Effects of Natural Exposure

Fig. 5 shows the various tensile properties of a CFRP sheet as a function of exposure time. As indicated, the tensile properties showed a slight decrease as the exposure time increased, and the tensile strength, tensile modulus, and ultimate strain of the CFRP specimens decreased by 9.9%, 3.4%, and 7.2% (compared to its original value) after 30 months of exposure, respectively. The tensile strength decreased more compared with the tensile modulus, and similar test results were reported in Refs. 17 and 21. The tensile modulus is a measure of deformation under external stress, which is determined based on the interaction forces between atoms or molecules. However, the tensile strength is more closely related to the initiation and development of defects in the materials, which is more sensitive to the existing defects [5].

In contrast, the tensile test results of the epoxy resin matrix are as shown in Fig. 6. The tensile strength and tensile modulus showed a nearly linear decrease as the exposure time increased, and decreased by 59.4% and 49.2% after 30 months of exposure compared to the initial value or 35.5 MPa and 2.5 GPa, respectively. The decrease in tensile strength can be attributed to the oxidation of the surface layer [22], as well as consolidation

TABLE 1. Summary of parameters along with number of specimens tested in the study.

		Wet-dry cycles				Natural environment			
Specimen	Control	DW60	DW120	DW240	DW360	NE6	NE12	NE18	NE30
CFRP sheet	7	7	7	7	7	7	7	7	7
Epoxy resin matrix	7	7	7	7	7	7	7	7	7

Note: DW60 = Wet-dry condition with 60 cycles; and NE6 = Natural exposure condition with 6 months.

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TABLE 2. Experimental results of tensile properties at room temperature.

No.	CFRP sheet Tensile strength (MPa)	CFRP sheet Elastic modulus (GPa)	CFRP sheet Ultimate strain (%)	Epoxy resin matrix Tensile strength (MPa)	Epoxy resin matrix Elastic modulus (GPa)	Epoxy resin matrix Ultimate strain (%)
1	4,428.83	233.41	1.82	35.64	2.49	1.98
2	4,629.20	239.57	2.02	36.90	2.40	1.73
3	4,318.29	226.74	1.93	34.72	2.32	1.82
4	4,841.09	238.71	2.04	33.08	2.58	2.12
5	4,626.90	221.42	1.92	37.20	2.60	1.99
Mean value	4,568.9	232.0	1.95	35.5	2.5	1.93
Standard deviation	202.18	7.81	0.09	1.68	0.12	0.15
Coefficient of variation (CV)	4.4%	3.4%	4.5%	4.7%	4.8%	8.0%

through the thickness of the specimen [23]. Regarding the ultimate strain, however, the natural exposure showed a reverse effect. The ultimate strain showed a slight fluctuation for an unknown reason, and increased by 18.1% compared with the original value of 1.93%. The reduction in the break strain of the epoxy resin matrix can be attributed to the post curing [22, 23], and the increase was attributed to the plasticization effect of the moisture ingress [24]. The results indicate that the plasticization had a greater influence on the ultimate strain compared with the post curing.

The properties of the FRP composite are governed not only by the fiber and resin matrix, but also by the interface between the fiber and epoxy resin matrix [5, 17]. Compared with the tensile test results of the CFRP sheets and epoxy resin matrix, more serious degradation of the tensile strength and tensile modulus was found in the epoxy resin matrix. These results indicate that the degradation of the epoxy resin showed only a slight effect on the tensile property of the CFRP sheets. For the control specimens, the ultimate strains of the CFRP sheets (1.95%) and the epoxy resin matrix (1.93%) were nearly the same, which means a good mechanical load-carrying capacity of the composite was achieved. For an exposure time of up to 30 months, the ultimate strain of the CFRP sheets (1.80%) was smaller than that of the epoxy resin matrix (2.28%), which indicates that the tensile strength was controlled based on the carbon fiber in the composites, and that interface damage occurred during the tensile test. Furthermore, the tensile modulus of unidirectional FRP composites along the reinforced fiber direction can be expressed as [25]:

$$E_c = E_m V_m + E_f V_f \tag{1}$$

where E_c, E_m, and E_f are the tensile modulus of the composite, resin matrix, and reinforced fiber, respectively; and V_m and V_f are the volume fraction of the resin matrix and reinforced fiber inside the composite, respectively.

It is assumed that the volume fractions of the carbon fiber and epoxy resin matrix remained constant. Based on this model and the experimental results, the theoretical tensile modulus of the carbon fiber for different exposure times is as listed in Table 3. It is assumed that there is no damage on the carbon fiber under natural exposure, as based on Ref. 17. The interface damage rate is defined as:

$$R = \frac{M_0 - M_t}{M_0} \tag{2}$$

where M_0 is the initial tensile modulus of the specimens, and M_t is the tensile modulus of the specimens at time T. The calculated value of R is also listed in Table 3. As shown, the theoretical tensile modulus of the carbon fiber increased by 1.1% after a 6-month exposure period, and the corresponding interface damage rate increased by 1.0%.

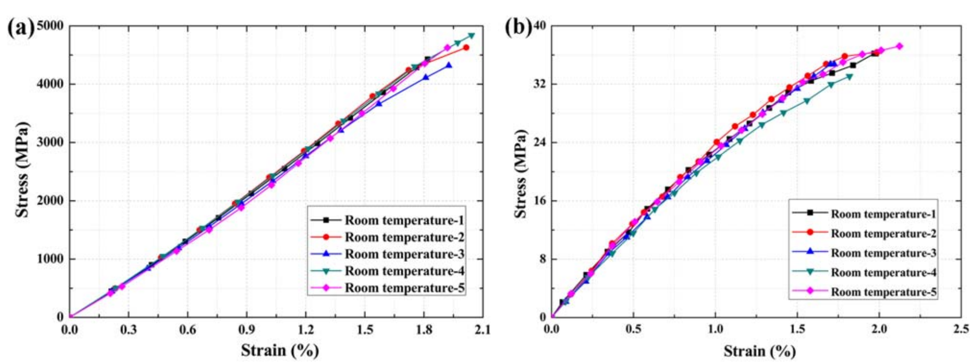

FIG. 3. Stress–strain relationship of the specimens at room temperature: (a) CFRP sheet and (b) epoxy resin matrix. [Color figure can be viewed at wileyonlinelibrary.com]

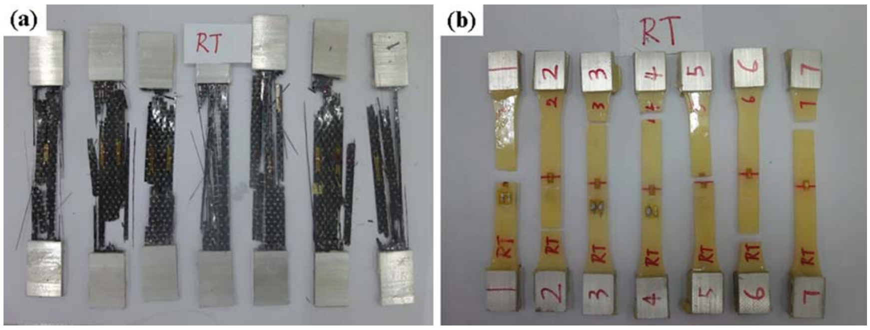

FIG. 4. Failure modes of the specimens at room temperature: (a) CFRP sheet and (b) epoxy resin matrix. [Color figure can be viewed at wileyonlinelibrary.com]

This phenomenon may be attributed to the cross-linking reaction between the size and epoxy resin matrix [17]. As the exposure time increased up to 12, 18, and 30 months, the interface damage rate increased by 0.6%, 1.3%, and 3.4%, respectively. The increased interface damage can be attributed to the difference in thermal expansion coefficients between the carbon fiber and resin matrix [23], which led to the degradation tensile strength of the CFRP sheets.

Fig. 7 shows the failure modes of the epoxy resin matrix after various exposure times. All of the specimens failed in the middle region, and there is no clear difference in the failure modes compared with the control specimens (see Fig. 4b). It is worth noting that the specimens showed a different morphology, and the color deepened after 30 months of exposure (Fig. 7d). This can be attributed to the thermal aging of the specimens [22].

Fig. 8 shows photographs of the CFRP sheets after the tensile test at various exposure times. As with the control specimens, these specimens fractured in a brittle manner. The failure mode of the specimens exposed to a natural environment for a 6-month period (Fig. 8a) was similar to that of the control specimen, although a splitting failure occurred. This failure mode often began at one of the loaded edges with the interface damage and propagated into the pane [3]. As shown in Fig. 8b, for the specimens exposed after 12 months, the specimens broke into many fragments. This phenomenon became more pronounced as the exposure time increased, as seen in the specimens exposed for an 18-month period (Fig. 8c). A difference in failure mode can be observed for the CFRP sheets after 30 months of exposure. As shown in Fig. 8d, the cross-section of the fractured specimens became regular. The

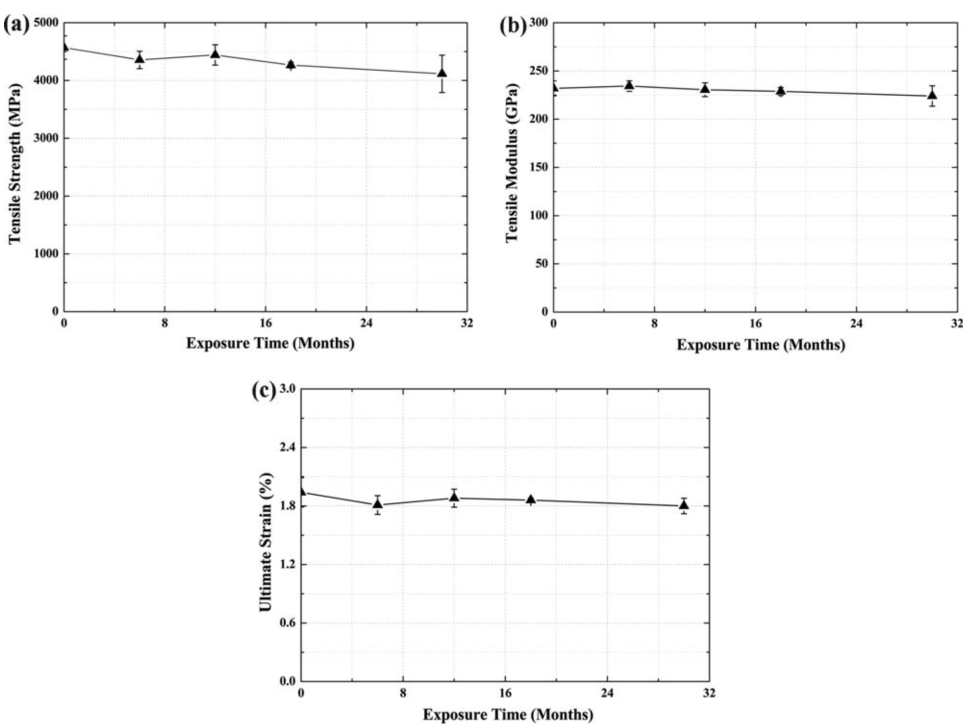

FIG. 5. Tensile test results of the CFRP sheet as a function of exposure time: (a) tensile strength, (b) tensile modulus, and (c) ultimate strain.

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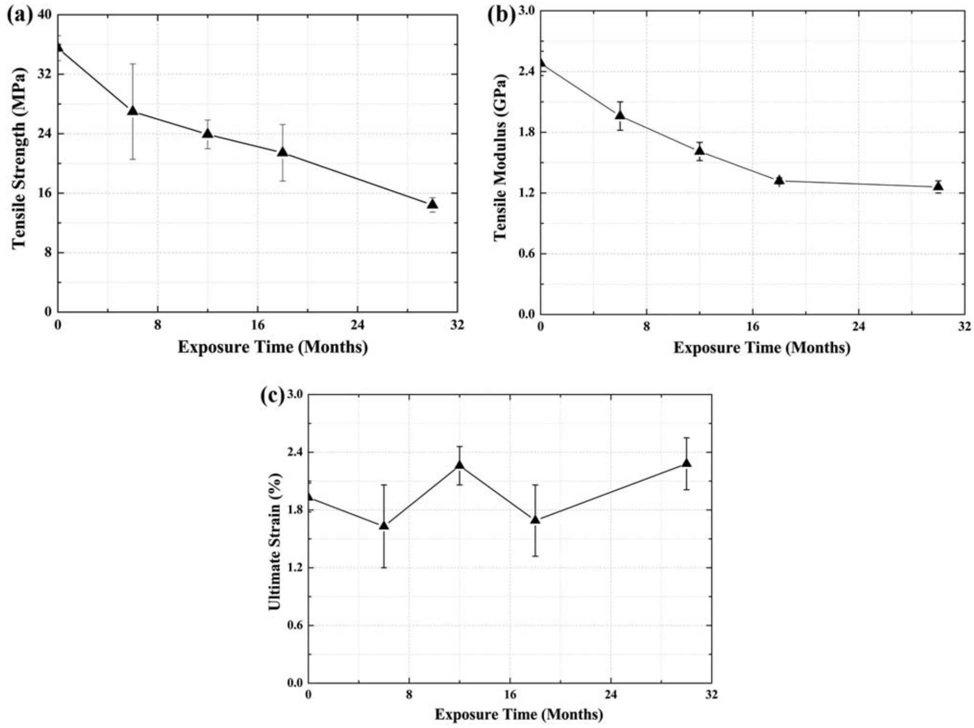

FIG. 6. Tensile test results of the epoxy resin matrix as a function of exposure time: (a) tensile strength, (b) tensile modulus, and (c) ultimate strain.

failure modes may be attributed to the degradation of the epoxy resin matrix and interface damage, as well as to a concentration of stress occurring at these locations [23].

The average stress–strain curves of the epoxy resin matrix are shown in Fig. 9a. As shown, the ultimate stress and the slope of these curves decreased as the exposure time increased, and the deformation increased at the same load level. An almost linear relationship between the stress and strain can be found for the control and 6-month exposure specimens. An obvious two-stage relationship can be found for the epoxy resin matrix exposed for 30 months, where the slope of the curve was consistent with the specimen exposed for 18 months during the first stage, and then decreased as the stress increased up to 8 MPa. The decreased slope may be attributed to the fracture of the thermally aged layer of the epoxy resin matrix, leading to a decrease in bearing capacity. The strain was controlled using a moisture-plasticized polymer [7, 23]. Thus, an increase in ultimate strain can be seen.

In contrast, the stress–strain curves of the CFRP sheets are as shown in Fig. 9b. A linear relationship can be found for all specimens after various exposure times. As shown, the ultimate stress showed a slight decrease as the exposure time increased. The variations of the slope in these curves agree well with the changes to the tensile modulus of the CFRP sheets. Compared with the epoxy resin matrix, the deformation of the CFRP sheets was smaller than that of the epoxy resin matrix at the same load level. This result indicates that the deformation was dominated based on the carbon fiber and that the contribution of the epoxy resin matrix to the tensile strength of the CFRP sheets was limited [21, 26].

Effects of Cyclic Wet-Dry Chloride-Containing Exposure

Fig. 10 shows the tensile test results of CFRP sheets as a function of the wet-dry cycle time. As the results of the tensile strength test indicate (Fig. 10a), the tensile

TABLE 3. Theoretical tensile modulus of the carbon fiber under natural environment.

Exposure time period (months)	Fiber volume fraction (V_f)	Epoxy resin matrix volume fraction (V_m)	Theoretical value (GPa)	Interface damage rate under natural exposure (%)
0	0.946	0.054	245.0	0
6	0.946	0.054	247.6	−1.0%
12	0.946	0.054	243.6	0.6%
18	0.946	0.054	241.8	1.3%
30	0.946	0.054	236.7	3.4%

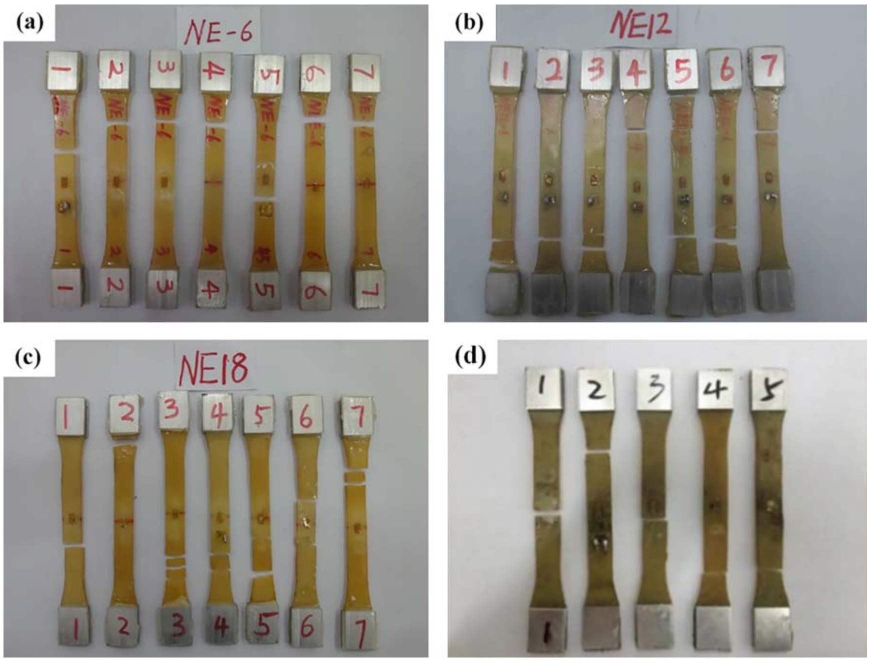

FIG. 7. Failure modes of the epoxy resin matrix after various exposure times: (a) 6 months, (b) 12 months, (c) 18 months, and (d) 30 months. [Color figure can be viewed at wileyonlinelibrary.com]

strength decreased by 4.0%, 3.0%, 6.4%, and 8.1% (compared with the initial value of 4,568.9 MPa) as the cycle times increased to 60, 120, 240, and 360, respectively. This observation likely indicates that the wet-dry cycles have a deleterious effect on the tensile strength of a CFRP sheet, and the longer the exposure time, the more serious the degradation. Regarding the tensile modulus, as shown in Fig. 10b, the tensile modules showed a linear increase with the exposure cycle, and the tensile modulus increased by 1.4% compared with the initial value of 232 GPa as the exposure cycles increased to 360. The ultimate strain decreased as the exposure time increased, and as the exposure cycle increased to 360, the ultimate strain decreased by 8.0%, as shown in Fig. 10c. The interface

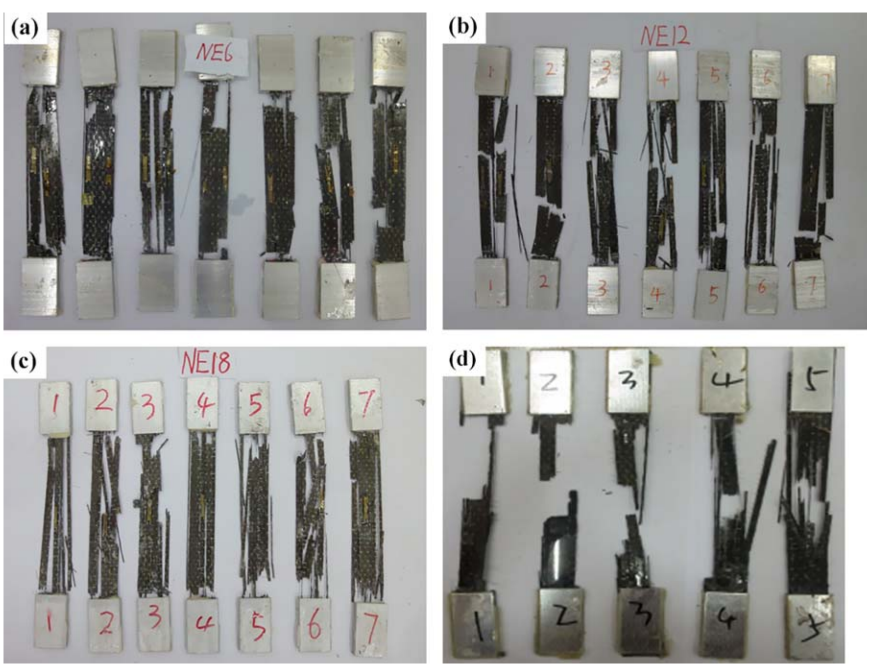

FIG. 8. Failure modes of CFRP sheet after various exposure times: (a) 6, (b) 12, (c) 18, and (d) 30 months. [Color figure can be viewed at wileyonlinelibrary.com]

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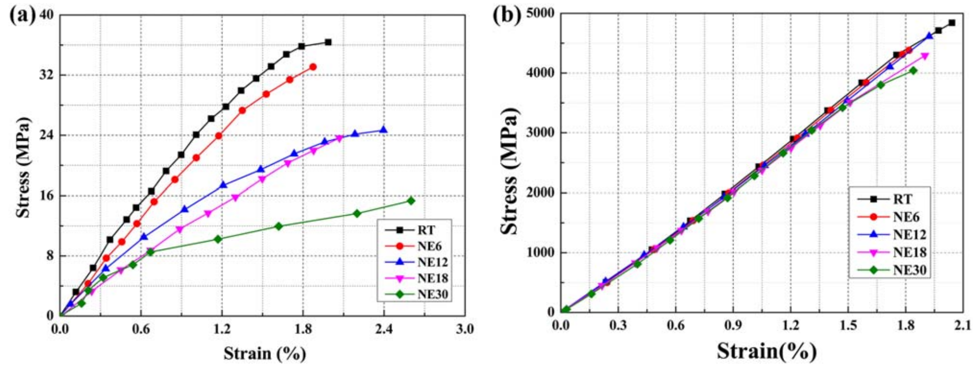

FIG. 9. Stress–strain relationship of the specimens after various exposure times: (a) epoxy resin matrix and (b) CFRP sheets. [Color figure can be viewed at wileyonlinelibrary.com]

damage of the fiber-matrix may lead to a degradation of the tensile property [5, 25]. Moreover, water molecules diffuse into the CFRP sheets and combine with water soluble molecules to form new larger molecules in the composite, which may lead to the tensile strength of the CFRP sheets to decrease [24].

Fig. 11 shows the tensile test results after various wet-dry cycles for the epoxy resin matrix. As shown, the tensile strength and tensile modulus decreased as the exposure cycles increased. However, the ultimate strain showed a slight increase. The degradation of the tensile strength is shown in Fig. 11a, and compared with the initial value of 35.5 MPa, the tensile strength decreased by 22.1%, 30.8%, 39.9%, and 43.1%, and the tensile modulus (Fig. 11b) decreased by 19.4%, 32.0%, 45.8%, and 46.3% (compared with the initial value of 2.5 GPa) as the number of cycles increased to 60, 120, 240, and 360, respectively. Regarding the ultimate strain, as the wet-dry cycle times increased to 360, the ultimate strain increased by 6.9% compared with the control value of 1.93%. The chloride ions can easily permeate into the epoxy resin through the existing voids and cracks, and destroy the epoxy resin matrix [17], resulting in degradation of the tensile strength [27].

Fig. 12 shows the failure modes of the epoxy resin matrix specimens after various exposure cycles. There is no clear difference in the failure modes compared with the control specimens. From the surface morphologies, it

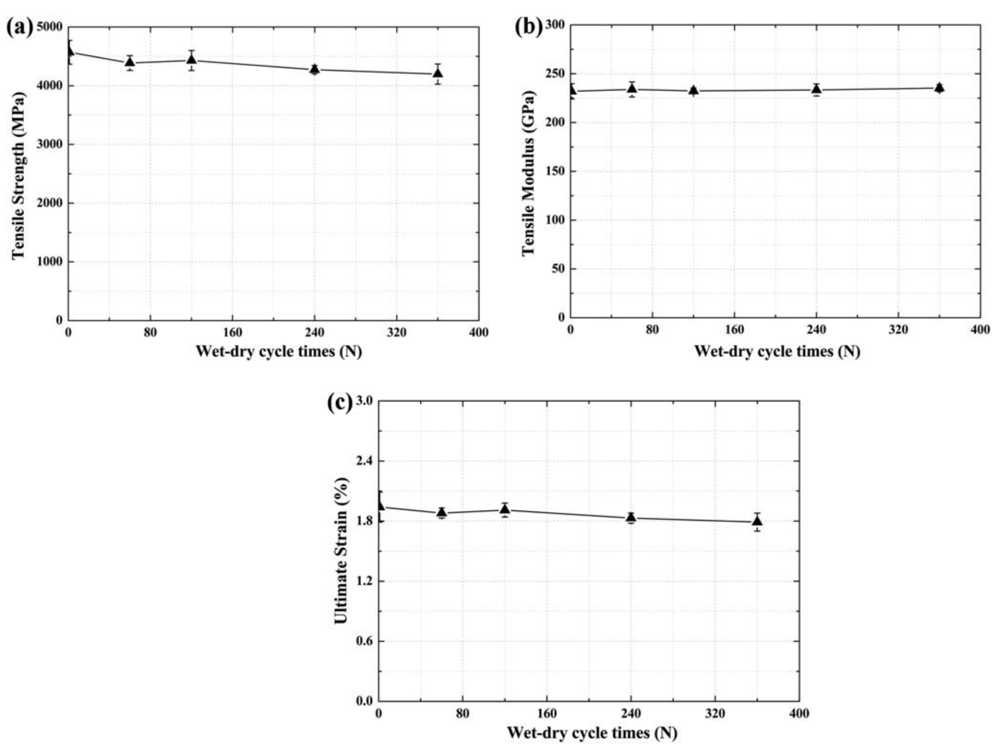

FIG. 10. Tensile test results of CFRP sheet as a function of exposure time: (a) tensile strength, (b) tensile modulus, and (c) ultimate strain.

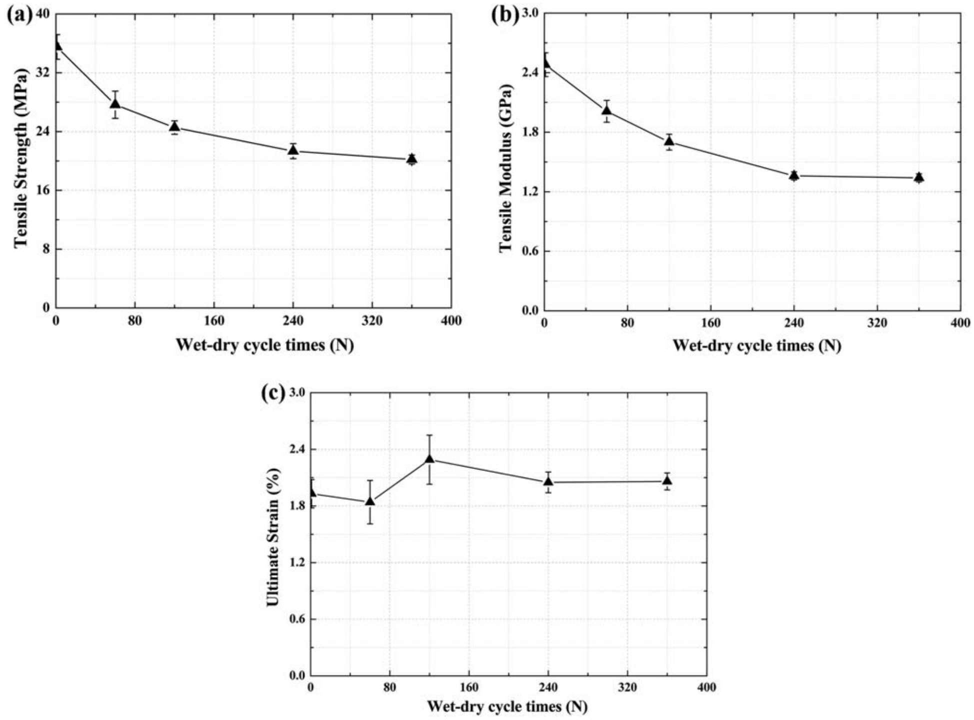

FIG. 11. Tensile test results of epoxy resin matrix as a function of exposure time: (a) tensile strength, (b) tensile modulus, and (c) ultimate strain. [Color figure can be viewed at wileyonlinelibrary.com]

is difficult to determine the effect of salt on the epoxy resin matrix.

Fig. 13 shows photographs of the CFRP sheets after tensile tests after various wet-dry cycles. Similar to the specimen exposed to a natural environment, the specimens fractured in a brittle manner. As the wet-dry cycle time increased, the specimens broken into many fragments. The results can be attributed the degradation of the epoxy resin matrix [21] or the defects that developed owing to the difference in thermal expansion

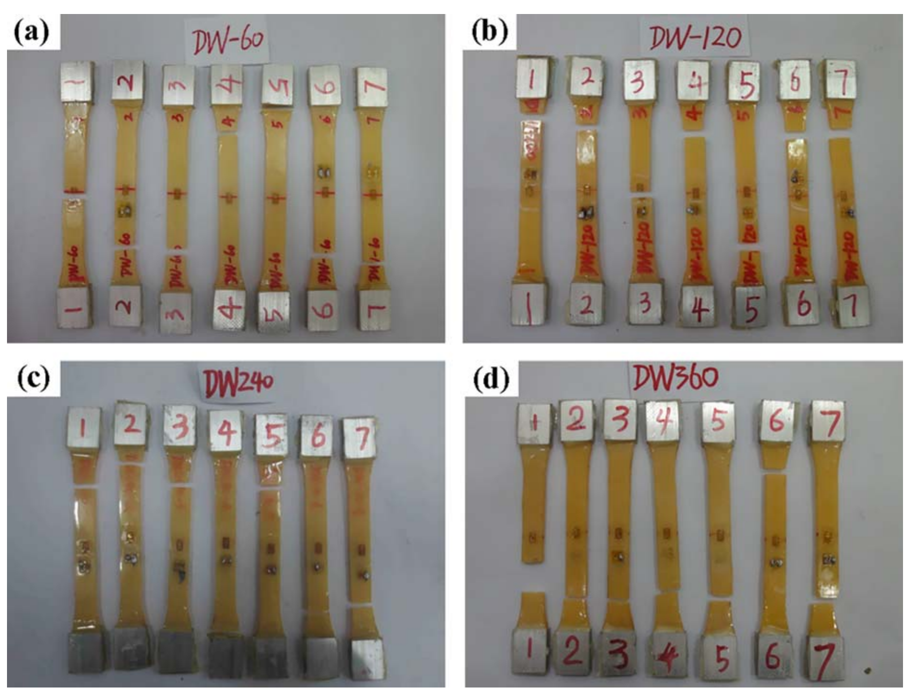

FIG. 12. Failure modes of epoxy resin matrix after various exposure times: (a) 60, (b) 120, (c) 240, and (d) 360 cycles. [Color figure can be viewed at wileyonlinelibrary.com]

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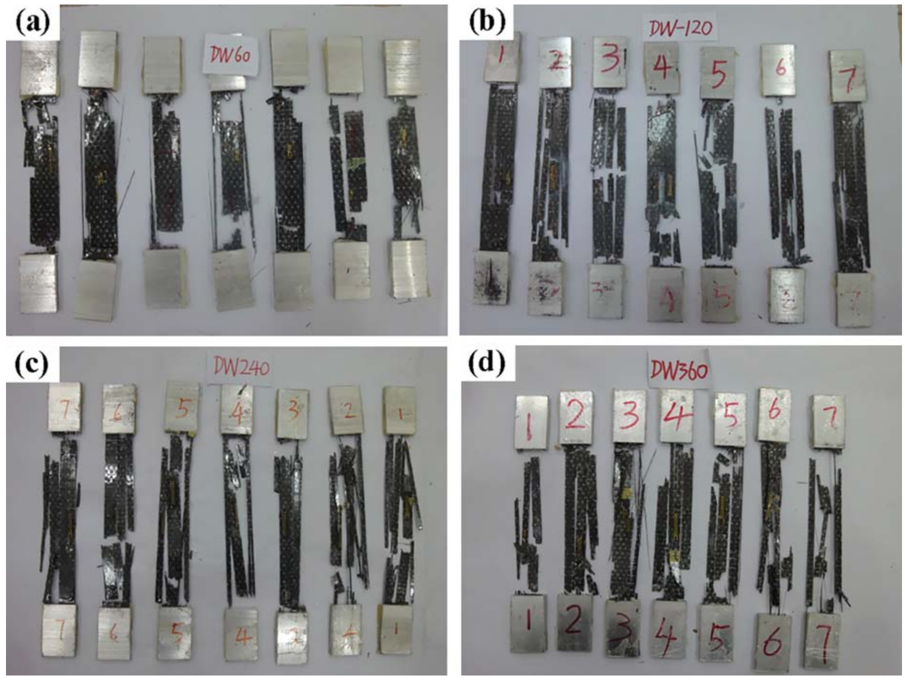

FIG. 13. Failure modes of CFRP sheet after various exposure times: (a) 60, (b) 120, (c) 240, and (d) 360 cycles. [Color figure can be viewed at wileyonlinelibrary.com]

coefficients between the carbon fiber and epoxy resin matrix [23]. The rate of interface damage was excluded from the calculation (by *Eq. 2*) owing to the discreteness of the tensile modulus data.

The stress–strain curves of the CFRP sheet are shown in Fig. 14. As Fig. 14a–d show, a linear relationship can be found between the stress and strain. The slope of these curves remained almost constant, which agrees well with the results of the tensile modulus. Moreover, the degradation of the epoxy resin matrix showed no effect on the stress–strain relationship of the CFRP sheets.

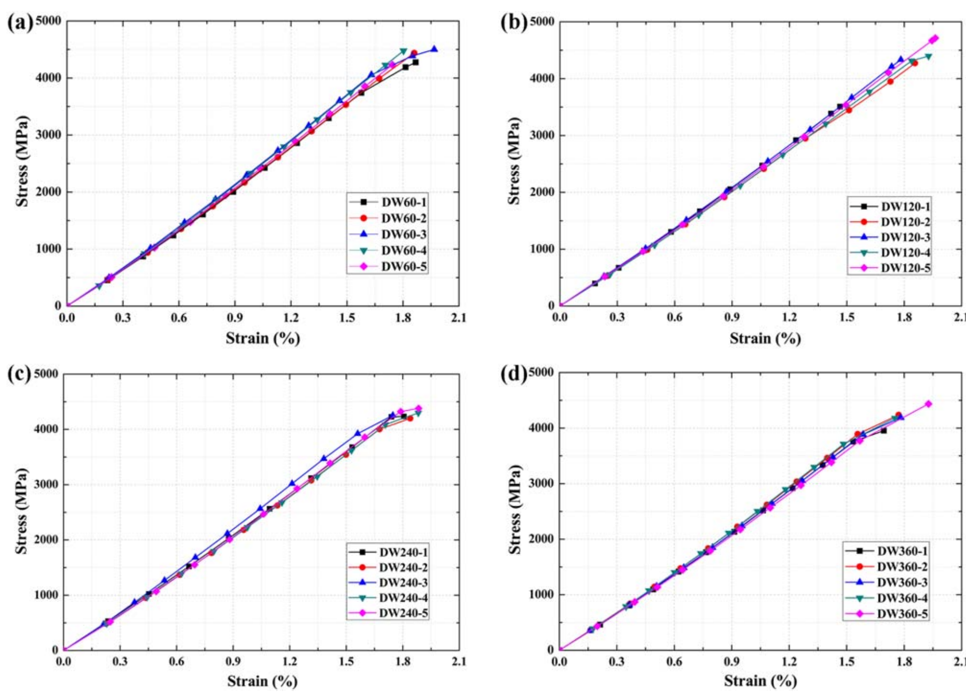

FIG. 14. Stress–strain relationship of CFRP sheet after various exposure times: (a) 60, (b) 120, (c) 240, and (d) 360 cycles. [Color figure can be viewed at wileyonlinelibrary.com]

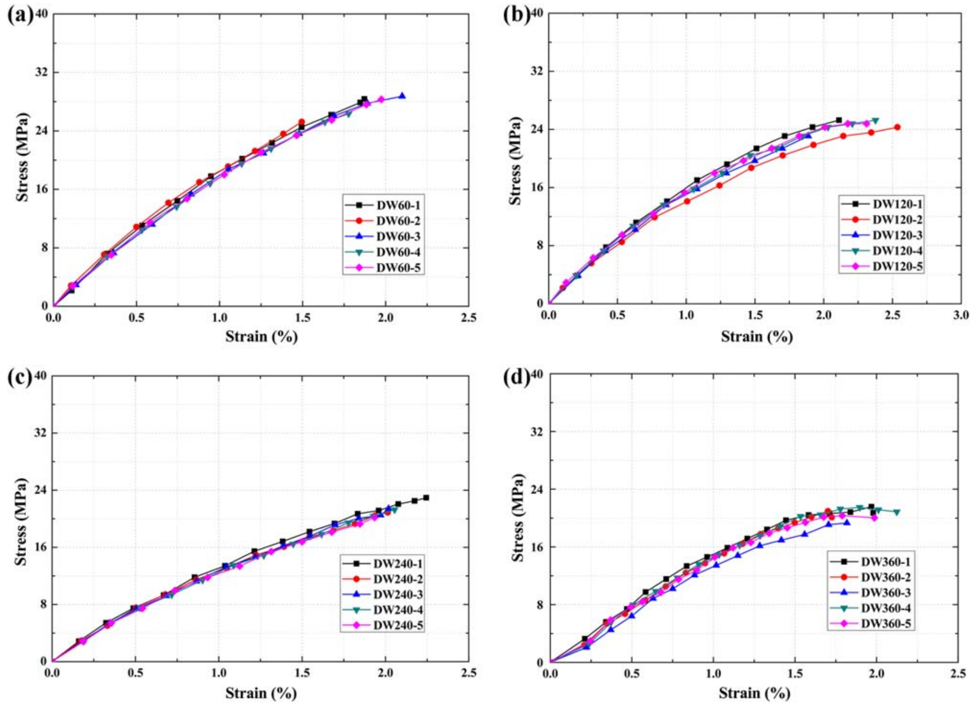

FIG. 15. Stress–strain relationship of epoxy resin matrix after various exposure times: (a) 60, (b) 120, (c) 240, and (d) 360 cycles. [Color figure can be viewed at wileyonlinelibrary.com]

For comparison, the stress–strain curves of the epoxy resin matrix are shown in Fig. 15. As Fig. 15a–d indicate, the ultimate stress showed a slight decrease as the exposure cycle increased. The various slopes of these curves agree well with the change in tensile modulus of the epoxy resin matrix. At the same load level, the deformation of the specimen increased. This may be attributed to the plasticization of the epoxy resin matrix [7, 24], resulting in a nonlinear relationship of the stress–strain curves (see Fig. 15d). Compared with the CFRP sheets, the deformation of the epoxy resin matrix is larger at the same load level. This result indicates that the deformation was controlled based on the carbon fiber, and that the contribution of the epoxy resin matrix to the tensile strength of the CFRPs sheet was limited owing to the aging of the epoxy resin matrix [21, 26].

Relationship of the Exposure Effects between Cyclic Wet-Dry and Natural Environment

Based on the above experimental results, it can be concluded that both a natural hygrothermal environment and a cyclic wet-dry chloride-containing environment can cause the tensile properties of the specimens to degrade. To compare the effects of these types of exposure environments, Table 4 shows the tensile properties of the CFRP sheet and epoxy resin matrix after 1 year of exposure.

It can be seen from Table 4 that the degradation of the specimens under a natural environment was lower than that of the specimens exposed to a wet-dry cycle environment. There are three possible reasons for this difference. First, the deterioration of the epoxy resin matrix is one reason for the degradation of the CFRP sheet, and carbon fiber played an important role in the development of the defect induced by the difference in thermal expansion coefficients between the carbon fiber and epoxy resin matrix, which led to the initiation of fiber-matrix debonding near the free surface [23]. Thus, more serious degradation of the specimens exposed to cyclic wet-dry conditions can be found owing to the relatively large difference in temperature. The other reason is that the chloride ions can easily permeate into the epoxy resin and lead to an increase in the hydrolysis of the epoxy resin

TABLE 4. Comparison of the tensile properties of the CFRP sheet and epoxy resin matrix after 1 year of exposure.

Exposure condition	Specimen	Tensile strength (MPa)	Tensile modulus GPa)	Ultimate strain (%)
Natural	CFRP	4,441.7 (175.4, 3.9%)	230.5 (0.09, 0.04%)	1.89 (0.09, 4.9%)
	Resin matrix	23.91 (1.93, 8.1%)	1.61 (0.09, 5.8%)	2.26 (0.20, 8.8%)
Cyclic wet-dry	CFRP	4,198.1 (171.8, 4.1%)	235.2 (3.68, 1.6%)	1.78 (0.09, 5%)
	Resin matrix	21.20 (0.61, 3.0%)	1.34 (0.04, 3.3%)	2.06 (0.09, 4.4%)

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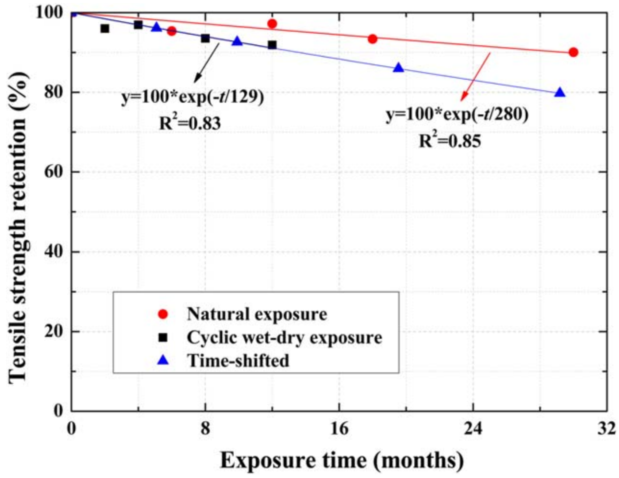

FIG. 16. Predicted results of the CFRP sheet under both exposure environments. [Color figure can be viewed at wileyonlinelibrary.com]

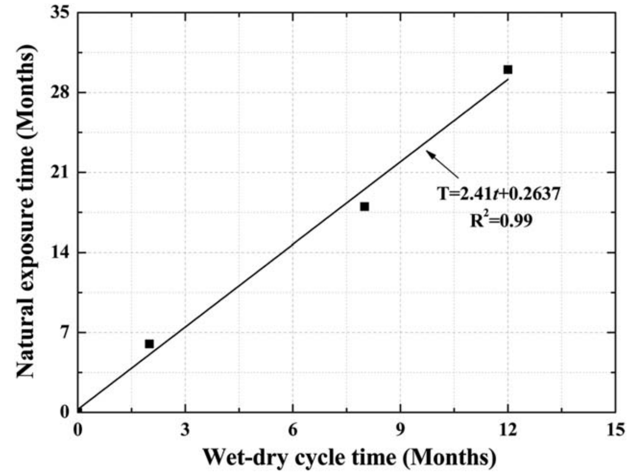

FIG. 17. Relationship between natural exposure and wet-dry exposure.

matrix, resulting in a degradation of the tensile property [21]. Regarding the CFRP sheet, the high carbon fiber volume fraction was an obstacle for the moisture uptake, and the fiber-matrix interface damage occurred during the chloride ion penetration into the specimen [3, 17]. The third reason is that salt precipitation during the drying process may lead to expansion stress at the fiber-matrix interface, which accelerates the degradation of the CFRP sheet under cyclic wet-dry exposure [3, 13].

In this study, the test parameters included the exposure duration, temperature, and chloride ions. It is unreasonable to consider the tensile degradation of the CFRP sheets under a complex environment as having occurred based solely on the time-shift factor. To predict the durability of the CFRP sheets, a new approximation method was used based on a tensile strength retention model defined by [28]:

$$Y = 100\ \exp\left(-{}^{t}/_{\tau}\right) \tag{3}$$

where Y represents the tensile strength retention (%), t is the exposure time, and τ is the fitted parameter. The prediction results of the CFRP sheets under both environments are shown in Fig. 16, and it can be seen that the fitted results agree well with the test data, the expression of which is as follows:

$$Y = 100\ \exp\left(-{}^{t}/_{129}\right) \tag{4a}$$

$$Y = 100\ \exp\left(-{}^{T}/_{280}\right) \tag{4b}$$

where *Eq. 4a* represents the tensile strength retention under a cyclic wet-dry environment, *Eq. 4b* represents the tensile strength retention under a natural hygrothermal environment, and t and T represent the exposure times (months were used in this study) under the corresponding exposure conditions.

Using *Eq. 4b*, the tensile strength retention can be obtained after natural exposure for a 50-year period, and is about 11.7%. Regarding the cyclic wet-dry exposure, the tensile strength retention is about 0.9% (*Eq. 4a*) after a 50-year exposure. The results indicate that serious damage occurred under accelerated exposure conditions. How can we obtain the tensile strength degradation based on a short-term accelerating test? A discussion of this question is given as follows.

The tensile strength retention of CFRP sheets exposed to the different environments is listed in Table 5. An interesting result can be seen in that there is a corresponding relationship regarding the tensile strength retention between both environments. The tensile strength retention after 2, 4, 8, and 12 months under cyclic wet-dry exposure was close to that after 6, 12, 18, and 30 months under natural exposure, respectively.

TABLE 5. Comparison of the tensile strength of the CFRP sheet under the exposure conditions.

Cyclic wet-dry exposure		Natural exposure	
Exposure time (month)	Tensile strength retention (%)	Exposure time (month)	Tensile strength retention (%)
0	100	0	100
2	96.0	6	95.4
4	97.0	12	97.2
8	93.6	18	93.4
12	91.9	30	90.1

TABLE 6. Calculated results using the obtained formula.

Accelerated exposure time	Equivalent accelerated in natural time (Eq. *5*)	Equivalent tensile strength retention (%, Eq. *4a*)	Natural exposure tensile strength retention (%, Eq. *4b*)
0	0	100	100
2	5.1	93.1	98.2
4	9.9	92.6	96.5
8	19.5	85.9	93.2
12	29.2	79.8	90.1

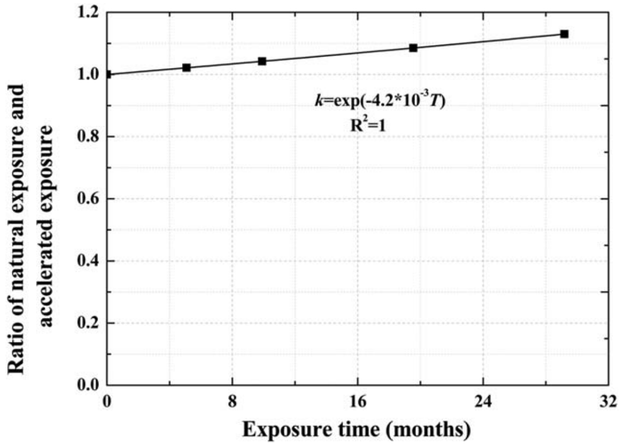

FIG. 18. Relationship between natural exposure and accelerated exposure.

The relationship based on a linear fitting between the natural exposure and wet-dry exposure is shown in Fig. 17. It can be seen that the tensile strength between the natural environment and cyclic wet-dry environment showed a linear relationship, which can be expressed through the following equation//:

$$T = 2.41t + 0.26 \quad (5)$$

where T represents the duration under natural exposure, and t represents the duration under cyclic wet-dry exposure. $t = 0$ means direct exposure of the composites at nature hygrothermal environment, T should be equal to zero. Thus, the limit $t > 0$ is put in place for this equation. Using this equation, the relationship between natural exposure and cyclic wet-dry exposure can be found.

As shown in Fig. 16, the time-shift equation (through *Eq. 5*) only changes the effect of the exposure time, and the degradation is higher than that under natural exposure. Based on *Eqs. 4a* and *5*, the tensile strength retention under natural exposure can be calculated based on that under accelerated exposure. That is, the tensile strength

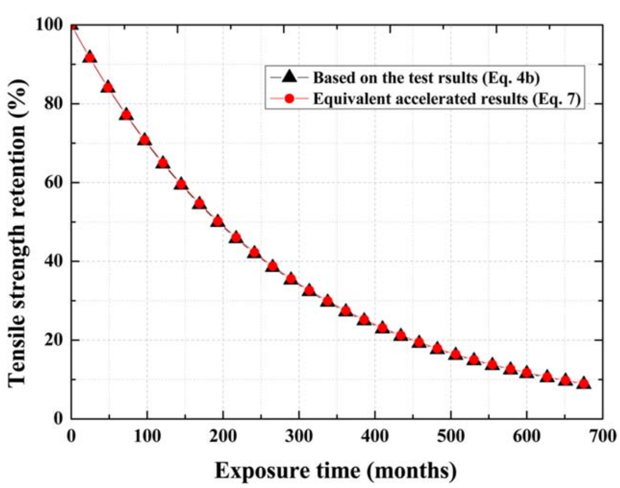

FIG. 19. Tensile strength retention of CFRP sheet under natural exposure. [Color figure can be viewed at wileyonlinelibrary.com]

retention under natural exposure can be obtained through *Eq. 4b*. The calculated results are listed in Table 6.

Compared to the test results between natural exposure and accelerated exposure, a difference can be found. As shown in Fig. 18, the difference between natural exposure and accelerated exposure increase as the exposure time increases. A parameter is defined as an environmental impact factor, and is obtained through the curve fitting.

Based on the above results, the environmental impact factor (k) can be obtained as follows:

$$k = \exp\left(-4.2 \times 10^{-3} T\right) \quad (6)$$

As can be seen, the environmental impact factor increases as the exposure time increases. Using *Eq. 4a* multiplied by the environmental impact factor, the following equation can be obtained:

$$Y = 100 \ \exp\left(-3.6 \times 10^{-3} T\right) \quad (7)$$

Based on *Eq. 7*, the predicted results of the tensile strength retention of the CFRP sheets under natural exposure are as shown in Fig. 19. For comparison, the calculated results of the tensile strength based on the tested data *Eq. 4b* are also shown in Fig. 19. Almost no difference can be found in the results, which indicates the reasonableness of the prediction method.

CONCLUSIONS

The durability of CFRP sheets and their constituents exposed to a natural hygrothermal environment or cyclic wet-dry chloride-containing environment was investigated in this study. The following conclusions were drawn from the experimental results:

1. The tensile property of the epoxy resin matrix showed more sensitivity to these two kinds of exposure environments than the CFRP sheets. When the exposure time increased under both exposure conditions, the tensile property of the CFRP sheets showed a slight decrease. The permeation of chloride ions into the epoxy resin matrix accelerates the hydrolysis of the specimen, which leads to more serious degradation compared with the natural exposure after 1 year.
2. Interface damage was found to be introduced based on the difference in thermal expansion coefficients between the carbon fiber and epoxy resin matrix, and the hydrolysis of the epoxy resin matrix. This is the main reason for the degradation of the CFRP sheets under wet-dry cyclic conditions in a chloride-containing environment.
3. Based on the parameters of the time-shift factor and the environmental impact, a relationship regarding the tensile strength degradation of the CFRP sheets between natural exposure and cyclic wet-dry exposure was proposed. The predicted results are in good agreement with the test results for the natural hygrothermal environment in Guangzhou.

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REFERENCES

1. S. Hong and S.-K. Park, *Polym. Compos.*, **38**, 2549 (2015).
2. Z. Yang, G. Xian, and H. Li, *Polym. Compos.*, **36**, 1590 (2015).
3. I. Kafodya, G. Xian, and H. Li, *Compos. B Eng.*, **70**, 138 (2015).
4. D. Borrie, H.B. Liu, X.L. Zhao, R.K. Singh Raman, and Y. Bai, *Compos. Struct.*, **131**, 799 (2015).
5. B.C. Ray and D. Rathore, *Polym. Compos.*, **36**, 410 (2015).
6. A.K. Al-Tamimi, R.A. Hawileh, J.A. Abdalla, H.A. Rasheed, and R. Al-Mahaidi, *J. Mater. Civ. Eng.*, **27**, 04014252 (2015).
7. Y. Pan, G. Xian, and M.A.G. Silva, *Constr. Build. Mater.*, **101**, (2015).
8. J. Shrestha, T. Ueda, and D. Zhang, *J. Mater. Civ. Eng.*, **27**, (2015).
9. J. Shrestha, D. Zhang, and T. Ueda, *J. Compos. Constr.*, **20**, 04016023 (2016).
10. R. Sen, *Constr. Build. Mater.*, **78**, 112 (2015).
11. M. Naderi and S.A. Hajinasri, *J Adhes.*, **89**, 559 (2013).
12. J.-G. Dai, H. Yokota, M. Iwanami, and E. Kato, *J. Compos. Constr.*, **14**, 834 (2010).
13. P. Böer, L. Holliday, and T.H.K. Kang, *Constr. Build. Mater.*, **48**, 360 (2013).
14. M. Heshmati, R. Haghani, and M. Al-Emrani, *T. Compos. B Eng.* **126**, 211 (2017).
15. M. Heshmati, R. Haghani, and M. Al-Emrani, *Compos. B Eng.*, **81**, 259 (2015).
16. C. Batuwitage, S. Fawzia, D. Thambiratnam, and R. Al-Mahaidi, *Compos. Struct.*, **160**, 1287 (2017).
17. V.M. Karbhari and G. Xian, *Compos. B Eng.*, **40**, 41 (2009).
18. J.R. Cromwell, K.A. Harries, and B.M. Shahrooz, *Constr. Build. Mater.*, **25**, 2528 (2011).
19. American Society for Testing and Materials, ASTM D3039. Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials (2000).
20. American Society for Testing and Materials, ASTM D638. Standard Test Method for Tensile Properties of Plastics (2000).
21. Z. Lu and G. Xian, *Polym. Compos.*, (2016). doi:10.1002/pc.24220
22. Y.M. Yang, G.J. Xian, H. Li, and L.L. Sui, *Polym. Degrad. Stab.*, **118**, 111 (2015).
23. D. Lévêque, A. Schieffer, A. Mavel, and J.-F. Maire, *Compos. Sci. Technol.*, **65**, 395 (2005).
24. M. Wrosch, G. Xian, and V.M. Karbhari, *J. Appl. Polym. Sci.*, **107**, 3654 (2008).
25. D.B. Marshall, B.N. Cox, and A.G. Evans, *Acta Metall.*, **33**, 2013 (1985).
26. G. Wu, X. Wang, Z.S. Wu, Z.Q. Dong, and G.C. Zhang, *J. Compos. Mater.*, **49**, 873 (2015).
27. S. Eslami, F. Taheri-Behrooz, and F. Taheri, *Polym. Compos.*, **33**, 467 (2012).
28. Z.K. Wang, X.L. Zhao, G.J. Xian, G. Wu, R.K.S. Raman, S. Al-Saadi, and A. Haque, *Constr. Build. Mater.*, **139**, 467 (2017).