Effect of Boiling Water Aging on Strength and Fracture Properties of Chopped Strand Mat–Polyester Laminates

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Synopsis

Four types of unsaturated polyesters and chopped strand mat laminates prepared from these resins were examined for their durability after immersion in boiling water. The boiling water aging of fiber-reinforced plastics (FRP) by use of a pressure cooker was found to be 3–4 times faster than boiling water immersion at atmospheric pressure. The weight gain of neat resins increased, and their tensile strength decreased with an increase in immersion time. No variation in the plane strain fracture toughness, K_{Ic}, of the neat resins was observed after boiling water immersion. The elastic–plastic fracture toughness J_{Ic} of the immersed FRP was measured by a partial unloading procedure. Although J_{Ic} showed considerable scatter, on the whole, J_{Ic} of FRP was found to be independent of the four types of matrix resins and also was not effected by immersion in boiling water at 116°C for 24 h.

INTRODUCTION

Recently the need for fiber-reinforced plastics (FRP) structural parts in the field of corrosive environments such as containers for water, chemical tanks, and chemical pipes have been increased remarkably, since FRP has many advantages over metal (relatively light and strong, and in particular corrosion resistant). In these corrosion-resistant FRP, it is generally considered that the glass fibers mainly support the load, and the matrix is responsible for the corrosion protection. When a FRP is allowed to stand in humid environments, it absorbs water and, consequently, some mechanical properties of the FRP change. Both the absorption of water into FRP and the reduction in the mechanical properties, generally increase with an increase in both time and temperature.[1,2]

The successful application of fracture mechanics to a variety of designs in metallic materials, have encouraged similar fracture-toughness studies of polyester resins[3–5] and their composites.[6,7] The fracture toughness of plastics is generally expressed in terms of the stress intensity factor or the strain energy release rate at the crack initiation, K_{Ic} or G_{Ic}. In FRP, the fracture toughness is measured not only by the stress intensity factor at maximum load, K_Q, but by the J-integral at the crack initiation, J_{Ic}.[8]

While K_{Ic} value is useful only in brittle fracture of a material, the fracture toughness J_{Ic} is applicable not only to brittle fracture but to ductile fracture. As the application of elastic–plastic fracture mechanics to the FRP increases in number,[8] the usefulness of J_{Ic} has become more evident. For metallic materials ASTM standards define the measurement of J_{Ic}.[9] However, no standard for the measurement of J_{Ic} in FRP has been established at this

time. In this paper, we applied Rice's simplified equation to a partially unloaded precracked FRP specimen. In practical application of FRP in corrosion environments, the fracture properties of matrix resins and FRP are considered to be an important factor as well as the strength properties.

EXPERIMENTAL

Materials

The polyesters used were Epolac G-180, Epolac N350-L, Epolac RF-1001, and Epolac RF-1 (Japan Catalitic Chemical Industry Co., Ltd.). These resins were chosen as representatives of orthophthalic polyester (O-resin), isophthalic polyester (I-resin), vinyl ester (V-resin), and bisphenol A polyester (B-resin), respectively. In the cases of O- and I-resins, the curing agents used were 1 phr of MEKPO (55%) and 0.5 phr of Co naphthenate (0.6%). V- and B-resins were cured with 2 phr of MEKPO and 0.5 phr of Co naphthenate. The polyester was mixed with curing agents, the mixture was degassed and casted between two glass plates. The cured neat polyester (6 mm thick) was postcured at 100°C for 2 h. The heat distortion temperature of O-, I-, V-, and B-resins were 100°C, 103°C, 103°C, and 109°C, respectively.

The glass chopped strand mat used was EM-450G-5 (Nippon Glass Fiber Co., Ltd.). The glass-fiber-reinforced laminates were fabricated by a hand-layup technique. The thickness of the FRP plate was adjusted to 6 mm. The glass contents of 8-plied chopped strand mat–polyester laminates were ca. 30 wt %.

Mechanical Testing

Dogbone-shaped tensile specimens, ASTM D638 type I, 12.6 mm wide and 165 mm long, were prepared by cutting polyester plates with a band saw and by abrading with a belt sander. The tensile strength of the resins was measured with an Instron Testing Machine Model 1114 with a grip separation of 115 mm and at a crosshead speed of 5 mm/min at 23°C. The three-point bending strength of the FRP was measured with specimens having dimensions of 20 or 22 mm wide and 110 mm long, with 80-mm span and at a crosshead speed of 5 mm/min.

The plane-strain fracture toughness K_{Ic} of neat resins was measured according to ASTM E399-81 and Carisella's procedure with three-point bending test specimens.[5,10] The dimensions of these specimens are shown in Figure 1. The specimens with dimensions of 6 mm (thick) × 12.5 mm (high) × 80 mm (long) had a 4.5 mm deep notch cut into them (by a band saw) followed by the introduction of sharp crack formed by tapping them with sharp razor balde at the base of the notch. The fracture toughness of the resins was measured with an Instron Machine (using a 50-mm span) at a crosshead speed of 1 mm/min at 23°C. The fracture toughness K_{Ic} of each specimen was calculated by

$$K_{Ic} = (P_Q S / B W^{3/2}) \cdot f(a/W) \tag{1}$$
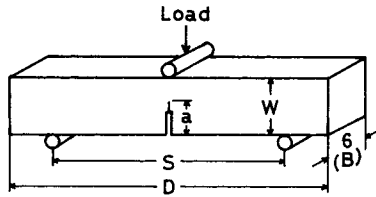
W = 12.5, S = 50, D = 80 for K_{Ic}

W = 20 , S = 80, D = 110 for J_{Ic}

Fig. 1.   Fracture test specimens (mm).

where P_Q is the maximum load[5] and $f(a/W)$ is a geometry factor.[10] The fracture toughness of the FRP was measured in a similar manner to that of resins. The initial crack length of FRP was varied from a/W = 0.4 to 0.8, which resulted in a/W = 0.61 on average, while in the resins the average value of a/W was 0.52.

The validity requirement[10] for the plane strain fracture toughness was satisfied in the resins; however, it did not hold in the FRP. In the case of the resins, in order to give valid K_{Ic}, both the thickness and initial crack length of the fracture specimens must be larger than 0.1–0.4 mm, while in the FRP these values must be greater than 8–14 mm. For comparison, the candidate stress intensity factor K_Q calculated in eq. (1) under 0.95 slope load conditions was used as a measure of fracture toughness in the FRP.[6,8]

The number of the specimens used for each measurement was 2–6 for the tension test, 4 or 6 for the three-point bending test, 4–6 for the fracture toughness test of the resins, and 8 for that of the FRP. Both the average and the range of these measurements will be presented in this article.

J_{Ic} Measurement

The elastic–plastic fracture toughness J_{Ic} of the FRP was measured with specimens having dimensions of 20 mm high and 110 mm long (Fig. 1). These specimens were notched to a depth of 11 mm with a band saw followed by the introduction of sharp crack by tapping with sharp razor blade at the base of the notch. The average value of a/W was 0.60.

The specimen was mounted on an Instron testing machine with 80-mm span under three-point bending; the specimen was loaded at the crosshead speed of 0.5 mm/min. Figure 2 shows the procedure for the determination of J_{Ic}. At an arbitrary midspan deflection, the loading jig was stopped, slightly unloaded, and stopped again. The crack length was monitored with a 50-fold traveling microscope. This operation was repeated until numerically meaningful crack propagation (0.02–0.03 mm) was observed. The number of unloadings was 10–15 for each specimen.

The displacement just before additional crack propagation was termed Δ_j, and that after crack initiation, Δ_{j+1}. The area under the load–displace-
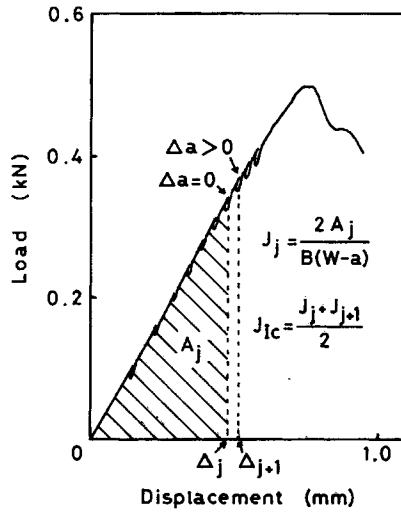
Fig. 2. J_{Ic} measurement of FRP by partial unloading procedure.

ment curve, A_j, was measured, and the energy necessary to displace the specimen by Δ_j was calculated using Rice's simplified equation[8,9] as $J_j = 2 A_j/[B(W - a)]$. The energy necessary to deflect up to Δ_{j+1}, J_{j+1}, was likewise calculated. As $\Delta_j < \Delta_i < \Delta_{j+1}$, the true J_{Ic} value lies between J_j and J_{j+1}. In this report the J_{Ic} value was determined to be $J_{Ic} = (J_j + J_{j+1})/2$.

As the amount of grown crack length at the crack initiation was usually too small, it was difficult to determine the exact displacement at the crack initiation, Δ_i, under constant loading conditions. The partial unloading procedure proposed above seemed to be adequate for the determination of J_{Ic} in FRP.

Immersion Test

The aging immersion test in boiling water was done both at atmospheric pressure and at slightly higher pressure by the use of a pressure cooker. At atmospheric pressure, the immersion vessels used were a conventional cooking kettle and a water bath with electric heater. The pressure cooker was 10 L in volume, and its water temperature was as ca. 116°C at an inner pressure of 0.18 MPa (Riken Light Metal Ind. Co.).

The specimens were immersed in boiling water at either atmospheric pressure or in the pressure cooker. After immersion for a certain time, the specimens were taken out, quickly wiped, and weighed. The specimens were put in a polyethylene film bag to avoid additional loss of water before mechanical testing. When the immersion test in the pressure cooker was extended more than 8 h, the specimens were kept in water for 16 h. Thus the specimens were subject to a cyclic immersion process. The mechanical properties of all of the immersed specimens were measured in a similar manner irregardless of their immersion history. The sharp crack tip of the fracture toughness specimens (cut with a razor blade) was introduced after the immersion process.

RESULTS AND DISCUSSION

Accelerating Aging of FRP by use of Pressure Cooker

It is well known that a pressure cooker is a useful tool for reducing food cooking time. It is interesting to examine if a pressure cooker would be useful in accelerating the degradation of FRP in aqueous environments.

Figure 3 shows the comparison between immersion tests of chopped strand mat/I-resin laminates (I-FRP) in boiling water and in the pressure cooker. The immersion of I-FRP in boiling water for 24 h corresponded to 5–8 h immersion in the pressure cooker on the basis of weight change and strength reduction. Fourty-eight hours immersion in boiling water corresponded to the immersion in the pressure cooker for ca. 16 h. In a separate experiment, I-FRP showed no change in flexural properties, after 500-h exposure in a weather meter with carbon arc-lights. Therefore, boiling water immersion was much more effective in accelerating the degradation of FRP than was exposure in a weather meter.

A brief environmental durability evaluation of FRP in boiling water for 24 h can be replicated by conditioning the specimens in a pressure cooker for only 8 h. This results in considerable savings in time and energy. In the following discussion, the immersion time was 8 h for boiling water exposure, and 8 and 24 h for exposure in the pressure cooker.

Effect of Boiling Water Immersion on Polyester Resins

Since the matrix is responsible for the corrosion resistance of FRP, the immersion tests were done for four types of polyesters. Figure 4 shows the weight change of polyesters after immersion in boiling water and after
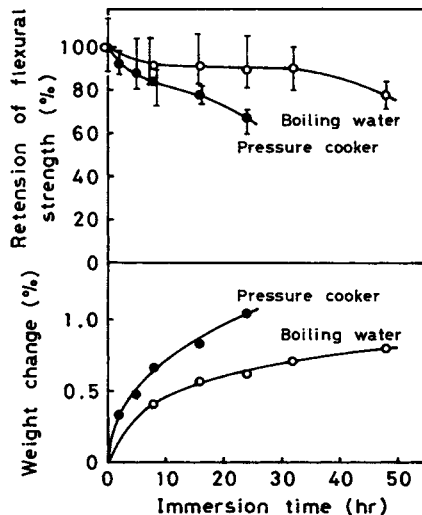

Fig. 3. Comparison between immersion of chopped strand matisophthalic polyester laminates both in boiling water and in pressure cooker.
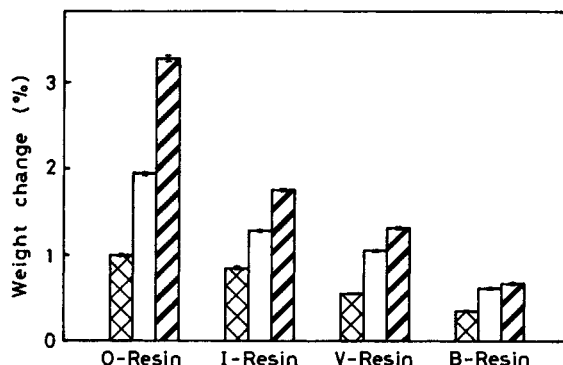
Fig. 4. Weight change of neat polyesters after immersion in boiling water [(⊠) 8h] and after heating in pressure cooker [(□) 8h; (▨) 24h].

heating in the pressure cooker. In any resin the weight gain increased in the order: boiling water 8 h, pressure cooker 8 h, and pressure cooker 24 h. The weight gain of the resins decreased in the order: O-resin > I-resin > V-resin > B-resin. The weight change of O-resin was very large, and an immersion time of 24 h in the pressure cooker resulted in a weight gain of 3.3%.

Figure 5 shows the tensile strength of neat resins after immersion in boiling water. In any resin the strength decreased in the following immersion conditions: boiling water 8 h, pressure cooker 8 h, and pressure cooker 24 h. The strength reduction of O-resin was particularly pronounced as a result of 24-h heating in the pressure cooker. In other resins the strength decreased gradually with increase in the immersion time.

Figure 6 shows the fracture toughness of neat resins before and after immersion. These fracture toughness values are consistent with those reported on similar resins.[4,5] The fracture toughness was in the decreasing order of V-, O-, I-, and B-resins. The K_{Ic} of V-resin was particularly larger than that of other resins, indicating that this material could be used as structural parts with a high degree of safety. Any reduction in the tensile strength or in K_{Ic} was not recognized after air-heating of V-resin at 116°C
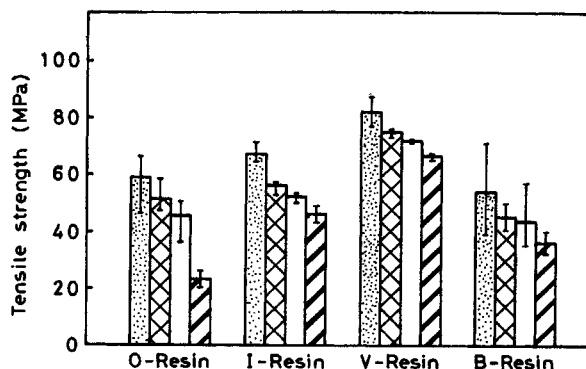

Fig. 5. Tensile strength of polyesters after immersion in boiling water [(⊠) 8h] and after heating in pressure cooker [(□) 8h; (▨) 24 h]: ▣ before immersion.
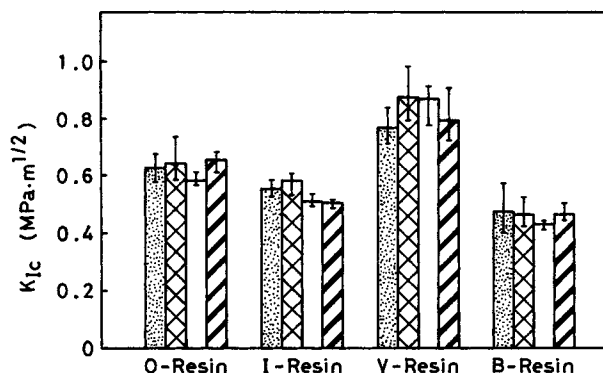
Fig. 6. Plane strain fracture toughness K_{Ic} of polyesters after immersion in boiling water [(⊠) 8h] and after heating in pressure cooker [(□) 8h; (▨) 24h]: (▧) before immersion.

for 8 h. It was surprising that none of these resins showed any appreciable variation in the fracture toughness after conditioning in either boiling water or in the pressure cooker, even though they had absorbed large amounts of water and their tensile strength was significantly reduced. This phenomena were particularly evident in O-resin. A visual inspection of the 24-h immersed O-resin specimens revealed that the edges of the tensile specimens were cracked slightly and a few small voids were formed on their surface. The tensile strength of a material usually is decreased by the formation of flaws or voids.

In the fracture toughness measurement, a sharp crack was introduced just before mechanical testing, and the stability of this cracked specimen was then evaluated. Since the crack tip was considerably sharper than the voids or flaws formed during immersion, the fracture toughness of immersed resins was found to be unchanged. On the other hand, in the previously cracked samples, the K_{Ic} was reported to decrease after immersion in water at 50°C for 500 h.[4]

The bending modulus was occasionally used for the calculation of the fracture energy in place of the tensile modulus.[11] The bending modulus of the resins was almost unchanged after immersion in boiling water except that of the O-resin. In the case of the O-resin, the flexural modulus was decreased considerably by the immersion process. Twenty-four-hour immersion in the pressure cooker reduced the flexural modulus of the O-resin to 66% of its initial value. The critical strain energy release rate of the immersed resins was given by

$$G_{Ic} = (1 - \nu^2)K_{Ic}^2/E \tag{2}$$

where E is the bending modulus of the immersed resin and ν is Poisson's ratio, assumed here to be 0.3.

Figure 7 shows the critical strain energy release rate calculated above. The G_{Ic} values in Figure 7 were in the same order as those obtained in the literature.[3,4] The G_{IC} value of the V-resin was particularly larger than those of other resins. A considerable increase in the G_{Ic} of the O-resin was observed after immersion in the pressure cooker for 24 h. In the other resins, the change in G_{Ic} was small after immersion.
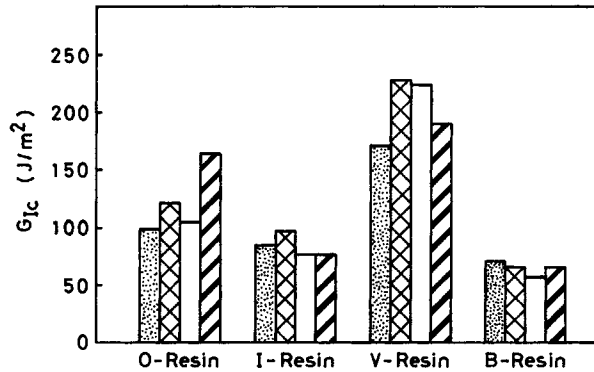
Fig. 7. Critical strain energy release rate G_{Ic} of immersed polyesters [($\boxtimes$) boiling water, 8h; ($\square$) pressure cooker, 8h; ($\boxslash$) pressure cooker, 24h]: G_{Ic} was calculated by $G_{Ic} = (1 - \nu^2)K_{Ic}^2/E$ assuming $\nu = 0.3$: ($\boxdot$) before immersion.

Effect of Boiling Water Immersion on Chopped Strand Mat–Polyester Laminates

In the same manner as the effect of the boiling water immersion on the properties of neat polyesters was investigated, the accelerating immersion of FRP prepared using these matrices was also examined. Figure 8 shows the weight change of chopped strand mat–polyester laminates after immersion in boiling water and after heating in the pressure cooker. In this figure O-FRP, I-FRP, V-FRP, and B-FRP represent the FRP prepared by O-, I-, V-, and B-resins, respectively. On the whole, the trends shown in Figure 8 are similar to those in Figure 4. However, in the case of the FRP, the amount of weight gain was smaller than that of the neat resins. In any FRP the weight change increased in the order of boiling water 8 h, pressure cooker 8 h, and pressure cooker 24 h. The weight change of FRP depended on the matrix, and this value decreased in the order of O-, I-, V-, and B-FRP.

Figure 9 shows the three-point bending strength of chopped strand mat–polyester laminates before and after immersion in boiling water. The reduction in the flexural strength of FRP after immersion in the boiling water of the pressure cooker was not large, even though the neat O-resin showed considerable drop in its tensile strength. The finding that the reduction in flexural strength of FRP after immersion was not so large as expected from
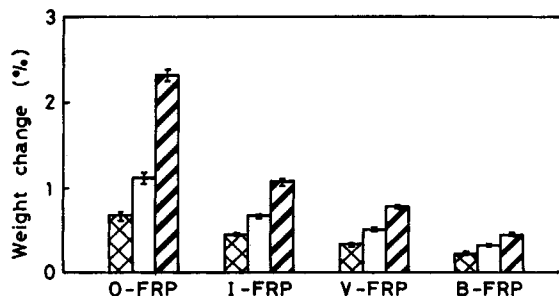
Fig. 8. Weight change of chopped strand mat–polyester laminates after immersion in boiling water [($\boxtimes$) 8h] and after heating in pressure cooker [($\square$) 8h; ($\boxslash$) 24 h].
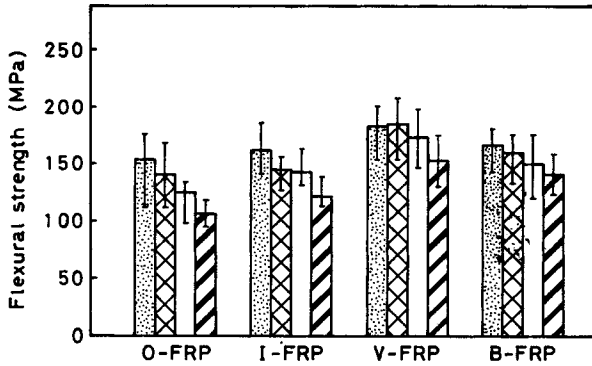
Fig. 9. Flexural strength of chopped strand mat–polyester laminates after immersion in boiling water [(□) 8h] and after heating in pressure cooker [(□) 8h; (▨) 24 h]: (▨) before immersion.

the behavior of the neat polyesters can be explained as follows: In chopped strand mat–polyester laminates, the glass fibers aligning to the stress direction still sustained a considerable part of the load; thus the reduction in the strength of immersed FRP was rather small.

Fracture Toughness of Immersed FRP

The plane strain fracture toughness K_{Ic} of immersed FRP was measured in a similar manner as in the case of the neat resins. However, the thickness of the FRP specimens was not large enough to give valid K_{Ic}. For comparative purpose, the candidate stress intensity factor K_Q[6] is shown in Figure 10 as a measure of fracture toughness of FRP. The K_Q values in Figure 10 were in good agreement with the literature values.[6,7] The K_Q value of 9.1–11.0 MPa · m$^{1/2}$ was obtained with notch bend specimens,[6] and that of 9.8–11.5 MPa · m$^{1/2}$ was reported in center-notched specimens.[7] The difference in K_Q value between these FRP was small, even though, in neat resins, the V-resin showed larger value in K_{Ic}. The variation in the K_Q value of FRP after heating in the pressure cooker for 8 h was small. With center-notched specimens, the effect of water absorption on fracture toughness was also reported to be small.[7]

Figure 11 shows the elastic–plastic fracture toughness J_{Ic} of FRP before and after immersion in boiling water by use of the pressure cooker for 24
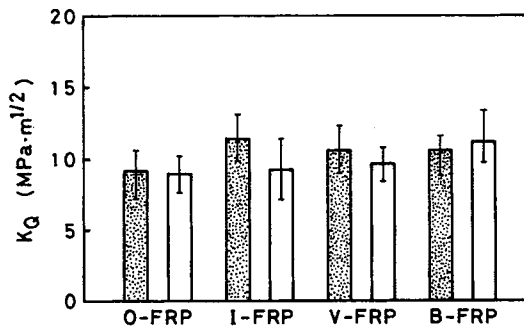

Fig. 10.   Candidate stress intensity factor K_Q of chopped strand mat–polyester laminates after heating in pressure cooker [(□) 8h]: (▨) before immersion.

TABLE I
Fracture Parameters for Neat Polyesters and Chopped Strand Mat²–Polyester Laminates

Material	Resin		FRP		
	K_{Ic} (MPa·m$^{1/2}$)	G_{Ic}^a (J·m^{-2})	J_{Ic} (kJ·m^{-2})	K_{Ic}^b (MPa·m$^{1/2}$)	K_Q^c (MPa·m$^{1/2}$)
Orthophthalic (O-)	0.63	98	2.8	4.9	9.2
Isophthalic (I-)	0.55	85	4.4	6.1	11.4
Vinyl ester (V-)	0.77	171	3.0	5.1	10.6
Bisphenol A (B-)	0.48	71	4.0	5.9	10.6

[a] Calculated by $G_{Ic} = (1 - \nu^2)K_{Ic}^2 / E$, assuming $\nu = 0.3$.
[b] Calculated by $J_{Ic} = (1 - \nu^2)K_{Ic}^2 / E$, assuming $\nu = 0.3$.
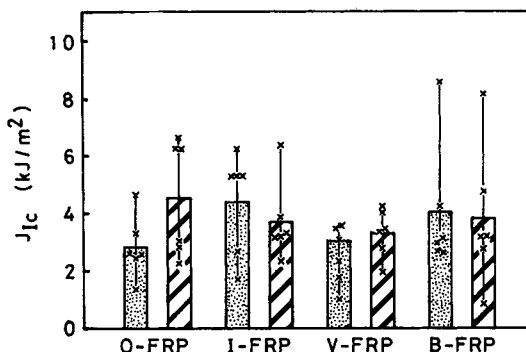[c] Candidate stress intensity factor: plane strain condition was not satisfied.

Fig. 11.   Elastic–plastic fracture toughness J_{Ic} of chopped strand mat–polyester laminates after heating in pressure cooker [(▨) 24 h]: (▧) before immersion.

h. There is a great deal of scatter in the measured data. In general, the J_{Ic} values of these FRP lay nearly in the same order. The J_{Ic} value of FRP seemed to be roughly unchanged after the immersion. From the measurement of J_{Ic} and also K_Q in Figure 10, the fracture toughness of FRP was found to be independent both of the matrix and of the immersion conditions used in this study.

Table I summarizes the fracture parameters for the neat polyesters and the chopped strand mat–polyester laminates before immersion. In the case of the neat resins, the plane strain fracture toughness K_{Ic} and the critical strain energy release rate G_{Ic} of the V-resin was larger than those of the other resins.

In the case of FRP, the elastic–plastic fracture toughness J_{Ic}, the equivalent K_{Ic} calculated from J_{Ic}, and K_Q were roughly independent of the matrix resins. The candidate stress intensity factor K_Q lay around 10 MPa · m$^{1/2}$, and this value is about twice as large as the equivalent K_{Ic}. The bigger values of K_Q than those of K_{Ic} can be explained as follows: In the K_Q measurement a maximum load was used in the calculation, while in J_{Ic} measurement the energy necessary just to initiate crack was calculated. The equivalent K_{Ic} of FRP was about 10-fold larger than K_{Ic} of neat resins.

References

1. H. H. Chung and A. Crugnola, Proc. 30th SPI Reinf. Plas./Composites Inst. 9-A (1975).
2. N. C. W. Judd, Proc. 30th SPI Reinf. Plas./Composites Inst. 18-A (1975).
3. L. J. Broutman and F. J. McGarry, J. Appl. Polym. Sci., 9, 589, 609 (1965).
4. G. Pritchard, G. V. Rhoades, and R. G. Rose, J. Mater. Sci., 15, 1635 (1980).
5. J. V. Carisella, R. D. Goolsby, and R. W. Hewitt, Proc. 36th SPI Reinf. Plas./Composites Inst. 7-B (1981).
6. S. K. Gaggar and L. J. Broutman, Proc. 30th SPI Reinf. Plas./Composites Inst. 9-E (1975).
7. M. J. Owen and R. J. Cann, J. Mater Sci., 14, 1982 (1979).
8. M. Suzuki, M. Iwamoto, and T. Maeoka, Trans. Jap. Soc. Mech. Eng. Ser. A, 47, 10 (1981).
9. "1981 Annual Book of ASTM Standards", Part 10, E813-81 (1981) p. 810.
10. "1981 Annual Book of ASTM Standards", Part 10, E399-81 (1981) p. 588.
11. W. D. Bascom, R. Y. Ting, R. J. Moulton, C. K. Riew, and A. R. Siebert, J. Mater. Sci., 16, 2657 (1981).