A Study on Mode I and Mode II Delamination Toughness of Carbon Fiber/Epoxy Composite with Short Kevlar Fiber and Nylon-6 Powder Reinforcement

B.Y.PARK, S.C.KIM*, S.K.CHUNG and B.JUNG
Agency for Defence Development
* Dept. of Chemical Engineering,
Korea Advanced Institute of Science and Technology

Introduction

The main advantages of polymer composites over conventional metals in primary structural applications are their superior fatigue resistance and strength- and stiffness-to-weight ratios. However, the primary deficiency of the current generation composites, such as graphite/epoxy, is their poor damage tolerance. The low in-plane and out-of-plane matrix-dominated mechanical properties often result in intraply matrix cracking and delamination in the composite in response to a low energy impact[1]. The initiation and growth of these cracks in composites may lead to severe reliability and safety problems. Stiffness, strength, environmental resistance, and durability may be reduced considerably. Understanding of the basic relationships between these failure mechanisms and material parameters is of great academic interest as well as of significant technical importance.

Research to improve the interlaminar fracture behavior of laminated polymeric composites has generally focused on the matrix material, the reinforcement and the fiber-matrix interface. Conventional toughening approaches that involve dispersing a rubbery phase in the matrix resin have led to an improvement in damage tolerance, but usually at the sacrifice of hot/wet compressive performance[2]. Interlaminar toughness involves incorporating usually heterogeneous organic or inorganic particles, short fiber, or film, between the prepreg plies of composite. Technology for achieving this, therefore, varies from simple spray coating on the prepreg, to quite complex filming processes. SKF and N6P were used as the interlaminar toughening materials in this work.

Seferis[3] suggested toughening by thin layers of matrix with modifier particles between plies in the carbon fiber/dicyanate composites. The unmodified mode-II fracture toughness had a value of 530 J/m^2 and the maximum mode-II fracture toughness obtained with 20-phr modifier was 1135 J/m^2. Above 20-phr particle concentration, the decrease in the mode-II fracture toughness was observed. No change was observed in the mode-I fracture toughness McGrail[4] used reactively terminated polysulphone as the particulate modifier in epoxy, bismaleimide, and cyanate ester resin based composites. Gic was improved from 0.51 ± 0.07 kJ/m^2 to 0.77 ± 0.10 kJ/m^2. Compression after impact testing rose from 223 ± 0.7 Mpa to 268.9 ± 15.9 Mpa. The thermoplastic particles were sieved onto the prepreg.

Browning[5] ascribed the improved

toughness to incorporation of an adhesive in-lay either by itself or in combination with a kevlar mat. The AS1/3502/163-Kev-163 contained an in-ply of one layer of AF-163 adhesive, one layer of Kevlar mat, and one layer of AF-163. This combination produced the highest Gic of 1855 J/m^2 that was greater by an order of magnitude over the control. Scanning electron microscopy (SEM) of the fracture surface showed a substantially lesser amount of fiber pull-out and the presence of the adhesive around kevlar fibers. Lin[6] have suggested the incorporation of SKF in a thermosetting resin before being used for impregnating the continuous fibers or fabrics. SKF had no effect on Gic, but increased Giic from 1.24 kJ/m^2 to 2.08 kJ/m^2. However, a high volume fraction of added short fibers could make it difficult to out-gas during compression, leading to a high void content and reduced mechanical properties of composites. Methods discussed above are not related to toughness improvement through short fiber-bridging. The phenomenon of fiber-bridging[7,8] has been reported extensively in the mode I delamination, but is less understood for mode II delamination. Shon[9] has reported that significant fiber bridging was observed for the Giic test whilst Gic exhibited lower fracture energies with less apparent fiber bridging. Giic of 16-ply Hercules carbon-fiber laminates of 5 to 7 mm kevlar fiber reached as high as 4.5 kJ/m^2 from the initial value of about 1.0 kJ/m^2 before it went down to 3.0 kJ/m^2. They examined at 33 mm crack growth from the initial crack length between 35 mm and 50 mm that was thought to be beyond the center load point of crack tip. This would give erroneous values due to blocking the natural crack propagation by the center load when the crack tip reached the center load point[10]. 12-ply T300 carbon-fiber laminates with 17 g/m^2 of 13 to 15 mm kevlar fiber showed no effect on Giic. Fiber bridging, in the context of crack propagation parallel to the fibers, refers to the phenomenon of unbroken fibers inclining and interconnecting the opposite fracture surface behind a crack tip. Most of the fiber-bridging phenomena have been reported in Mode I fracture[7,8] which arose from misalignment of the fibers across the crack plane and/or the growth of the crack in more than one plane.

From the studies reported in the literature, no general conclusion can be drawn about the effect of SKF's bridging on Gic and Giic of carbon-fiber/epoxy composites. Further studies on hybrid addition of SKF and N6P are undoubtedly necessary. A range of SKF or SKF and N6P in equal weight ratio was considered in order to examine the influence of fiber bridging on Gic and Giic. The complex fracture path by different kind of reinforcement was expected to result in a strong increase in the fracture resistance. The role of SKF was thought to induce fiber bridging that can absorb large energy than any fracture mechanism. Ductile deformation and debonding from matrix of N6P were also thought to absorb large amount of fracture energy.

Experimental

Materials Preparation

The carbon fabric was eight-harness satin woven type. The epoxy resin used in this study was 0510 from Ciba-Geigy Corp. it was mixed with a hardener HT 976 at a weight ratio of 100:38 and the mixture was heated for the complete dissolution of hardner in the epoxy for 20 min at 120^{0}C. The prepreg was made by impregnating the resin mixture in the carbon fabric with a hand roller, heated during 2.0 hr at 120^{0}C for B-stage condition and had fiber weight percent-fractions of 55.0 % to 60.0 %. Kevlar-29 was chopped to 6 mm in length and used as the interlaminar reinforcement The particles used were semicrystalline Nylon 6 (1002D NAT, Atochem Corp) with an average particle of 20 μm. SKF was spread manually after impregnating the resin in the carbon fabric. N6P was uniformly sieved onto the prepreg having SKF. The amount of SKF and N6P in equal weight ratio, SKF or N6P used was 4.0 g/m^2, 8.5 g/m^2, 17.0 g/m^2 and 25.5 g/m^2. The laminate consisted of 8-plies of prepreg. The prepreg with SKF was in the mid-plane of laminate where the starter crack was implanted. The folded sheet of aluminum foil of 35 μm was used for this purpose.

Laminates were prepared by autoclave molding. Each specimen (150 mm × 24 mm × 3.2 mm) was cut from laminates by using a radial diamond saw. The metallic end blocks made of steel were bonded to the precracked specimen as a means of applying the load perpendicular to the interlaminar layer for measuring Gic. The surface of the specimen and the steel end block was prepared for bonding after carefully scraping with sand paper until the surfaces were uniformly dull. The surface of the specimen was cleaned with acetone and that of the end blocks with 1,1,1-trichloroethane. The adhesive used for bonding end blocks was adhesive film (FM73, Cyanamid Corp), which was cured at 120^0 C for 120 min. Care was taken to ensure that both hinges on each specimen were in alignment since the direction of applied load for the mode I crack opening within the specimens would be dictated by this alignment. The hinges must be free to rotate so that minimal stiffening of the Gic specimen is introduced when attached to the instron grips.

The edges of each specimens before testing were polished manually with sandpaper down to 1000 mesh to produce flat and smooth surface. To assist the observation of the crack propagation, the edges were then coated with a thin layer of a diluted white correction fluid. Such a thin coating created a good contrast between a dark crack and the white intact area of the laminates. Marks of 1 mm apart were made on the white background.

Test Procedure

The double cantilever beam (DCB) test was performed at a constant crossed displacement rate of 2 mm/min. During the test, the transverse tensile load was applied to the end of the beam specimen by steel block bonded adhesively to the upper and lower side. Approximately 15 - 20 crack length values were obtained , including the corresponding displacement and the load being carried by the double cantilever beam.

The end notched flexure (ENF) test was performed with the aid of a three-point bending apparatus with a fixed support distance of 100 mm. Crack growth in the ENF tests has been shown to be unstable without SKF and stable with SKF. The specimens were loaded until the crack propagated, the machine was stopped to measure the actual crack length and unloaded. This procedure was repeated until the crack reached near the center load point. Approximately 2 - 7 crack length values were obtained. The critical load was obtained as the maximum value in the linear portion of load-displacement curve. Instron tensile tester machine was used in the experiment under constant crosshead speed of 2 mm/min.

For DCB and ENF test, the first load application was applied on the specimen until the crack extended from the tip of the aluminum foil. The machine was then stopped and the specimen was unloaded to zero load. This precracking procedure was carried out in order to avoid the resin-rich areas in front of the started crack. The traveling optical microscope(× 25) was used to determine the length of the crack propagation.

The mode I delamination toughness Gic was calculated by the equation (1 - 3) based on the linear elastic beam theory

$$C = \frac{2a^3}{3E_{11}I} = \frac{\delta}{P} \quad (1)$$

$$Gic = \frac{P^2a^2}{BE_{11}I} \quad (2)$$

$$Gic = \frac{3P\delta}{2Ba} \quad (3)$$

where P was the load required to extend a crack length a in the specimen of width B with the displacement δ. This method and other alternatives have been reviewed and analyzed in detail by Hashemi[11].

The normal loading and unloading technique was employed to stabilize crack growth and allow compliance measurement. The equation for evaluation of Giic as a function of the applied load P and the crack length are readily available for various delamination modes. Details can be found , for instance, in the work of Hashemi[11]. The Young's modulus, E_{11}, along fiber direction in unidirectional fiber composites, can be obtained from initial compliance C_0 determined from load and displacement curve. For the ENF specimens, C_0 is given by

$$C_0 = \frac{\delta}{P} = \frac{3a_0^3 + 2L^3}{8BhE_{11}} \quad (4)$$

where δ is the displacement generated under the applied load P, a_0 is the initial crack length, L is the length from the central load point to the end support, h is the half thickness of the specimen, and B is the width. the mode II delamination toughness Giic is given by

$$Giic = \frac{9Pa^2}{16B^2h^2\overline{E}_{11}} \quad (5)$$

where a is the instantaneous crack length corresponding to the fracture load P, and $\overline{E}_{11}$ is the average Young's modulus determined from several compliance values obtained by equation (4). Equation (4) and (5) are the simplified forms of the original equation with $\chi = 0$.

Results and Discussion

SEM observation

In the case of composites having SKF, the following fracture mechanisms[1] are of special importance: (1) matrix deformation and fracture; (2) fiber and matrix debonding; (3) fiber pull-out; (4) fiber bridging and fracture. All of these mechanisms consume energy and contribute to the toughness of the composite. Which of them and to what extent actually occur during the failure of the material depends largely on the partial properties of the three microstructual elements of the composite: matrix, fiber, and interface, and on the geometrical arrangement and form of the reinforcement. No apparent matrix plastic deformation in this study was observed because the deformation zone was limited to the thin geometrical spacing between the SKF or N6P in the matrix resin. Due to poor interfacial bond strength between SKF or N6P and matrix resin, it was not expected to increase fracture toughness by debonding. To obtain a high crack resistance, the fracture mechanism should occur by fiber bridging and fiber fracture that can absorb large energy than the other[7,8].

The fracture surfaces for ENF test specimens were also examined by SEM. Fig.1 shows the fracture surface of the control sample. A clean fracture surface with a few hackle structures around the continuous fibers can be seen on the micrograph of the control sample. A large hackle structure always occurs in the brittle composite system subjected to in-plane shear loading.

The SEM fractrographs of the composite with SKF, Fig.2 to Fig.4, show that new surfaces were created in random direction without any fixed pattern. These include the fracture of the matrix, fiber debonding and fiber bridging. Therefore, SKF orientation would be expected to be placed at small angle or parallel to in-plane orientation. The SKF that was placed initially parallel to in-plane moved by resin flow during curing, oriented to other direction. In addition, as shown in Fig.3, many SKF were pulled-out by another interlocking SKF underneath and debonded from the matrix. There existed no hackle structure around pulled-out and fractured SKF. This implied that the matrix resin had little plastic deformation under shear loading. The fracture surface around debonded SKF showed the hackle due to the possibility of plastic deformation of the matrix. The fracture surface with N6P, Fig.5, showed debonding between N6P and the matrix with the hackle around N6P. Less hackle found around N6P for the fracture surface having SKF. Because the SKF constrained the plastic deformation of the matrix, the fibrillation and fracture of SKF were the evidence of SKF's bridging.

Effect of SKF or N6P on Gic

The only difference between Gic and Giic test[13] is the orientation of principal tensile stress under which microscopic failure occurs. The principal tensile stress during Gic and Giic tests is oriented at 90° and 45° to in-plane orientation. In general, the fracture plane in any loading condition of the carbon fiber/epoxy composite is perpendicular to the maximum resolved tensile direction. When the fibers lay perpendicular to the maximum tensile direction, a single cleavage plane parallel to the fibers results. The river pattern and feather pattern features found on mode I failure surface fall into this category. However, when the fibers are not perpendicular to the maximum tensile, the fracture plane intersects the plane of the fibers. the fiber plane generally restricts any further growth of the crack, resulting a series of parallel hackles in the region between the fiber plane.

In this study, most of the SKF in interlaminar layer was oriented between 45 ° and 90 ° to the principal stress' plane of mode I. The effect of fiber pull-out, fiber bridging, and fiber fracture was not expected. In addition, the carbon fabric used did not show any fiber bridging due to fabrication-induced fiber misalignment, since the specimen had uniform Gic values irrespective of the crack length. Fig.6 to Fig.9 show that the Gic values are low for all samples irrespective of the presence of SKF or N6P. The control had Gic of 0.5 kJ/m^2. For composites having SKF, both the increase in fracture surface area through SKF and the more tortuous path of crack growth would suggest greater resistance to crack growth for increasing mode I loading. A fairly large experimental scatter was noticeable on composites with SKF, probably due to the difficulty encountered in fixing the random orientation of SKF during resin curing. Thus, within the experimental scatter, very little effect with the amount of SKF was observed. SKF and N6P showed lower Gic values compared with SKF alone, but had smaller experimental scatter. N6P showed no improvement in Gic due to the poor bonding between N6P and matrix.

Effect of SKF or N6P on Giic

The orientation of some SKF shown in the SEM was placed to be parallel to the principal stress' plane of mode II. SKF's bridging means the bridged zone of unbroken fibers inclining and interconnecting the opposite fracture surfaces behind a crack tip. Therefore, SKF's bridging requires a higher load or more energy to produce the critical condition at the crack tip.

For fracture mechanics except fiber bridging[7,8], Gic and Giic are independent of crack length and thus also of the position of the pre-crack. In contrast, for the accurate computation of Giic values for materials in which substantial fiber bridging occurs, it is important to place the tip of aluminum foil pre-crack at the accurate center from support point to loading point in the loading fixture. This requirement is the case in this work since small difference in the initial crack length will result in values of changed Giic that are strongly dependent on the crack length.

Fig.10 and Fig.11 show that the Giic values exhibited a pronounced dependence for the specimens containing either 8.0 to 25.5 g/m^2 of SKF, or 8.0 to 17.0 g/m^2 of SKF and N6P. Typically, the Giic values were in the range of 1.0 - 4.0 kJ/m^2. It was observed that the values commenced well around 1.0 kJ/m^2 and rose sharply to the 3.0 - 4.0 kJ/m^2 range with increasing crack propagation. The visual inspection of the samples, after fracture, indicated that substantial SKF's bridging had occurred across the crack propagation. Thus, the fiber bridging is responsible for the increased Giic. It is possible that Giic of the laminate with SKF could be enhanced further if the tests were continued permanently. The Giic tests could not be continued due to the flexural mode fracture in the specimen when the crack tip passed beyond the loading point. But, Slepetz[13] found that the Gic value measured with fiber-bridged specimens showed an initial increase with crack length and then leveled off at a value more than double the value without fiber bridging. This stabilized energy level is thought to correspond to the full development of the fiber-bridged zone. Thus, For this system, the leveled-up Giic with crack length is expected

The results with 8.5 g/m^2 and 17.0 g/m^2 of SKF did not indicate any difference in Giic. The Giic of composites having 25.5 g/m^2 of SKF was lower than that with 8.5 g/m^2 and 17.0 g/m^2 of SKF. The out-of-plane orientation of SKF decreaseed due to the interference between SKF during resin curing by increased amount of SKF. The value of Giic was constant with crack length for the specimens containing 4.0 g/m^2 of SKF, 4.0 g/m^2 or 25.5 g/m^2 of SKF and N6P. In the case of 4.0 g/m2 of either SKF or SKF and N6P, the absolute amount of SKF oriented towards out-of plane was too small to have significant fiber bridging. 25.5 g/m2 of SKF and N6P had relatively large volume of N6P and prevented the orientation of SKF to out-of plane. The Giic of composites having SKF and N6P was lower than that of SKF alone because N6P had negative effect on the orientation of SKF to out-of plane. With N6P, Giic increased gradually with the amount added and showed lower values compared with similar case[2] due to the uneven distribution of N6P in the interleaf layer. One possible explanation for the uneven distribution of N6P was the manual sieving method adopted in this study.

The composite with SKF produced large improvement in Giic, but no increase in Gic. In addition, several researchers have shown Giic to have approximately linear correlation with compressive strength after impact values for composites[2,12]. Thus, the presence of SKF should correspond to a large improvement in composite impact properties.

Reference

1. Schulte, K.and Stinchcomb.B.B., Damage mechanism - including edge effects - in carbon fiber - reinforced composite materials. In Application of Fracture Mechanics to Composite Materials, ed. K.Friedrich. *Composite Materials*. vol. 6, Elsevier Science Publishers, Amsterdam, 1989
2. Evans, R.E., and Masters,J.E., A new generation of epoxy composites for primary structural applications: Materials and Mechanics. in *Toughened Composites*, ASTM STP 937, ASRM, Philadelphia (1987) 413-436
3. Zeng, S., Hoisington, M., and Seferis, J.C., Particular interlayer toughening of dicyanate matrix composites. *Poly Comp*, 14 (1993) 458-466
4. McGrail, P.T., and Jenkins, S.D., Some aspects of interlaminar thoughening: reactively terminated thermoplastic particles in the thermoser composites. *Poly*, 34 (1993) 677-683
5. Browning, C.E. and Schwartz, H.S., Delamination resistant composite concepts. in *Composite Materials. Testing and Design* (Seventh Conf.), ASTM STP 893, ASRM, Philadelphia (1986) 256-265
6. Lin, T.L. and Jang, B.Z., Mechanical prop. of hybrid composites containing both short and continuous fibers. *Ann. Tech. Conf. (ANTEC)*, 35 (1989)1552
7. Hung, X.N. and Hull, D., Effect of fiber bridging on Gic of a unidirectional glass/epoxy composite. *Comp. Sci. and Technol.*,35 (1989) 283-299
8. Xiao-Zhi Hu and Yiu-Wing Mai, Mode I Delamination and fiber bridging in carbon-fiber/epoxy composites with and without PVAL coating. *Comp. Sci. and Technol.*,46 (1993) 147-156
9. Min-Seok Sohn and Xiao-Zhi Hu., Mode II delamination toughening of carbon-fiber/epoxy composites with chopped kevlar fiber reinforcement. *Comp. Sci. and Technol.*, 52 (1994) 439-448
10. Zhao.S, Gaedke. M and Prinz.R., Mode II delamination behavior of carbon/epoxy composites. *Adv. Comp. Mater.*, 4 (1994) 111-127
11. Hashemi, S., Kinloch, A.J., and Williams, J.G., The analysis of interlaminar fracture in uniaxial fiber-polymer composite. *Proc. R. Soc.Lond.* A427 (1990) 173-199
12. John E.Masters., Improved impact and delamination resistance through interleafing. *Key Engineering Materials.*, 37 (1989) 317-348

13. Hibbs, M.F., and Bradley, W.L., Correlation between micromechanical failure processes and delamination toughness of graphite/epoxy systems. *Fractography of modern engineering materials: Composites and Metals*, ASTM STP 948, J. A. Masters and J.J. Au, Ed., ASTM, Philadelphia, (1987) 68-97
14. Slepetz, J. M., and Carlson, L., In *Fracture of Composite*. ASTM STP 593, 1975, 143-162

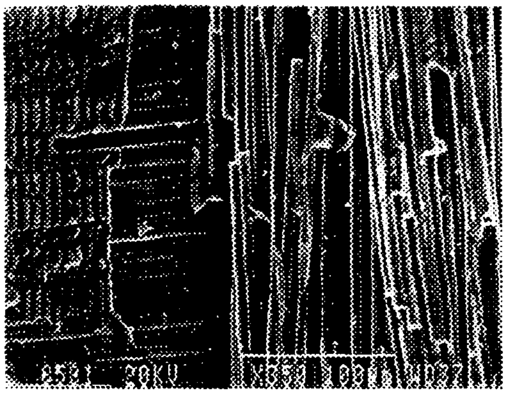

Fig.1 Mode II fracture surface of carbon/epoxy composite with no modifier

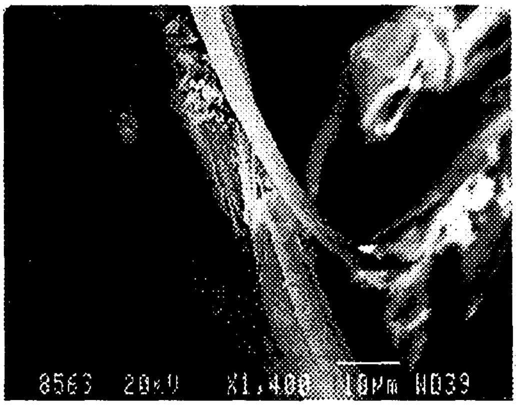

Fig.2 Fractured SKF by Mode II fracture of carbon/epoxy composite having SKF of 17.0 g/m^2

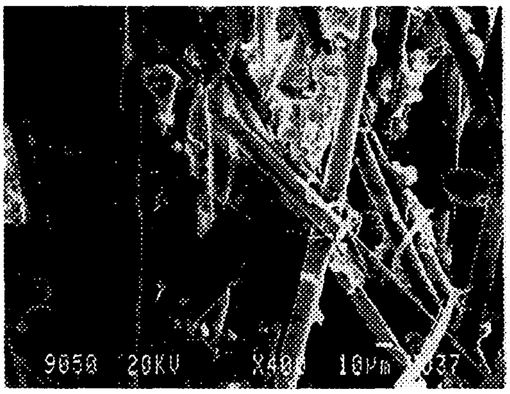

Fig.3 Pull-out of interlocking SKF by Mode II fracture of carbon/epoxy composite having SKF of 17.0 g/m^2

Fig.4 Fracture of SKF oriented in the z-direction by Mode II fracture of carbon/epoxy composite having SKF of 17.0 g/m^2

Fig.5 Debond between N6P and the matrix with hackle by Mode II fracture of carbon/epoxy composite having N6P of 17.0 g/m^2

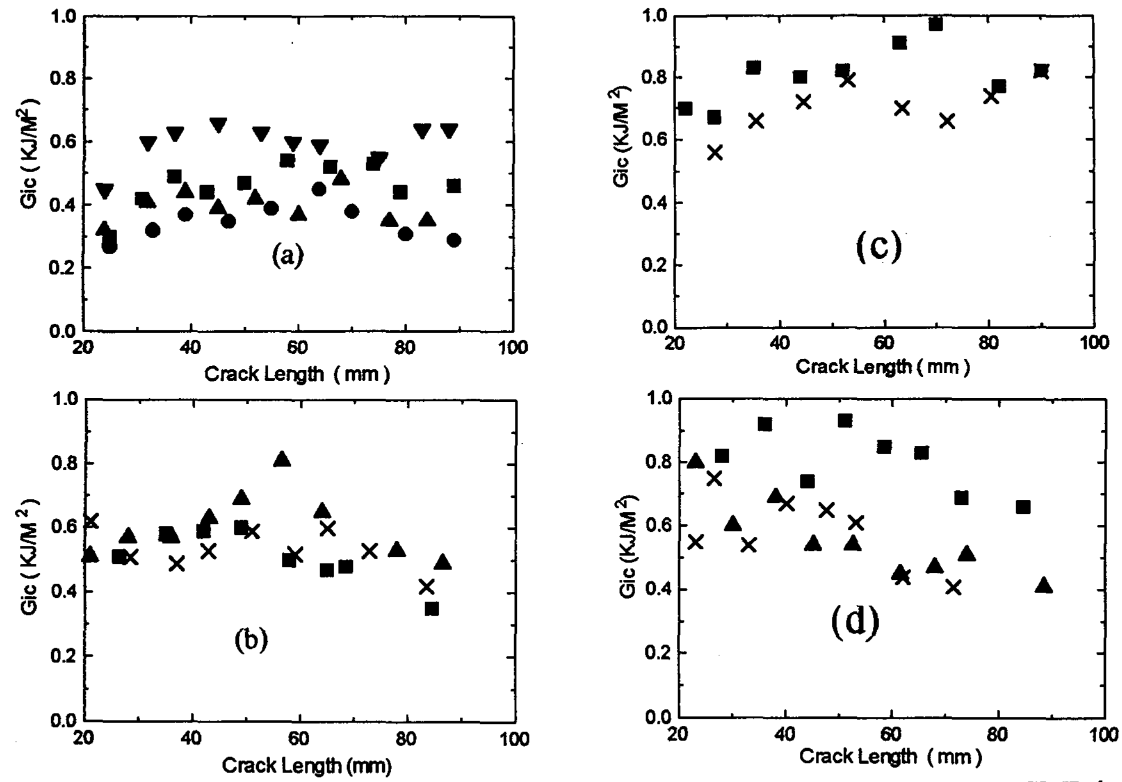

Fig.6 Mode I crack growth resistance of carbon/epoxy composite having SKF in varying amount (a: 4.0 g/m^2, b: 8.5 g/m^2, c: 17.0 g/m^2, d: 25.5 g/m^2)

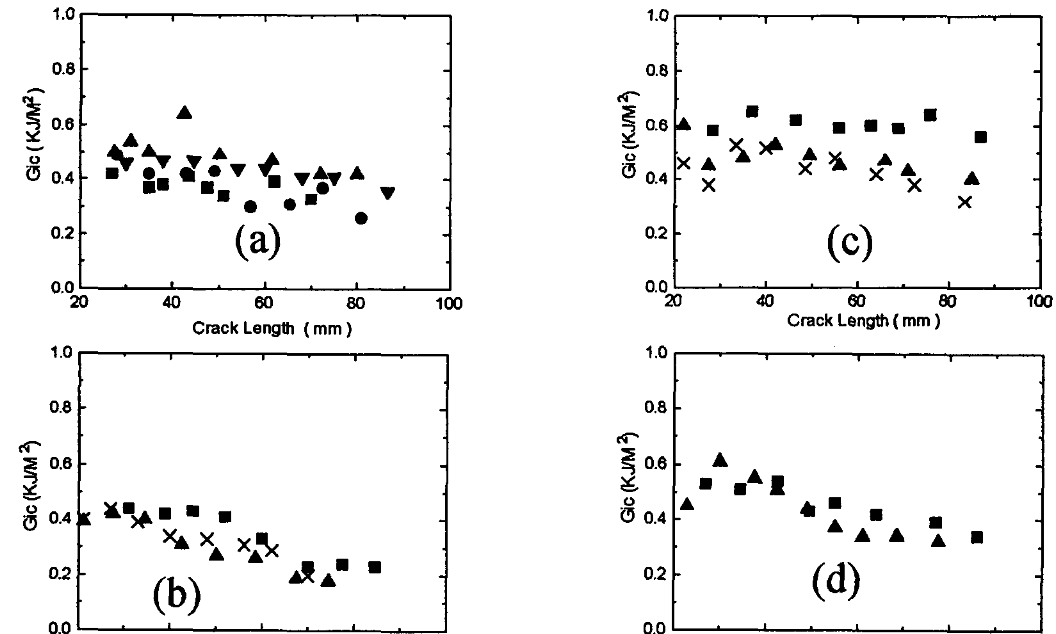

Fig.7 Mode I crack growth resistance of carbon/epoxy composite having SKF and N6P in equal weight ratio in varying amount
(a: 4.0 g/m^2, b: 8.5 g/m^2, c: 17.0 g/m^2, d: 25.5 g/m^2)

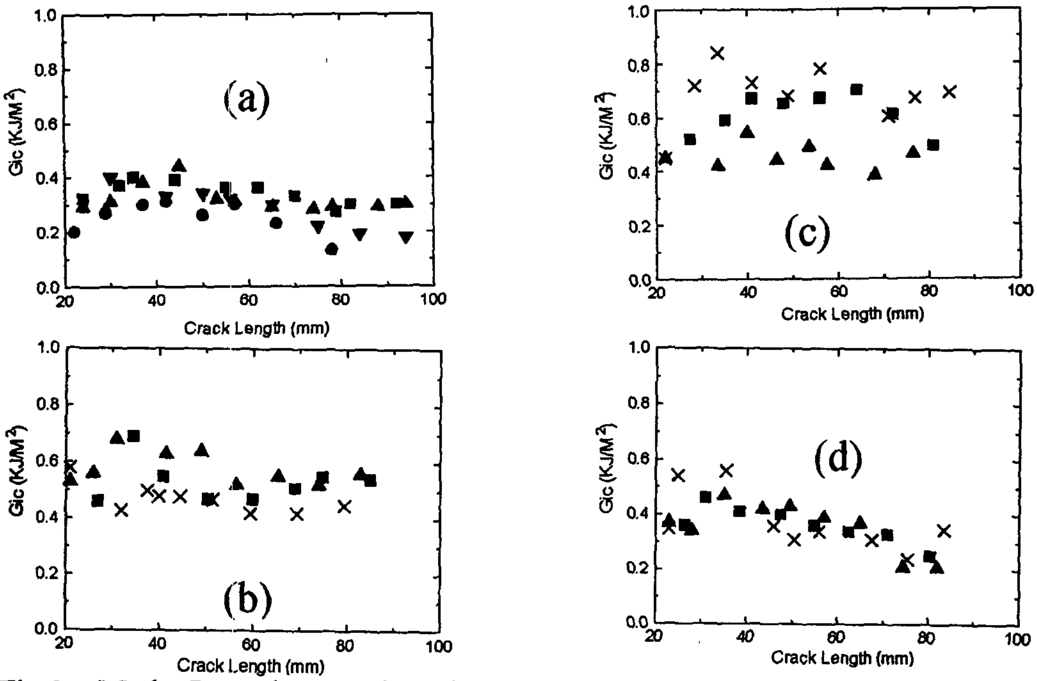

Fig.8 Mode I crack growth resistance of carbon/epoxy composite having N6P in varying amount
(a: 4.0 g/m^2, b: 8.5 g/m^2, c: 17.0 g/m^2, d: 25.5 g/m^2)

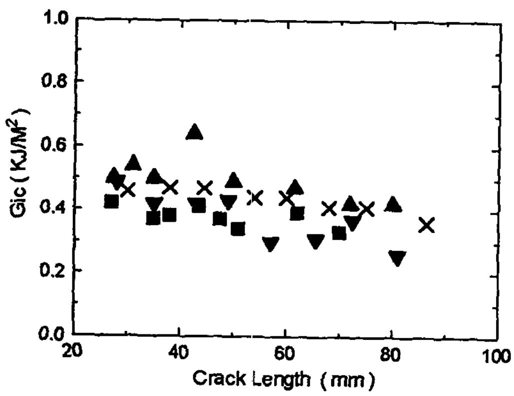

Fig.9 Mode I crack growth resistance of carbon/epoxy composite with no modifier

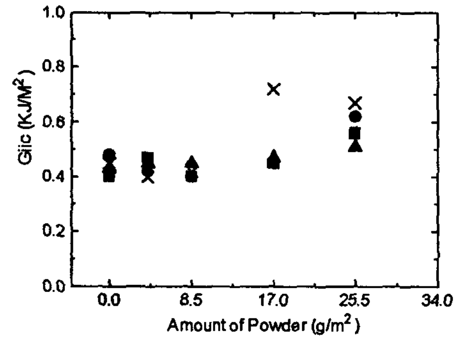

Fig.12 Mode II interlaminar fracture thoughness as a function of the amount of N6P modifier

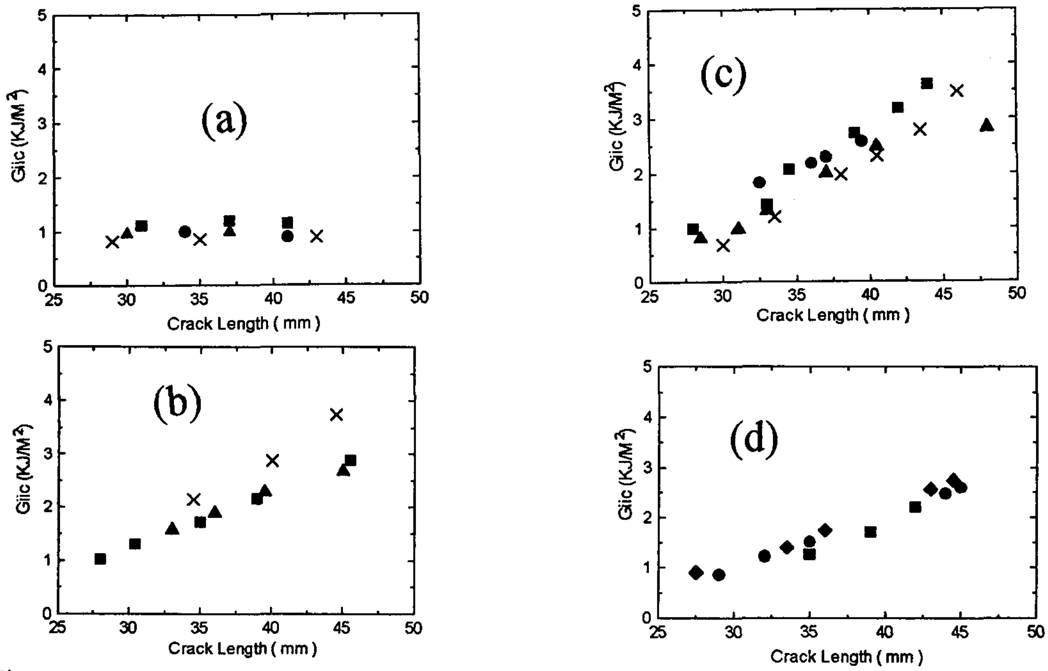

Fig.10 Mode II crack growth resistance of carbon/epoxy composite having SKF in varying amount
(a: 4.0 g/m^2, b: 8.5 g/m^2, c: 17.0 g/m^2, d: 25.5 g/m^2)

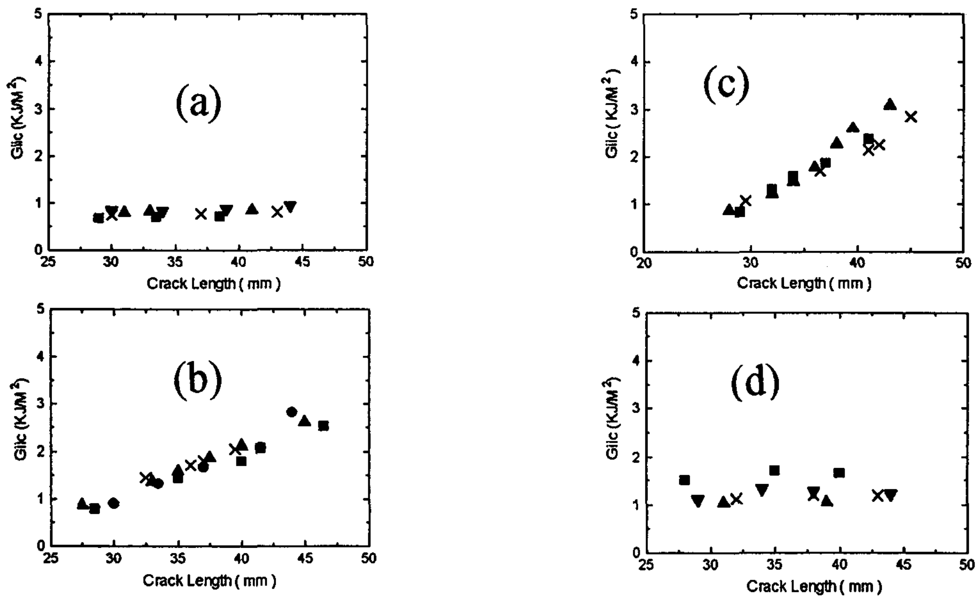

Fig.11 Mode II crack growth resistance of carbon/epoxy composite having SKF and N6P in equal weight ratio in varying amount
(a: 4.0 g/m^2, b: 8.5 g/m^2, c:17.0 g/m^2, d:25.5 g/m^2)