A Study on Stress-Corrosion Cracking Using Single Fiber Model Specimen* (Degradation Properties of GFRP Caused by Water Absorption)

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Recently the crack propagation properties of GFRP on the stress corrosion cracking (S.C.C.) are investigated, and the threshold stress intensity factor K_{Isc} is verified in some environmental solution. From the investigation, it was found that GFRP reinforced by C-glass fiber has a superior acid resistance. However the microscopic crack propagation mechanisms caused by the material corrosion are not verified, and the microscopic mechanisms are necessary to assure the durability. Therefore the degradation mechanisms of the inner fiber and the matrix and the fiber/matrix interface should be quantified. In this study, the degradation of the fiber strength and the fiber/matrix interfacial shear strength are investigated using a single fiber composite previously immersed into environmental solutions, distilled water and acid solution. The effects of solution diffusion into the matrix resin on the fiber strength and the interfacial shear strength have been evaluated as a function of immersion time by fragmentation test in the room air. It is found that the diffusion of distilled water influences the degradation earlier than the acid solution. And the diffusion behavior is confirmed by Fickian diffusion analysis. The calculated concentration distribution showed that the water concentration around the fiber is saturated much earlier than the saturation of the acid ion due to the lower diffusion coefficient. Furthermore the crack propagation mechanisms are discussed based on the degradation estimated by the fragmentation test.

Key Words: GFRP, Stress Corrosion Cracking, Single Fiber, Interface, Degradation, Diffusion

1. Introduction

Glass fiber reinforced plastics (GFRP) have been used for a variety of chemical applications, since they have an outstanding performance as structural materials. However, it is said that the glass fiber suffers from chemical attacks in corrosive environments although it is embedded in composite materials, and such degradation is accelerated by applied stress. The degradation mechanism should be solved in the GFRP caused by stress-corrosion from the point of reliability. In the last decade, the properties of stress corro-

sion cracking (S.C.C.) in the GFRP have been studied by some institutes⁽¹⁾⁻⁽⁷⁾.

Crack-propagation properties of woven GFRP laminates have been investigated in our laboratory. The crack propagation behavior on the stress intensity factor, and crack propagation rate, da/dt , diagram was separated into two stages and then the threshold stress intensity factor, K_{Isc} , was confirmed on crack propagation behaviors in each environmental solution. The K_I - da/dt diagram of the C-glass/Vinyl ester systems under various environmental solutions is shown in Fig. 1^{(1),(2)}. As the acid concentration increased, the crack propagation was accelerated, and the crack propagation behavior in water was largely enhanced in comparison with that in air. Figure 1 implies the GFRP degradation mechanism based on the water diffusion is indispensable.

In this study, in order to investigate the relation-

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Fig. 1 Comparison of crack propagation behaviors for various conditions and fracture surface C/VE composite

ship between the diffusion properties of solutions and the degradation mechanism, the single fiber strength that is embedded in the matrix resin and the fiber/matrix interfacial shear strength were evaluated by a fragmentation test using a single fiber composite after an immersion in solutions, such as water and acid. Furthermore, the fiber degradation properties caused by water diffusion were emphasized in order to consider the resistance of fibers against the acid corrosion. To compare the resistance of fiber after immersing in water, an E-glass fiber and an NCR-glass fiber were employed, and also an NCR-glass fiber was said to have a good resistance against acid corrosion.

2. Evaluation of Fiber Strength

2.1 Fragmentation test specimen

Considering the degradation of a fiber embedded in a composite near the crack tip caused by the solution diffusion, the fragmentation test using a single fiber model specimen was employed. The specimen is constituted by an E-glass fiber as the reinforcement and a vinyl ester resin as the matrix. The mechanical properties of these materials are shown in Table 1. And the geometry of a specimen is a dog-bone shape shown in Fig. 2. Dog-bone shape specimens for the fragmentation test were obtained by casting the liquid resin into metal moulds of a cross section of 4×2 mm

Table 1 Mechanical properties of materials

	Reinforcement	Matrix resin
Material	E-glass fiber	Vinyl ester
Young's modulus	78 GPa	3.6 GPa
Poisson's ratio	0.14	0.37

Fig. 2 Geometry of dog-bone specimen

with a glass fiber allocated to the center line. The interface exposing to the solution is sealed at the end of the specimen in order to reduce the water immersion through the interface.

2.2 Experimental procedure

Specimens were immersed in the solution. The immersion conditions are shown in Table 2. A tensile testing machine that was controlled by the computer was installed on the sample stage of an optical microscope. This machine was used to conduct the single fiber fragmentation tests at a cross-head speed of 0.1 mm/min. A gauge length of 25 mm in the middle of the specimens was used for optical observation of the fiber fragmentation process. The tensile load was continuously applied until the number of fiber fragments was saturated.

2.3 Fiber tensile strength

To determine the fiber strength, the number of fragments of the fiber was plotted against the applied stress using Weibull parameters⁽⁸⁾. Based on the calculated Weibull parameters, the average fiber strength at a fiber length 25 mm was evaluated.

The fiber strength decreased against the immersion time shown in Fig. 3. The fiber degradation behavior did not change in respect to each environmental condition, although the E-glass fiber failed due to the acid corrosion. It seems that only the water diffusion into the matrix influenced the fiber degradation, and the acid would not reach the fiber/matrix interface in the immersion time in this test. It implies that the effect of the water diffusion on the degradation of fibers embedded in a composite is important in this case.

3. Water Diffusion and Absorption of Matrix

3.1 Test specimen and experimental procedure

To investigate the water absorption ratio of the

Table 2 Immersion condition

Solution	H ₂ SO ₄ 1mol	H ₂ O
Temperature	323 K

Fig. 3 Change of the fiber strength as a function of immersion time

resin and the stress dependence on diffusion coefficient, immersion tests in water were carried out according to the testing conditions shown in Table 3. The water diffusion coefficient is determined based on the Fickian diffusion using the FEM analysis. The Fickian second law shows the concentration distribution using the diffusion coefficient, and the surface integral of the concentration gives the absorption ratio. In this study, the concentration distribution is obtained by the FEM analysis, and the diffusion coefficient is decided to match the calculated absorption ratio to the experimental result. Since it is difficult to estimate the acid diffusion coefficient, $D = 2.0 \times 10^{-11} \text{ mm}^2/\text{sec}$ ⁽⁹⁾ was employed in this study.

3.2 Results and Fickian diffusion analysis

Figure 4 shows the history plots of the water content as a function of the immersion time. It shows that the weight gain rate is saturated over about $\sqrt{700}$ sec. The diffusion coefficient was determined to be $2.0 \times 10^{-6} \text{ mm}^2/\text{sec}$ without stress. And at the applied stress 15 MPa it was calculated $3.0 \times 10^{-6} \text{ mm}^2/\text{sec}$, at 23 MPa it was $3.4 \times 10^{-6} \text{ mm}^2/\text{sec}$. These results reveal that the water diffusion coefficient is accelerated by the applied stress. It was reported that the diffusion coefficient depended on hydrostatic stress⁽¹⁰⁾. The acid diffusion coefficient is said to be $2.0 \times 10^{-11} \text{ mm}^2/\text{sec}$. It seems that the effect of water absorption appears earlier than acid diffusion, since the acid diffusion coefficient is negligibly smaller than water. It was conducted that the crack propagation properties were influenced by the solution as shown in Fig. 1. However, Fig. 3 shows that there was no

Table 3 Immersion time

Solution	H ₂ O
Temperature	323K
Immersion time	0-200hour
Applied stress	0, 15, 23MPa

Fig. 4 History plots of water absorption rate as a function immersion time

difference on the degradation behavior of the fiber strength between in H₂SO₄ and H₂O. Figure 5 shows the degradation behavior considering the water concentration around the fiber by the Fickian diffusion analysis using the diffusion coefficient obtained from the diffusion test. And it was believed that the acid causes the corrosion of an E-glass fiber, however water also causes the degradation of a fiber. It seems that the acid causes the corrosion of a fiber after the saturation of the water concentration around the fiber due to the lower acid diffusion coefficient, therefore the water diffusion causes the degradation of the fiber strength without the acid diffusion.

4. Degradation Mechanisms and Water Absorption

4.1 Mechanical degradation of matrix

Considering the water absorption ratio of a composite, the degradation of mechanical properties of each constituent will be predicted, therefore the matrix Young's modulus will decrease against the water absorption ratio. Thus, the relationship between the matrix Young's modulus and the water absorption ratio into the matrix were investigated. The Young's modulus is evaluated by a tensile test at a cross-head of a speed 0.1 mm/min using a tensile test machine. The geometry of a specimen is the same as a fragmentation test shown in Fig. 2. Figure 6 shows the degradation behavior of the matrix Young's modulus. The horizontal axis is the water absorption

Fig. 5 History plots of water absorption ratio, water concentration and fiber strength

Fig. 6 History plot of Young's modulus as a function of the water absorption ratio

ratio to the amount of saturation water absorption. It shows that the Young's modulus decreases against the water absorption ratio, and it decreases by about 500 MPa at the water absorption ratio of 0.8 wt%.

4.2 Fiber strength degradation caused by water absorption

To emphasize the effect of the water absorption on the fiber degradation properties, an E-glass fiber and an NCR-glass fiber were used as reinforcement. An NCR-glass fiber has a different component compared with an E-glass fiber, and it is said to have a good resistance against acidic corrosion. The fiber strength degradation caused by water absorption was evaluated. The geometry of the specimen and experimental procedure are similar 2.1 and 2.2. Also, the

Fig. 7 History plots of fiber strength against the water absorption ratio

Fig. 8 History plots of interfacial shear strength against the water absorption ratio

immersion conditions are shown in Table 3. Figure 7 shows the degradation behaviors of the fiber strength of E-glass/Vinyl ester (E/VE) and NCR-glass/Vinyl ester (NCR/VE) systems. The fiber strength of both systems decreased similarly as a function of the water absorption ratio. It implies that the diffusion properties of the matrix effect on the degradation of the fiber strength.

4.3 Degradation of interfacial shear strength

The maximum interfacial shear strength is estimated by the Cox formula⁽¹¹⁾, which assumes that the fiber/matrix interface was perfectly bonded. The maximum interfacial shear strength is,

$$\tau_{\max}^{rz} = \left(\frac{a\beta}{2} \right) \left[\frac{\sinh(\beta L_c/2)}{\cosh(\beta L_c/2) - 1} \right] \alpha_0 \left(\frac{L_0}{L_c} \right)^{1/\beta_0} \quad (1)$$

where

$$\beta^2 = \frac{(r_m^2 - r_f^2)^2 (1 + a/\gamma)}{(1 + \gamma) [r_m^4 \ln(r_m/r_f) - (r_m^2 - r_f^2)^2/2 - (r_m^4 - r_f^4)/4]} \quad (2)$$

and $\alpha = E_m/E_t$, $\gamma = r_t^2/(r_m^2 - r_t^2)$, L_0 is the gauge length, L_c is the critical fiber length, α_0 is the Weibull scale parameter, β_0 is the Weibull shape parameter, r_t is the fiber radius and r_m is the effective radius of the matrix. Figure 8 shows the maximum interfacial shear strength as a function of the water absorption ratio. And the interfacial shear strength decreases against the water absorption ratio. The maximum interfacial shear strength is influenced by the matrix Young's modulus. Therefore the interfacial shear strength decreases as a function of the water absorption ratio, and it depends on the mechanical degradation of a matrix.

5. Application to Macroscopic Crack Propagation Properties

Based on the results of the fragmentation test that considers the influence of the environmental solution, it was clarified that the maximum interfacial shear strength decreases against the water absorption ratio. When a crack propagates in a composite immersed in environmental solutions, solutions diffuse into a composite and diffusion is promoted by applied stress around the crack tip. The fiber and the fiber/matrix interface degradations were caused by the water absorption of a matrix resin earlier than the acid influences. After the water concentration around the fiber is saturated, the acid diffusion reaches around the fiber. Therefore the results of this study emphasize the need of investing based on considering the water diffusion and absorption ratio. Generally it is said that the interfacial shear strength degradation causes the crack deflection by interfacial debonding around the crack tip, and the deflection is one of the resistant factors against the crack propagation. Hence from the evaluation of the relationship between the water absorption ratio and the crack propagation behavior, it seems that the relationship clarifies the crack propagation behavior strictly in the environmental solution.

6. Conclusion

(1) The degradation of the fiber strength and the interfacial shear strength by environmental solutions were evaluated by the fragmentation tests. The fiber degradation behavior did not change in respect to both the water and the acid. It was confirmed by the Fickian analysis that water diffusion reaches around the fiber earlier than acid diffusion.

(2) Water absorption influences the degradation of composite contributions, matrix, fiber and fiber/

matrix interface. The degradation behavior did not depend on corrosion resistance of the fiber. Furthermore the matrix degradation is dominated by water absorption.

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