THE ROLE OF INTERLEAF/BASE LAMINA INTERPHASE IN TOUGHENING MECHANISM OF INTERLEAF-TOUGHENED CFRP

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SUMMARY: Interlaminar fracture toughness under mode I and II loadings was investigated for unidirectional CF/epoxy laminates with ionomer interleaf of the thickness of 12 to 200 μm. Ethylene based ionomer resin used in this study has high bonding strength with base epoxy resin. EPMA analysis revealed that interphases were formed between the ionomer layer and the base laminas. These interphases contain a mixture of ionomer, epoxy and carbon fibers. The fracture toughness of ionomer interleaved CF/epoxy laminates was much higher than that of base CF/epoxy laminates both under mode I and II loadings. For mode I loading, the high level of the toughness was kept constant with the crack growth. For mode II loading, the toughness reached 9 to 10 kJ/m^2, which is one of the highest among already reported results. Microscopic observation showed that the crack path was at the interface of the ionomer/interphase or inside the interphase region, arrested by fibers. Thus, cracks never propagated through the non-toughened region and this is responsible for the higher toughness, giving a new concept of interleaf toughening.

KEYWORDS: Delamination, Interlaminar fracture toughness, CFRP, Interleaf, CF/epoxy, Ionomer, Interphase, Mesoscopic fracture mechanism

INTRODUCTION

Although almost twenty years have passed since the importance of delamination was recognized [1], interlaminar strength is still one of the design limiting factors in structural composite laminates. Some levels of toughening have already been achieved by replacing matrix resin to a tougher system [2-4]. A well known example is AS4/PEEK with tough thermoplastic resin system [4-6]. This is rather a homogenized approach.

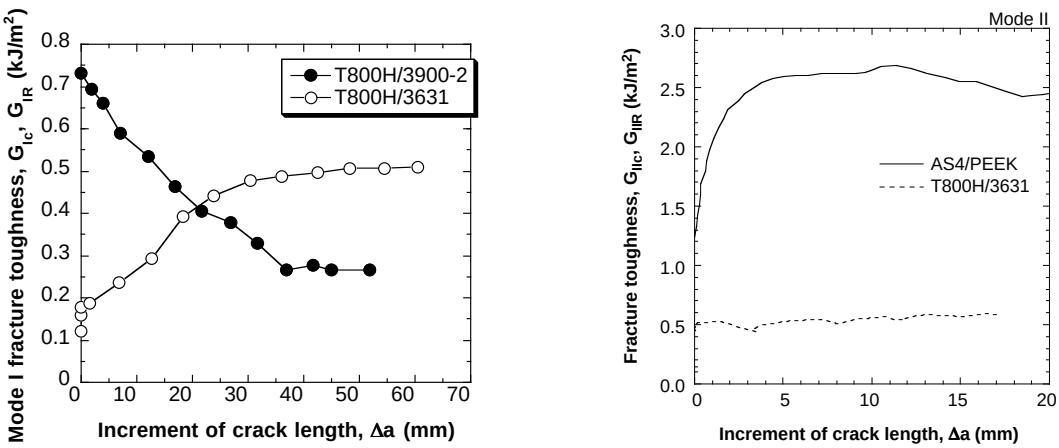
The fracture behavior of CFRP laminates is sensitive to its mesoscopic structure[7] such as the microscopic geometrical arrangement (misorientation, inhomogeneity in density) of fibers, the thickness of resin rich layers at the prepreg interface, etc[5,8]. Delamination crack path is often localized to the prepreg interface region. Then, one of the most promising way to increase the interlaminar properties is to control the mesoscopic structure by replacing only the resin layer at the prepreg interface to a tougher system. This way is often called as "interleaf" or "interlayer" method. Original way of this concept is simply to insert conventional thermoset or thermoplastic interleaves [9,10].

The new commercial product with a heterogeneous interlayer including fine thermoplastic particles, T800H/3900-2, has shown excellent compressive strength after impact (CAI), and has already been applied for primary structures of Boeing 777[11]. Figure 1 shows the R-curves under mode I and II loadings. The propagation values of the mode II fracture toughness for T800H/3900-2 (solid line) was about four times higher than that of the base CFRP laminates without interlayers (T800H/3631, dashed line) [12]. However, the mode I fracture toughness decreased gradually with the increment of crack length and levelled off where the increment of the crack length was more than 35 to 40 mm. This converged values [13] was lower than the propagation values of the fracture of the base CFRP laminates. It is also reported that the low adhesion between thermoplastic interleaf and matrix resin caused similar poor toughness for interleaved CFRP [9]. These facts suggest that both high ductility and high adhesion strength are necessary for the interleaf materials to improve the interlaminar fracture toughness.

In the present study, a new type of thermoplastic resin, ionomer, was used as the interleaf materials for CF/epoxy laminates [14], and the mode I and II interlaminar fracture properties of the interleaved CFRP were investigated. Ionomer reacts with epoxy, and higher adhesion is expected. Toughening mechanisms were discussed on the basis of microscopic observation and EPMA analysis.

EXPERIMENTAL PROCEDURE

Laminates used in this study were made from Toho Rayon UT500/111 prepregs. Unidirectional laminates, $(0)_{24}$, of the nominal thickness of 3 mm were molded by a hot press. The curing temperature was 140°C. Ethylene based ionomer film was inserted at the mid-thickness during



(a) Mode I (b) Mode II

Fig. 1: Comparison of R-curves for interlayer toughened CFRP (T800H-3900-2) and base CFRP (T800H/3631).

molding process as interleaf. Here, ethylene methacrylic acid copolymer was ionized partially by zinc iron [14]. The thickness of ionomer film was 12, 25, 100 and 200 μm. The laminates without interleaf were also prepared for comparison. Starter slits were introduced into the laminates by inserting single 13 μm thick polyimide film during molding at midplane.

Fracture toughness tests under mode I loading were carried out by using double cantilever beam (DCB) specimens (width=20mm)[15,16]. The load was applied to the specimen through pins and aluminum blocks attached to the specimen. The length of the initial crack was 30 mm. Tests under mode II loading were carried out by using end notched flexure (ENF) specimens (width=20) [15,17]. The span of the supports was 100 mm, and the length of the initial crack was 25 mm. The tests were carried out in a computer-controlled servohydraulic testing system (Shimadzu 4880, 9.8kN)[5-7]. The cross head speed was controlled to be 0.5 to 1.0 mm/min in DCB tests [15], and the crack shear opening displacement speed was controlled to be 0.03 mm/min in ENF tests [15]. The crack length was computed from the measurement of the compliance by using the calibration relation between the compliance and the crack length [16,17]. The tests were carried out in laboratory air. The energy release rate under mode I loading was calculated using modified compliance calibration method [15]. That under mode II loading was calculated using compliance calibration curves for each specimen [12]. The distribution of resin around interfaces between ionomer and epoxy was investigated using electron probe microanalyser (EPMA, JEOL JXA-8800M) by energy dispersion method.

RESULTS AND DISCUSSION

EPMA Analysis

The element distribution for the chloride and zinc element was investigated near the ionomer/ base lamina interface. There were distinct areas where Cl element and Zn element were highly detected. The Cl-highly-detected area corresponds to the original epoxy matrix region, and the Zn-highly-detected area corresponds to the original ionomer region[18]. Figure 2 shows the secondary electron image of the analyzed area. The upper side of the upper line is the original ionomer region, and the lower side of the lower line is the original epoxy matrix region. Thus, there existed an area where the density of both Zn and Cl elements decreased between ionomer/ base lamina interface, and one or two fibers inside the base lamina region. This indicates that the

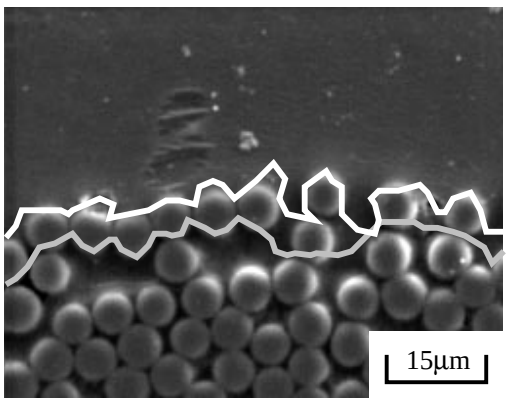


Fig. 2: Boundary of Zn- and Cl-highly-detected area at ionomer/base lamina interface.

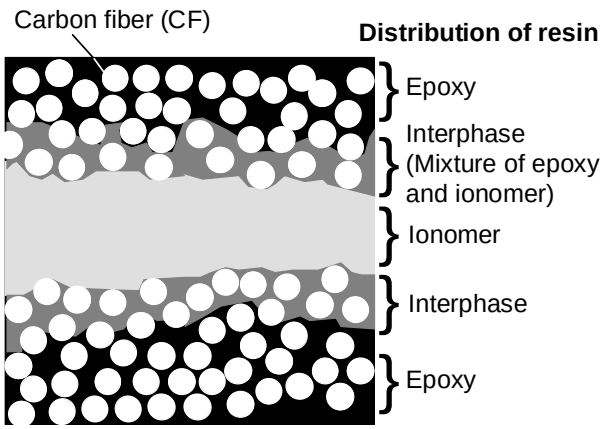


Fig. 3: Schematic structure of transverse section near ionomer/base lamina interface.

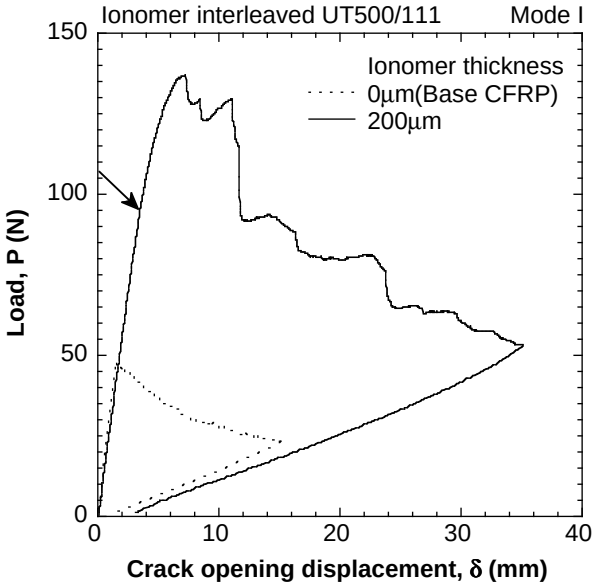


Fig. 4: Load-COD curves for laminates with ionomer thickness of 0 and 200 μm.

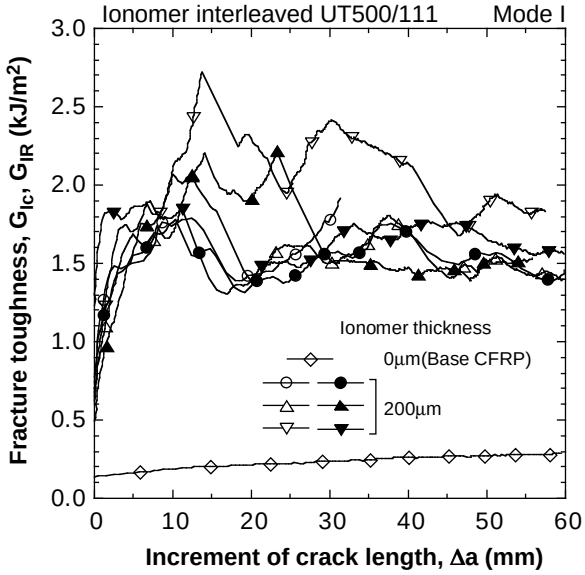


Fig. 5: Relation between fracture toughness and increment of crack length for each specimen (Ionomer thickness: 200 μm).

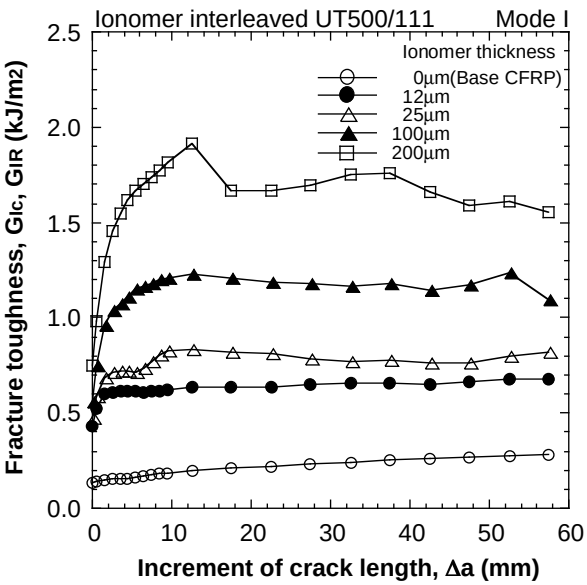


Fig. 6: Averaged relation between fracture toughness and increment of crack length under mode II loading.

ionomer resin penetrated into the base lamina region during molding, forming the interphase where epoxy and ionomer were mixed. This structure is schematically indicated in Fig. 3.

Mode I Interlaminar Fracture Toughness

Figure 4 shows the relation between load and load line displacement for 200μm-ionomer-interleaved laminates. The arrow indicates the onset of nonlinearity on the initial loading line (NL point). The corresponding relation between the interlaminar fracture toughness and the increment of crack length is shown in Fig. 5. The data points at Δa=0 mm indicate the initial values of the fracture toughness, G_{Ic}, at NL point. The scatter for each specimen is rather large. Then, the average of several specimen was calculated over subsequent 1 mm increment of the

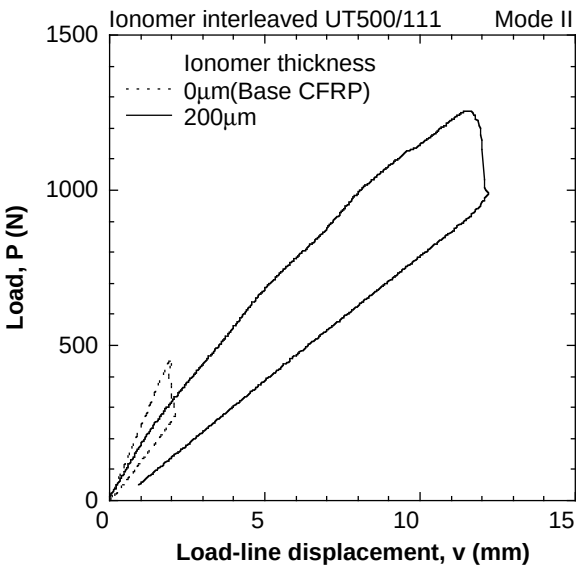


Fig. 7: Load-COD curves for laminates with ionomer thickness of 0 and 200 μm.

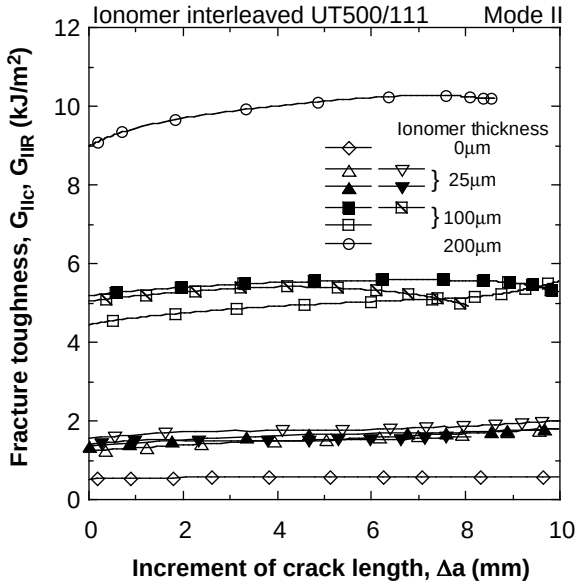


Fig. 8: Relation between fracture toughness and increment of crack length for each specimen .

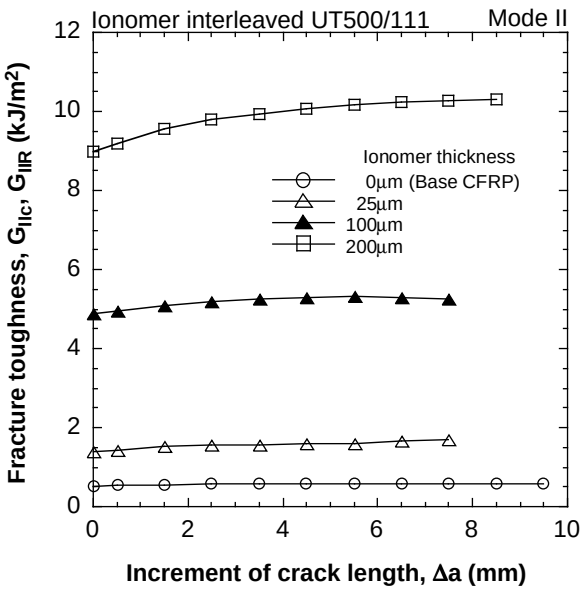


Fig. 9: Averaged relation between fracture toughness and increment of crack length under mode II loading.

Table 1. Comparison of crack growth resistance between area method and compliance calibration method.

Ionomer thickness (μm)	Crack growth resistance (kJ/m^2)	
	r	G_{IIs}
0	0.55	0.57
25	1.5	1.6
100	5.2	5.2
200	9.5	10

crack length for Δa < 10mm and subsequent 5 mm for Δa > 10 mm. Figure 6 shows the effect of interleaf-film thickness on the R-curve. Both the initial values, G_{Ic}, and the propagation values, G_{IR}, increased dramatically with the increase of the interleaf thickness. For the ionomer thickness of 200μm, the toughness increased about ten times from the base laminates. Another important point is that the G_{IR} values kept a higher plateau value without respect to the crack length. This behavior was completely different from that for T800H/3900-2 where the R-curve decreased, and converged to the base laminate value as shown in Fig. 1(a).

Mode II Interlaminar Fracture Toughness

Figure 7 shows the relation between load and load-line displacement for laminates with 200 μm-thick ionomer. The results of base CFRP laminates were also shown by dashed line. Initial loading line indicated rather large nonlinearity. Here, the compliance was determined by the higher load part of the initial loading line(for the case of Fig. 7, P > 300 N). In-situ microscopic observation on the side surface of the specimen indicated that the visual onset point of the crack growth agreed with the maximum load point of the load-displacement curve. Then, the initial values of the fracture toughness was only calculated at the maximum load point under mode II loading. The obtained relation between the fracture toughness and the increment of the crack length for each specimen, was shown in Fig. 8. In Fig. 9, each G_{IIR} data point was calculated as the average value over subsequent 1 mm increment of crack length. Similar to the results under mode I loading, the whole R-curve increased markedly with the increase of the interleaf thickness. For the ionomer thickness of 200μm, the toughness increased about twenty times from the base laminates. The actual toughness value of 10 kJ/m^2 was also one of the highest among the already reported results for CFRP laminates.

Figure 7 suggests the influence of the nonlinearity in the calculation of the energy release rates. In order to verify this possibility, the average of the propagation values of the fracture toughness, G_{IIs}, was compared with the crack growth resistance evaluated by the area method. Work of fracture during crack growth was calculated by the area between the load-displacement curves of a and a+da. Then, this area, *Π*, is related to the crack growth energy per unit area, *r*, as follows:

$$\Pi = \int (rB)da \qquad (1)$$

where B is the width of the specimen. Since the change of G_{IIR} with Δa was small in Fig. 9, we calculated *r* values supposing that *r* values are constant during crack growth. Table 1 shows that the agreement between G_{IIs} and *r* is quite good, showing that the effect of nonlinearity was small in the present study.

Crack Path and Toughening Mechanism

Crack path was investigated by in-situ optical microscope observation, observation of transverse section by an optical microscope, and scanning electron microscopy of the fracture surfaces. The results are schematically shown in Fig. 10 under mode II loadings. The crack path was usually at the lower ionomer/base lamina interface. When the thickness of the interleaved ionomer was thin (12-25 μm, Fig. 10(b)), the crack path was at the ionomer/interphase interface or inside the ionomer region. When the thickness of the interleaved ionomer was thick (100-200 μm, Fig.

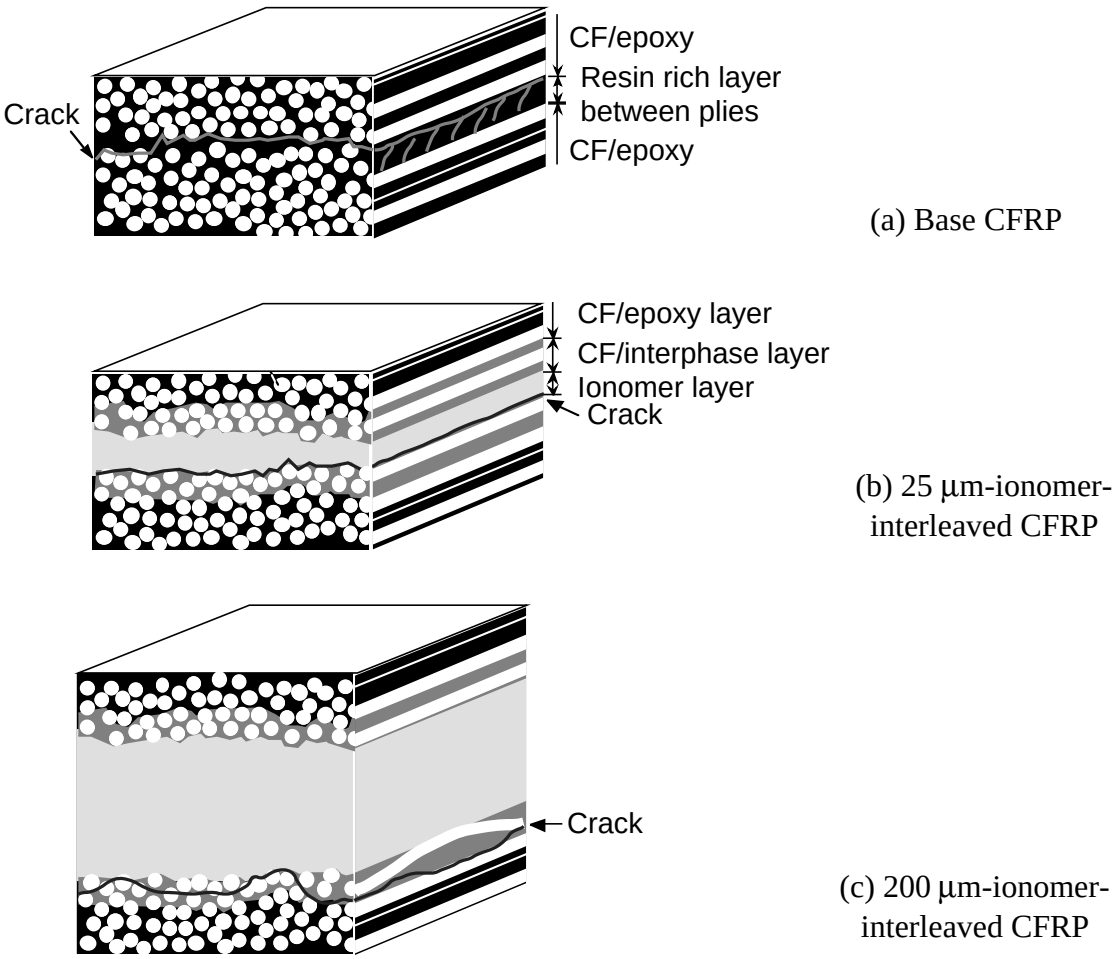


Fig. 10: Schematic models of crack path in the transverse and longitudinal sections of ionomer-interleaved CFRP

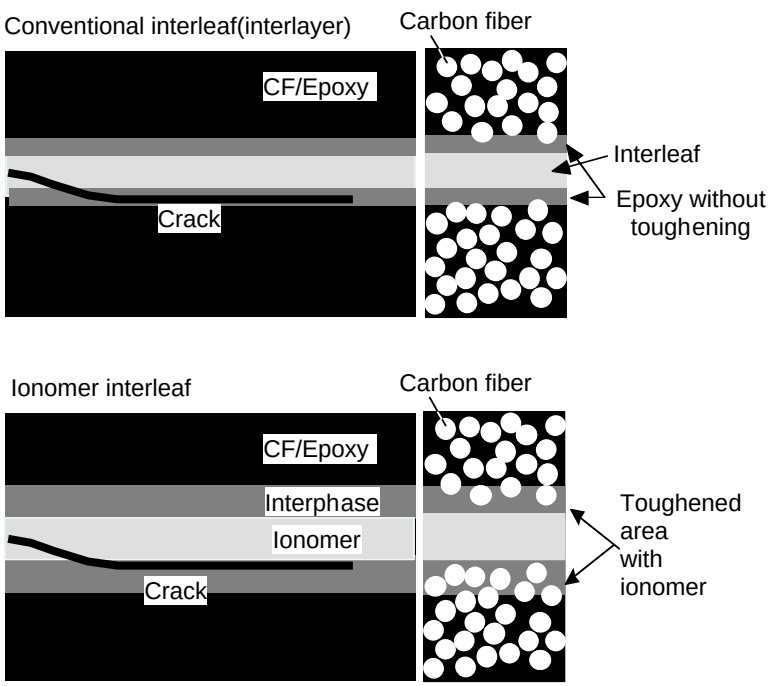


Fig. 11: Difference of toughening mechanism between conventional interleaved and ionomer interleaved laminates.

10(c)), crack went mainly through interphase region. The results under mode I loading were similar to those under mode II loading. Under mode I loading, the crack path was both at upper and lower interfaces, bridging ionomer film. The reason why the ionomer thickness affected the crack path is closely related to the size of the process zone at the crack tip. Since thicker-ionomer-interleaved CFRP has higher fracture toughness, the highly deformed region can not be localized inside the toughened zone (interlayer + interphase). The arrest of the crack path by fibers was not enough, and the fracture occurred mainly inside the interphase and partially in the CF/epoxy region inside the base lamina. SEM observation showed that the morphology of the fracture surface at the interface between the interlayer and the base CF/epoxy lamina, and at the interphase was very ductile and completely different from the base laminates. This ductility is mainly responsible for the dramatic increase of the fracture toughness.

Figure 11 explains the difference of the toughening mechanism between conventional interleaved and ionomer interleaved laminates. The transition of the crack path from the interleaf to the interface was common for both laminates. The crack path was arrested by the rigid carbon fiber at the surface of the base lamina. For conventional interleaved laminates, there were no toughened resin at the surface of the base lamina, and this caused the decrease of the toughness. On the other hand, the crack was still inside the toughened region for ionomer interleaved laminates. This is responsible for the non-decrease of the propagation values of the fracture toughness with the increment of the crack length as shown in Fig. 6.

Difference of Ionomer Thickness Effect between Mode I and II Loadings

Figure 12 indicates the relative increase of the initial values, G_{ic}, at the maximum load point and the propagation values, G_{is} (i=I, II), with the interleaf thickness. Here, G_i^B indicates the corresponding toughness for the base laminates. For mode I loading, the effect of the interleaf thickness was initially very large at the ionomer thickness of 12μm, and then the effect was decreased with thicker ionomer. On the other hand, the toughness under mode II loading

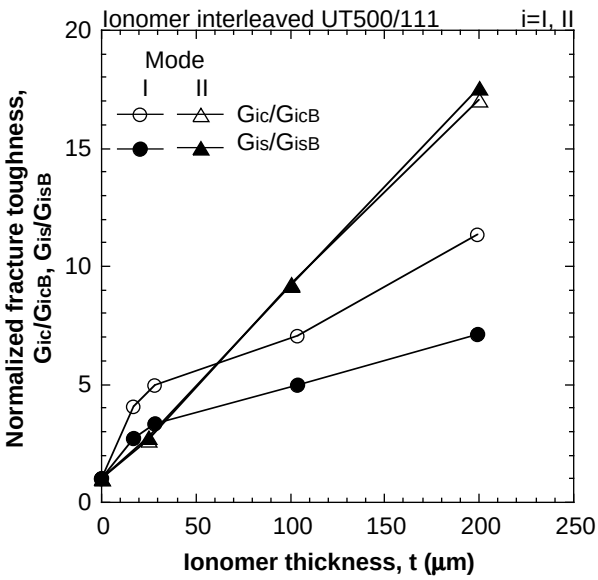
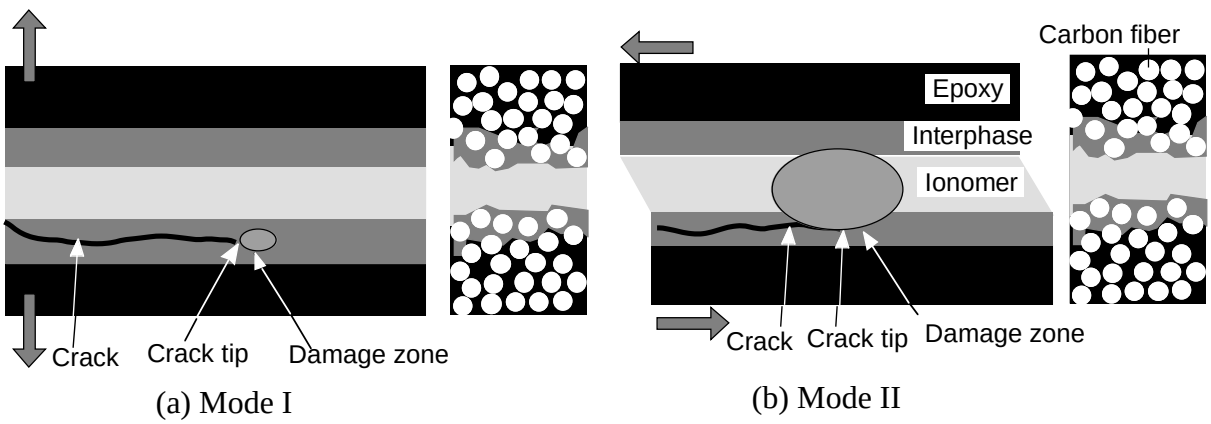


Fig. 12: Effect of ionomer thickness on mode I and II fracture toughness.



(a) Mode I (b) Mode II

Fig. 13: Comparison of damage zone size and location between mode I and II loadings.

increased linearly with the interleaf thickness. These facts suggests the toughening mechanism is different between mode I and II loadings.

The side surface of the specimens at the same location before and after the tests were observed by SEM using the replica method. The summarized results were shown schematically in Fig. 13. For mode I loading, the permanent deformation of the ionomer was localized in the vicinity of the crack path. This feature was almost the same without respect to the ionomer thickness. In this case, the reduced stress intensity factor by the introduction of the ionomer interleaf is responsible for the toughening mechanism [19], and only the existence (not the thickness) of the interleaf contributes the increase of the toughness as shown in Fig. 12. For mode II loading, the deformation was expanded to the whole interlayer indicated by large permanent shear deformation. This means the deformation of whole interleaf thickness contributes the increase of the toughness, and is related to the linear increase of the toughness with the interleaf thickness as shown in Fig. 11.

CONCLUSIONS

Interlaminar fracture toughness of ionomer-interleaved CF/epoxy laminates was investigated under mode I and II loadings. These laminates indicated dramatic increase of the toughness from base CF/epoxy laminates both under mode I and II loadings. The propagation values of the fracture toughness did not decrease from the initial values with the increment of the crack length under mode I loading.

EPMA analysis showed the existence of the toughened interphase at the interlayer/base lamina interface. Then, although the crack path shifted from the interleaf region to the interface, crack was still inside the toughened region. This is why the toughness was very high.

The difference of the effect of ionomer-interleaf thickness on the toughness under mode I and II loadings was due to the different size of plastic zone at the crack tip.

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