Study of PMCs on Stress-Corrosion Cracking
(Effect of Interfacial Debonding Energy on Matrix Cracking)

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ABSTRACT

Fiber-bridging behavior has been studied for stress-corrosion cracking (SCC) of Polymer matrix composites (PMCs). It has been believed so far that the fiber-bridging depends on an interaction between the matrix cracking and the interfacial debonding. Particularly we measured a relationship between the fiber-bridging phenomena and degradation of both a matrix and an interface. Thus effect of water absorption and diffusion on the fiber-bridging were estimated with direct measurements of a crack tip. A limited number of fibers were embedded in a matrix to facilitate the direct measurements of microscopical failures such as interfacial debonding during a crack propagation. Conventional tests for a measurement of fracture toughness were difficult to obtain stable crack-propagation for brittle materials. In this study, Double Cleavage Drilled Compression test was conducted for a specimen to be bridged partially by fibers. Two types of matrices were prepared to compare on diffusivity of the water, one is Epoxy, and the other is Vinylester. The specimens were immersed in the water at 60 for a range of time from 0 to 672 hours just before conducting DCDC test. As a result, a critical energy release rate of a matrix, G_{mat} decreased with increase of weight change due to the water absorption. An energy release rate of bridged crack-propagation, G_{bri} was also obtained. It was confirmed that G_{bri} exceeded G_{mat}. Finally we calculated bridging stress σ_{t} and ΔG that was defined as $\Delta G = G_{\mathrm{bri}} \quad G_{\mathrm{mat}}$, substituting the interfacial debonding length and the interfacial debonding energy from a micromechanics perspective. Results of the calculation showed that increase of the interfacial debonding length influences to improve the effect of the fiber-bridging.

1. Introduction

Stress-corrosion cracking (SCC) of Polymer Matrix Composites (PMCs) reinforced by glass-fibers has been studied by many researchers [1-5], because the PMCs have been used for applications in some hostile environments due to their good environmental resistance and their high specific strength and stiffness. However it is well known that E-glass fibers in the matrix are corroded in acidic environments. In our laboratory, studies on SCC of PMCs have been reported in the last decade [5]. In the studies, increase in an acid corrosion resistance of a C-glass/Vinylester composite (C/VE) was confirmed compared with an E-glass/Vinylester composite (E/VE). Subsequently, microscopic observations showed that there was no effect of acid on fracture surface of C/VE, because fracture surface of the C-glass fibers showed that brittle fracture occurred. It was found that the SCC of the PMCs depended on acid resistance properties of fibers. Although the effect of acid decreased in C/VE, the results also showed that the water-diffusion affected the SCC of the PMCs. SCC caused by the water is extremely important, because the water is a common environmental factor.

Therefore we performed a model examination to investigate an interaction between mechanical fracture and degradation by the water. Previously we measured an interaction between interfacial degradation and the water-diffusion by a fragmentation test [6]. As a result, it was

clearly indicated that the water diffusion affected the interfacial degradation.

To consider the SCC of the PMC from a fracture-mechanics perspective, a key factor is a relationship between each material's toughness. If the interface is weak enough for the matrix crack to be deflected along the interface, the fibers remain intact and bridge on crack plane, thus the composite can be tough. Therefore the crack-propagation behavior at the interface is critical to toughening in composites. Fiber-bridging is well known to be the key factor for obtaining the enhanced toughness and it has been investigated both theoretically and experimentally by many researchers to measure the magnitude of toughness enhanced by bridging. On the bridging, Fuller et. al. measured effect of a single fiber on the fiber-bridging behavior by DCDC test measuring change of stress intensity factor [7, 8]. Sun et. al., measured stress on the fiber-bridging by direct measurements of interfacial debonding lengths [9]. Xu et. al. estimated effect of the fiber-bridging on a critical energy release rate theoretically [10].

In this study, we investigated effect of the water on an interaction crack-propagation with embedded fibers. Therefore we have performed the DCDC test to measure degradation of a critical energy release rate of the G_{mat} as a function of water uptake. Subsequently Degradation of effect of the fibers caused by the water on the crack-propagation was also measured. We prepared a model specimen to be bridged partially on the crack plane. Additionally, we have done direct measurements of the interfacial debonding using the interfacial degradation data to estimate stress in a fiber at the crack plane and toughening effect by a fiber from a micromechanics perspective.

2. Experiment
2.1 DCDC test

It is difficult to observe a crack tip directly using a laminate as the specimen for measurements of matrix cracking, fiber failure and interfacial debonding. Therefore we have prepared a specimen, fibers of which bridged partially on the crack plane, although a commercial composite has fibers continually on the crack plane. Conventional testing method for a measurement of fracture toughness was not proper for the specimen, because the fiber volume fraction of the specimen was extremely low to obtain stable crack-propagation. In contrast, DCDC test is an easy testing method to evaluate fracture toughness of brittle materials. The DCDC test was considered by Jennsen and many following authors to measure toughness of brittle materials [7, 8, 11-13]. Especially, Fuller et. al. investigated an interaction between a single fiber and crack-propagation in a CMC by the DCDC test. Therefore, we modified the DCDC test for an experiment of a PMC to obtain stable crack-propagation and measured interfacial debonding lengths by in-situ direct observation of a crack tip.

2.2 Experiment procedure

Fig.1 shows geometry and dimensions of DCDC test specimen in this work. We prepared two types of specimens. The Epoxy and Vinylester were used as the matrices, and ECR-glass fibers as the reinforcement were embedded in the matrices. It is well known that C-glass fibers that

were used in past studies, are common for an acid resistant reinforcement. In this study, the ECR-glass fibers are employed, because they show the same mechanical properties with the E-glass fibers and are almost equal to the C-glass fibers regarding the acid resistance. The number of ECR-glass fibers was about 300. Furthermore silane-coupling agent was used on the ECR-glass surface.

Table1 shows mechanical properties of each constituent prepared for specimens. Fibers were located as shown in Fig.2 and they were embedded to be perpendicular to a crack-propagation direction. To estimate effect of the water-diffusion, we immersed specimens in purity the water at 60　for a range of time from 0 to 672 hours just before conducting the DCDC test. All tests were performed under displacement control. The interfacial debonding was accompanied with the matrix cracking, so that the debonding length was measured in-situ using photographing and video recording methods without unloading the specimen. The crack-propagation during the DCDC test was directly observed from the direction that was parallel to the crack plane. The crack tip shape was also observed and photographed.
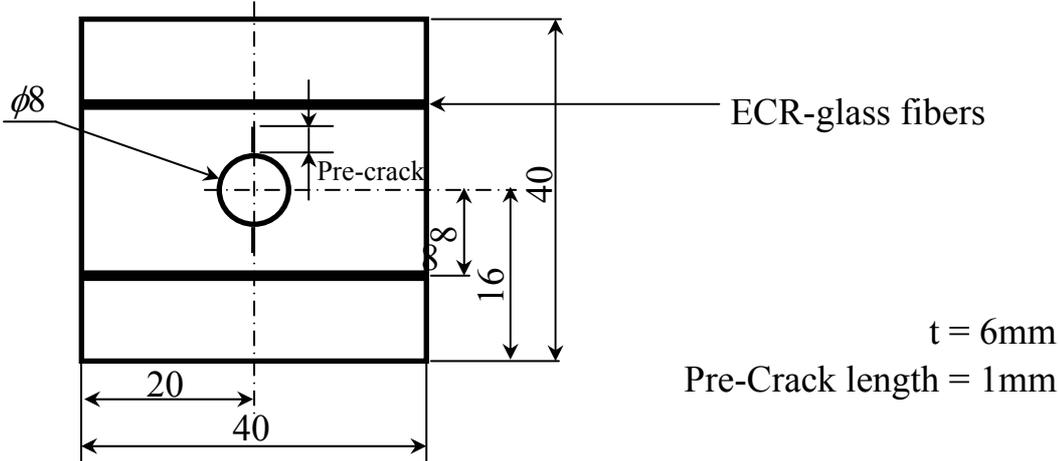

Fig.1 Specimen geometry of DCDC test.

Table1 Mechanical properties of materials.

	Reinforcement	Matrix	
Material	ECR-glass fiber	Vinyl ester	Epoxy
Young's modulus	78 GPa	3.6 GPa	4.0 GPa
Poisson's ratio	0.15	0.30	0.30

3. Results and discussion

3.1 Matrix cracking behavior

Specimens were immersed in the water at 60　. During immersion, we periodically weighed the specimens and recorded the amount of the water uptake as a function of time. Fig.2 shows the amount of the water uptake as a function of immersion time for both the Epoxy and the Vinylester specimen. The percent weight gain was calculated as

$$\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad\qquad (1)$$

where W_{wet} is the weight of the wet specimen and W_{dry} is the weight of the dry specimen. The time to reach saturation level was 20 hours$^{0.5}$ for the Vinylester. For the Epoxy, weight change did not reach saturation level in the time range of this work.

During the DCDC test, it was confirmed that the crack propagated stably, in other words, the crack-propagation velocity was controlled by the cross-head speed of the testing machine. To
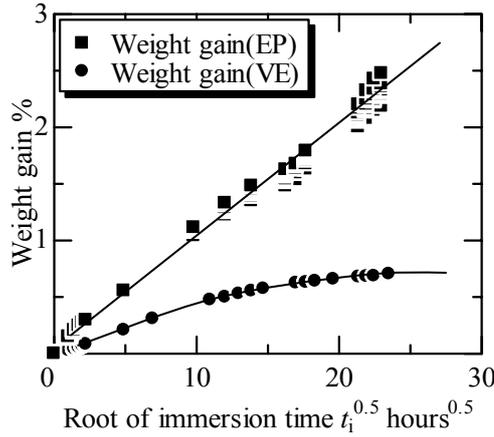
Fig.2 Water absorption rate as a function of root of immersion time for Vinylester and Epoxy.

qualify crack-propagation properties, an energy release rate, G, at the crack tip was calculated.

$$G = \frac{(1-\nu)^2}{E}\left(K_{\text{I}}^2 + K_{\text{II}}^2\right) \qquad\qquad (2)$$

We obtained G by Eq. (2) with an assumption that a crack propagated under only mode I. The K_{I} is described as $K_{\text{I}} = f(c/r)\sigma\sqrt{c}$, where c is the crack length and r is the radius of the drilled hole of the DCDC specimen, $f(c/r)$ is a geometry function of the specimen geometry. We defined the crack length at a mid-point of the crack plane through a thickness as the crack tip. Because a
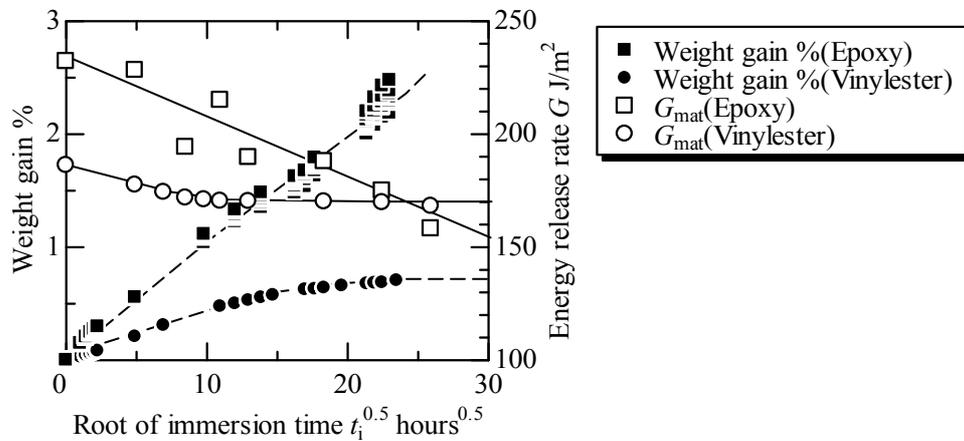

Fig.3 Critical energy release rate of matrix and water absorption rate as a function of root of immersion time for Vinylester and Epoxy.

stress intensity factor at a crack tip is fracture toughness that is material constant during the stable crack-propagation, we can obtain the $f(c/r)$ by a relationship between the applied stress and the crack length, Therefore we obtained fracture toughness of the Vinylester by Double Torsion (DT) test and the result of the DT test showed the fracture toughness, $K_{IC}=0.87\,MPa\sqrt{m}$. Finally, on the basis of a relationship between the σ_{app}, the c and the K_{IC}, the $f(c/r)$ is described as follows,

$$f(c/r) = -0.0580\,(c/r)^3 +0.3129\,(c/r)^2 -0.5860\,(c/r)+0.4627.$$
$$(0.75 \le c/r \le 2) \qquad (3)$$

Fig.3 shows a relationship between the immersion time and G_{mat}. An energy release rate of a matrix, G_{mat}, of the Epoxy was larger than one of the Vinylester when they were intact. As increasing the water uptake, G_{mat} of The Epoxy decreased. Because The Epoxy was not saturated with the water, the G_{mat} of The Epoxy kept decreasing. It was clear that there existed a crossing point of the energy release rate in this experiment. Decreasing properties of the energy release rate were concerned with the amount of the water uptake for each matrix. We found that the water absorption reduced fracture toughness of a polymer.

3.2 Bridging effect

In a model specimen to do a direct observation of the fiber-bridging, the crack tip showed a bowing behavior when a crack tip reached the fiber position, subsequently the crack was bridged by intact fibers. Two types of crack tip shapes were shown in Fig.4. Fig.4 (a) shows a typical bowing shape, (b) shows a typical bridging-shape. The bridging fibers failed after a crack length extended. The regions where both the bowing and the bridging were observed, are shown in Fig.5 and 6. Furthermore we calculated applied energy release rates G_{bri} using the same equations with G_{mat}. The crack-tip was defined as the edge of fiber bundle (the origin of x axis shown in Fig.4) when bowing behavior was observed. When bridging behavior was observed, the crack-tip was defined as a crack tip similarly to a matrix crack tip. The energy
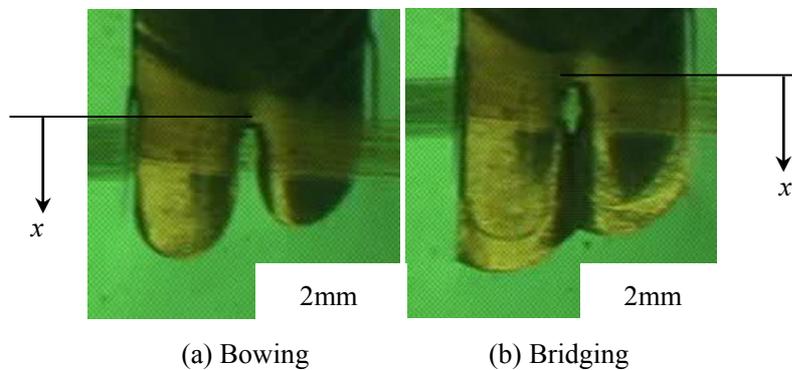

2mm	2mm
(a) Bowing	(b) Bridging

Fig.4 Photograph of crack tip shape obtained by in situ measurements.

release rate G_{bri} of the Epoxy are shown in Fig.5 and one of the Vinylester are shown in Fig.6.

The horizontal axes in both figures are the distance from fiber location. The origin of the distance is the edge of fiber bundle as shown in Fig.4 (a) and (b). Fig.7 shows G_{mat} and G_{bri} as a function of the immersion time. Reduction of G_{bri} was similar to one of G_{mat}. Because the Epoxy was not saturated with the water, G_{bri} decreased similarly to G_{mat}. When the fiber-bridging was observed, we considered G_{bri} was described as $G_{bri} = G_{mat} + \Delta G$. Here, ΔG is a term of the fiber-bridging effect. On the basis of the result of the Vinylester, it is predicted that the interfacial debonding length caused the increase of bridging effect. It was found that the interfacial debonding influenced crack-arrest by the fiber-bridging effectively. To consider the effect, we considered the relationship between the interfacial debonding and the fiber-bridging.

4. Increase of toughness

Longitudinal fibers in a specimen bridged through the crack planes partially. The experimental phenomena are verified on the basis of a micromechanics-point of view. Therefore we calculated fiber-stress distributions on the crack plane to consider the bridging effect based on
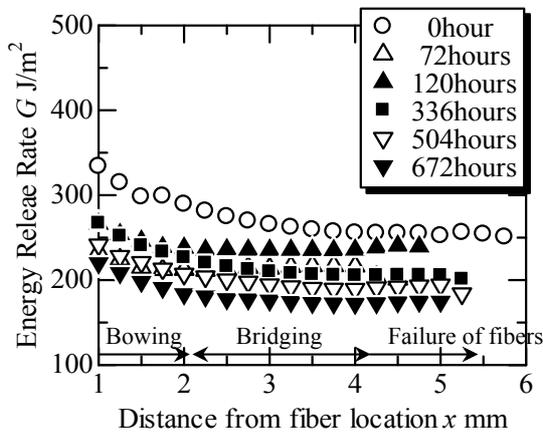

Fig.5 Energy release rate of Bridged crack-propagation of Epoxy as a function of distance from fiber location.
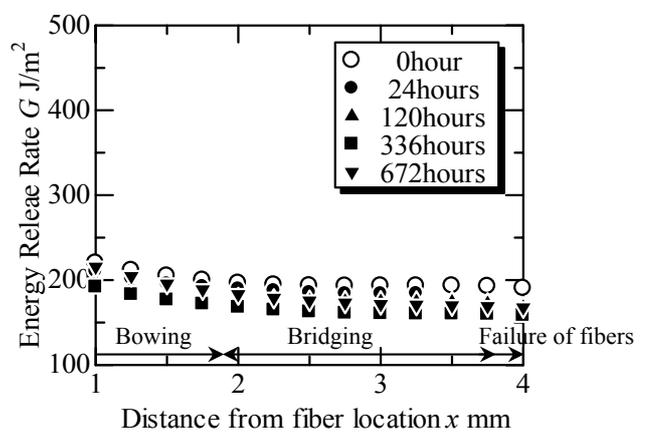
Fig.6 Energy release rate of Bridged crack-propagation of Vinylester as a function of distance from fiber location.
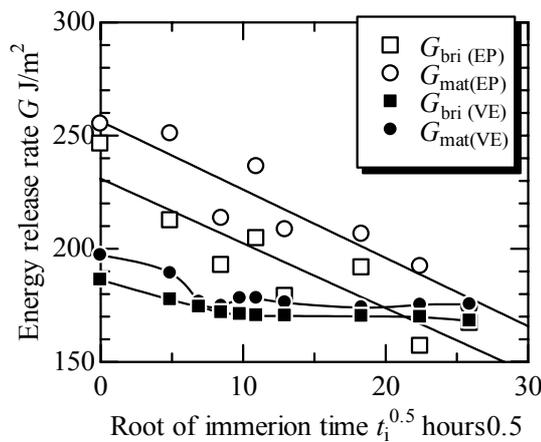

Fig.7 Critical energy release rate of matrix and bridged specimen as a function of root of immersion time.

the micromechanics. Furthermore the bridging effect ΔG was obtained using the distributions. The stress was obtained with an assumption that the stress caused the interfacial debonding

observed by direct measurements and the stress on the crack surface acted as traction to prevent crack-opening. With the stress on the crack surface, we determined the ΔG as work done by the bridging fiber. An actual PMC has fibers continuously, thus the crack would be bridged on whole crack surface. It was predicted that some of the fibers would fail with increase of a matrix crack length. The fiber failure required to be described with a failure probability function [14]. Therefore, effect of the fiber-bridging based on micromechanics, ΔG_{the} would be described theoretically as follows;

$$\Delta G_{the} = 2V_f \int (1-q)\sigma_t(u)\mathrm{d}u \tag{4}$$

where σ_t is the fiber-stress on the crack surface, q is the failure probability function, u is a half of the crack opening displacement. The σ_t is considered with micromechanics. The micromechanism of the fiber/matrix interfacial debonding/sliding has been studied theoretically by many researchers. These models were also experimentally examined recently by Sun and Singh [9]. In the model, the σ_t is described as follows;

$$\sigma_t = \frac{2E_c\tau_f L_d}{r_f V_m E_m} + \frac{2E_c\tau_f}{E_m V_m \rho} + \sqrt{\frac{4E_f E_c \Gamma_d}{r_f E_m V_m}} \tag{5}$$

where r_f is the radius of a fiber, τ_f is the interfacial frictional stress, E_f, E_m is the Young's modulus of a fiber and one of a matrix respectively, V_f, V_m is the volume fraction of a fiber and a matrix respectively, E_c is described as $E_c = E_f V_f + E_m V_m$ and

$$\rho^2 = \frac{4E_c G_m}{V_m E_m E_f \phi}, \tag{6}$$

and

$$\phi = -\frac{2\ln V_f + V_m(3-V_f)}{2V_m^2}. \tag{7}$$

Here V_f is determined as 2% from a observation of the crack plane and τ_f is assumed as 5MPa. The r_f of the ECR-glass fiber is 12.25μm. Subsequently the failure probability function is described as,

$$q = 1 - \exp\left[\frac{r_f}{L_0\sigma_0{}^m\tau_f(m+1)}\left\{\left(\sigma_t - \frac{2\tau_f L_d}{r_f}\right)^{m+1} - \sigma_t{}^{m+1}\right\}\right]. \tag{8}$$

where m and σ_0 is a weibull parameter respectively. We substituted $m=4.7$, $\sigma_0=2400$MPa and $L_0=25$mm. They were determined by tension test of the ECR-glass fiber. Using these equations, we can obtain bridging-stress with a debonding length and corresponding interfacial debonding energy, Γ_d. In early study, values of the Γ_d data in early study in ECR-glass/Vinylester specimens by the fragmentation tests were taken. Therefore following calculations are

conducted for the DCDC specimen which of a matrix is the Vinylester. In the early study, we obtained a relationship between the immersion time in the water and the Γ_d. The result of the fragmentation test is shown in Fig.8. This figure shows a relationship between Γ_d and immersion time t_i and a relationship between moisture-concentration at fiber/matrix interface in a specimen of the fragmentation test and t_i. Because the specimen geometry of the DCDC test was different from one of the fragmentation test, a distribution of moisture-concentration in a matrix also differs from previous test. We assumed that decrease of Γ_d was obtained as a function of the moisture-concentration before a matrix was saturated with the water. Thus, we approximately described the moisture-concentration with the previous fragmentation test as a function of the immersion time. On the basis of the function, we obtained Γ_d distribution as a function of the moisture-concentration. And a relationship between the moisture-concentration distribution and the immersion time in the DCDC specimen was obtained by conducting a Fickian analysis. A diffusion constant was determined as 6.0×10^{-6} mm^2/sec from the relationship between the water uptake and the immersion time. Consequently, a relationship between the Γ_d and the immersion time is described approximately as follows;

$$\Gamma_d = 0.00339t_i^3 + 0.0194t_i^2 - 2.41t_i + 432 \tag{9}$$

And a relationship between Γ_d and moisture-concentration is shown in Fig.9. And the interfacial debonding length L_d during the DCDC test was observed as shown in Fig.10. A magnitude of the L_d was taken as half of the length of the white band in Fig.10. The relationship between the L_d and fiber location, ξ, is shown in Fig.11. We performed the observations when the crack length was 6mm. In the Figure, the origin of the ξ and the direction are shown in Fig.10. By substituting the values of the Γ_d and the L_d at each immersion time, we calculated σ_t at the DCDC test. On the basis of the σ_t, we obtained ΔG_{the} and $G_{bri}' = G_{mat} + \Delta G_{the}$ as shown in Fig.12. We found that G_{bri}' increased after 7 9 hours$^{0.5}$ of root of the immersion time. This result shows the increasing the immersion time causes effect of crack-arrest, because energy
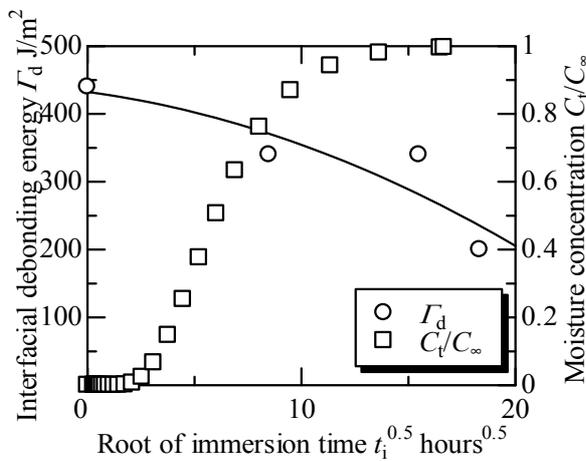

Fig.8 Interfacial debonding energy obtained by fragmentation test as a function of root of immersion time and corresponding moisture-concentration.
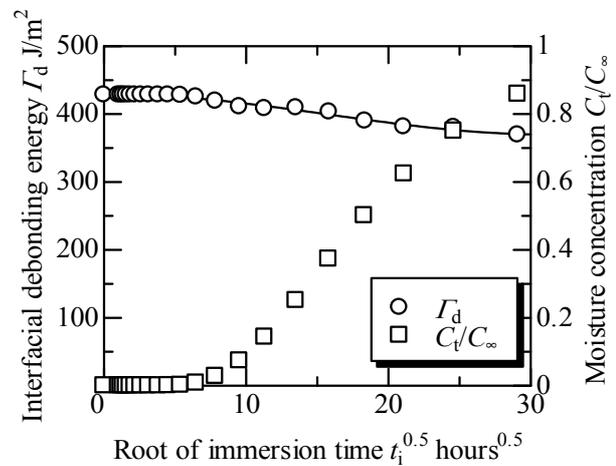
Fig.9 Interfacial debonding energy obtained by DCDC test as a function of root of immersion time and corresponding moisture-concentration.

that was stored in bridging-fiber increases due to the interfacial degradation and debonding behavior.
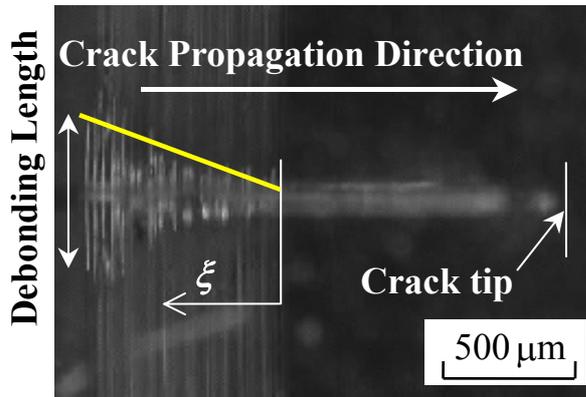

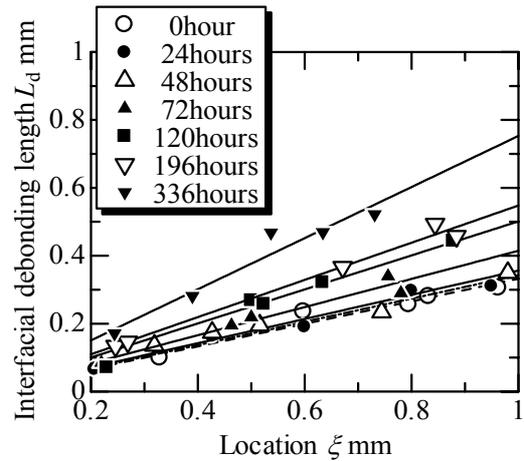Fig.10 Photograph of crack tip and interfacial debonding during DCDC test

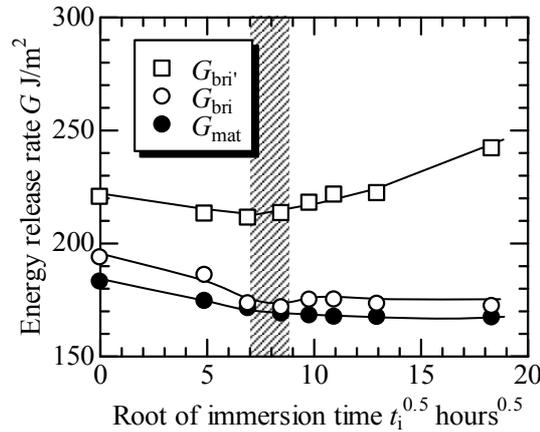Fig.11 Interfacial debonding length as a function of location.

Fig.12 Energy release rate of matrix and bridged specimen obtained experimentally and bridged specimen obtained by theoretically based on interfacial debonding.

5. CONCLUSION

It was found that decrease of the critical energy release rate of a matrix, G_{mat}, depended on the water uptake. A saturation level of the water uptake of the Epoxy was higher than one of the Vinylester. Additionally, the decrease of G_{mat} of the Vinylester converged relatively early. Therefore, although the G_{mat} of the Epoxy was larger than one of the Vinylester at an early stage of the immersion time in the water, finally the Vinylester exceeds the Epoxy at the saturation level of the water uptake.

An interaction between bridging-fibers and the interfacial debonding on crack-propagation of the matrix was measured with conducting the DCDC test. Change of bridging effect caused by water absorption was confirmed experimentally. Especially the change of bridging effect was estimated theoretically on the Vinylester matrix specimen. In Vinylester it was found that bridging effect recovered although it was vanished once. And the bridging effect was calculated based on micromechanics with the measurements of interfacial debonding. Results of the

calculation also showed that the toughening obtained by the bridging changed similarly to the results of the experiment.

REFERENCES

(1) J. N. Price and D. Hull, "Effect of Matrix Toughness on Crack Propagation during Stress Corrosion of Glass Reinforced Composites", *Composites Science and Technology*, 28, 211(1987)

(2) Klaus Freiedrich, "Stress corrosion crack propagation in glass fibre reinforced /thermoplastic PET", *Journal of Material Science*, 16(1981), 3292

(3) P. J. Hogg, "A Model for Stress Corrosion Crack Growth in Glass Reinforced Plastics", *Composites Science and Technology*, 38(1990), 23

(4) P. J. Hogg, S. N. Sapalidis and S. J. Youd, "High temperature acidic stress corrosion of glass fibre composites", *Journal of Material Science*, 32(1997), 309

(5) Hiroyuki Kawada, Akiyoshi Okada, Hironori Ueno, Ikuhiko Hayashi, "Stress Corrosion Cracking of Nothched GFRP Laminates (Microscopic Fracture Model and Crack Propagation Rate)", *Transactions of the Japan Society Mechanical Engineers*, A-61(1995), 2566

(6) Hiroyuki Kawada and Daisuke Inoue, "Study on Stress Corrosion Cracking o GFRP using Single-fiber Model Specimens (Evaluation of Interfacial Degradation by energy-balance Model)", *JSMS COMPOSITES-32*(2003), 75

(7) E. Butler, et. al., "Interactions of Matrix Cracks with Inclined Fibers", *Ceram., Eng., Sci., Proc.*, 13(1992), 475

(8) T. W. Coyle, "Fracture Mechanics Characterization of Crack/Fiber Interactions in Ceramic Matrix Composites", *Ceram., Eng., Sci., Proc.,* 8(1987), 630 (7) G. Xu, "The influence of crack trapping on the toughness of fiber reinforced composites", J. Mech. Phys. Solids, 46(1998), 1815

(9) Y. Sun and R. N. Singh, "Determination of fiber bridging stress profile by debond length measurement", *Acta Materialia*, 48(2000), 3607C.

(10) G. Xu, A. F. Bower and M. Ortiz, "The influence of crack trapping on the toughness of fiber reinforced composites", *J. mech. Phys. Solids,* 46(1998), 1815

(11) Jannsen, "Specimen for fracture mechanics studies on glass", *Proceedings of the Xth Intrnational Congress on Glass*, Kyoto, Japan, July 8-13(1974), 23

(12) M. Y. He, M. R. Turner, A. G. Evans, "Analysis of the double cleavage drilled compression specimen for interface fracture energy measurements over a range of mode mixities", *Acta Metallurgica et Materialia*, 43(1995), 3453

(13) J. E. Ritter, "Moisture-assisted crack growth at epoxy-glass interfaces", 33(1998), 4581

(14) H. L. Oh and I. Finnie, "On the Location of Fracture in Brittle Solids-I", International Journal of Fracture Mechanics" *Journal of Fracture Mechanics*, 6(1970), 287