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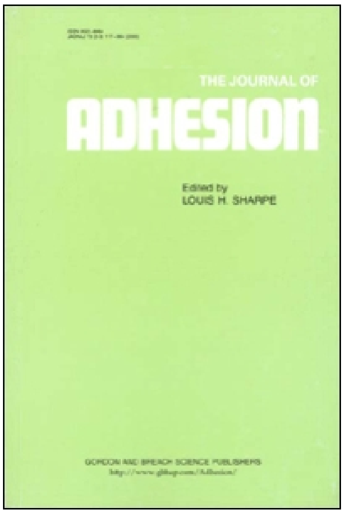

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Fracture Behaviour of Thermoplastic Modified Epoxy Resins*

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This work has shown that the addition of polyetherimide (PEI) can significantly increase the toughness of highly cross-linked epoxy resins, whilst retaining a high T_g and modulus. These combined properties indicate the potential of PEI modified epoxy resins for use as matrices for advanced composite materials. In terms of G_{IC}, addition of 20wt% PEI raised the toughness by a factor of eight. Evidence from SEM fracture surfaces suggests that the toughening mechanism operating in bulk PEI modified epoxy resin is ductile drawing of the PEI. Carbon fibre composites based on 30wt% PEI modified epoxy resin matrices show considerable improvement in toughness at low and high strain rates when compared with CFRP possessing unmodified or 20wt% modified PEI content epoxy resins.

KEY WORDS epoxy resin; thermoplastic modifier; polyetherimide; fracture toughness; CFRP; interlaminar fracture toughness.

1 INTRODUCTION

Highly cross-linked epoxy resins are used as the base material for carbon fibre reinforced composite materials (CFRP) because of their high elasticity, ability to withstand high temperatures and low water absorption. However, these epoxy resins display low resistance to fissure spread because of their extreme brittleness. Accordingly, the development of an advanced composite material for aerospace applications in which the toughness has been increased without sacrificing the superior cross-linking of epoxy resin has become a major objective.

It is known that rubber modification is extremely effective in toughening epoxy resin.[1-3] However, such rubber-modified epoxy resins have many drawbacks, such as high water absorption, poor heat resistance and a low elasticity ratio; moreover, it is not possible to improve the toughness of highly cross-linked epoxy resins.[4-5]

It has been proposed recently to increase the impact toughness and fracture

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toughness of highly cross-linked epoxy resins by modification using thermoplastic resins.[4,6,7] However, not enough is known to allow manufacturing applications of thermoplastic-modified epoxy resins as the base material for fibre-reinforced composite materials. In particular, it is important to determine the relationship between the cross-linking structure and phase separation configuration of epoxy resins on one hand, and the breakdown fracture toughness which is so important for the strength of the material on the other.

In the research reported on in this paper, we modified epoxy resin using a highly heat resistant thermoplastic polyetherimide resin (PEI, $T_g = 213°C$), and studied the effect exerted by the cross-linking density on breakdown fracture toughness and phase separation configuration in the resultant material. In addition, we made CFRP using these resins and evaluated interlaminar fracture toughness G_{IC} and G_{IIC}, as well as perforation impact characteristics.

2 EXPERIMENTAL METHOD

Figure 1 shows the tri-functional p-aminophenol epoxy resin (ELM-100) and the bi-functional bisphenol epoxy resin. By varying the proportions of the mixture, the density of the cross-linking in the resultant material was adjusted. The thermoplastic polyetherimide (PEI, ULTEM 1000) was used as the modifier, and Dicyandiamide (Dicy) was used as the curing agent. The test material was prepared in bulk by dis-

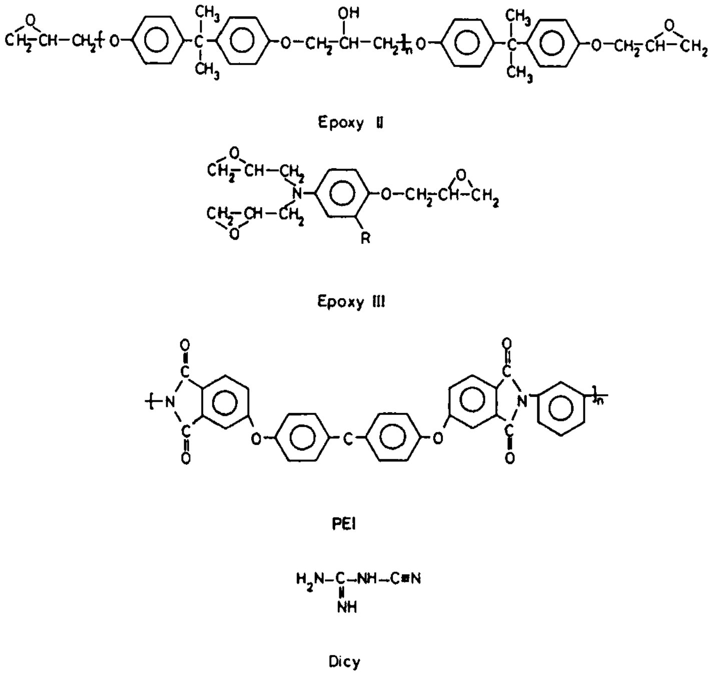


FIGURE 1 Chemical structures of epoxy resins, thermoplastic modifier and curing agent.

solving the PEI resin in five times the volume of methylene chloride, and after mixing with a set amount of epoxy resin and Dicy curing agent (six parts per hundred parts of epoxy resin), the methylene chloride was driven off by eight hours of reduced pressure evaporation at 95°C, and the material cured in a thermostatic bath for four hours at 150°C, and two hours at 200°C. CFRP was prepared using trifunctional epoxy resin (ELM-1000) and PEI and cross-woven carbon fibre. The fibre volume of the composite material was around 53%.

For the purpose of the CFRP interlaminar fracture test, delamination film was interposed at the layering stage, and the delamination section was artificially arranged. For the bulk material fracture toughness test, the compact tension specimen shown in Figure 2 was used, and an Instron tension test machine was used employing the ASTM E-399-72 method, with a cross-head speed of 0.5 (mm/min) at an atmospheric temperature of 23 ± 2°C.

$$K_{IC} = \frac{P}{B\,W^{1/2}} \cdot F \tag{1}$$

Here, P is load, B is the thickness of the test specimen, W is the width of the test specimen, and F is the shape factor. G_{IC} of the test material was derived by calculation using Equation 2.

$$K_{IC}^2 = EG_{IC} / (1 - V^2) \tag{2}$$

Here, E is the modulus of elasticity, and V is the Poisson ratio (here a value of 0.4 was used).

For the interlaminar fracture test, specimens shaped as shown in Figures 3 and 4 were used, in an Instron test machine, in accordance with recommendations of ASTM Committee D30.02, at an atmospheric temperature of 23 ± 2°C and a cross-

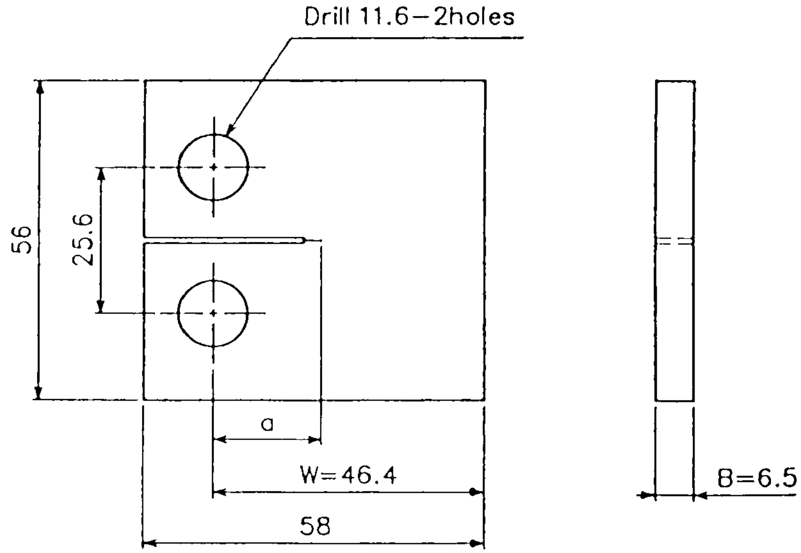
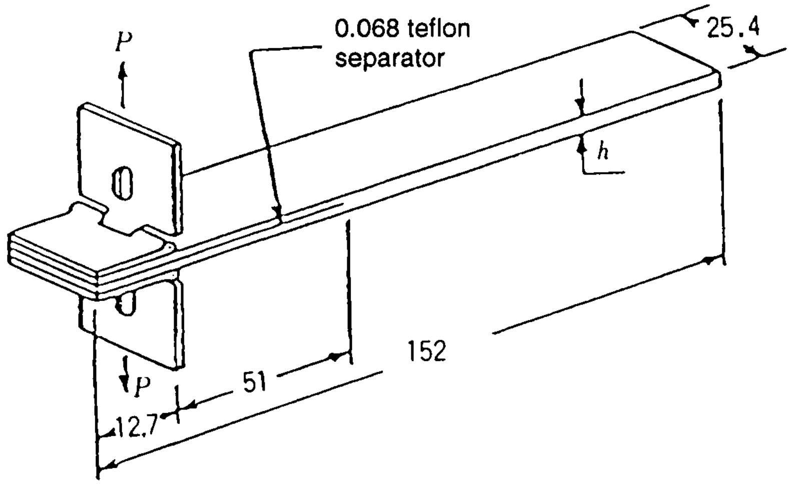
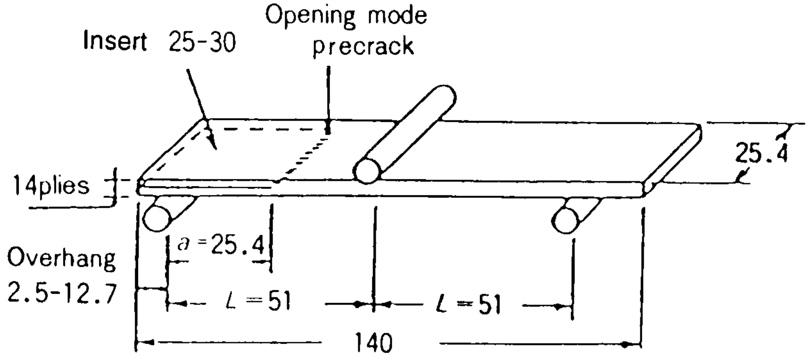


FIGURE 2 Compact-tension specimen used for crack growth studies (all dimensions in mm).



$$G_{\mathrm{Ic}} = \frac{P_c^2}{2b} \cdot \frac{nC}{a} = \frac{P_c n\delta}{2b \times a}$$

FIGURE 3 Double cantilever beam test set-up; Mode I (all dimensions in mm).



$$G_{\mathrm{IIc}} = \frac{9a^2 P_c^2 C}{2b(2L^3 + 3a^3)}$$

FIGURE 4 Edge notch flexure test set-up; Mode II (all dimensions in mm).

head speed of 0.5 (mm/min), and values were obtained for separation toughness G_{IC} and internal shear peeling toughness G_{IIC}. G_{IC} was calculated according to Equation 3.

$$G_{IC}=\frac{P_c n\,\delta}{2\,ba} \tag{3}$$

Here, P_c is load, δ is DCB opening deformation, b is the thickness of the test specimen, and a is the length of the interlaminar peel section.

G_{IIC} was calculated according to Equation 4.

$$G_{IIC}=\frac{9a^2\,Pc^2\,C}{2b\,(2L^3+3a^3)} \tag{4}$$

Here, C is compliance, and L is the length of load point interval.

For the CFRP perforation impact test, a Dynatup hanging weight impact test device with a 6.4 mm diameter striker was used, the impact speed was variously changed, and the perforation load and perforation energy respectively were calculated by means of computer processing. The test sample was 3 mm thick, 40 mm across and 60 mm long. Observation of the phase separation configuration of the fracture surface was made using a scanning electron microscope, and the mechanism of toughening was examined.

3 RESULTS AND OBSERVATIONS

Figure 5 shows the effect on glass transition temperature T_g of mixing bi-functional and tri-functional epoxy resins with both unmodified epoxy resin and 20wt% PEI modified epoxy resin. For both unmodified and modified systems, as the proportion of tri-functional epoxy resin increases, that is to say as the cross-link density increases, T_g increases. In the PEI modified system too, in the areas of high cross-link density, a high value of 200°C is shown. In terms of heat resistance, it is necessary to use an epoxy resin with high cross-link density containing a high proportion of tri-functional epoxy resin as the base material for composite materials.

BENDING MODULUS

Figure 6 shows the relationship between bending modulus and the amount of bi-functional and tri-functional epoxy resin combined with 20wt% PEI modified epoxy resin. As the amount of tri-functional epoxy resin decreases, that is to say as the density of cross-linking decreases, bending modulus decreases. Furthermore, as the proportion of PEI increases, fracture toughness decreased slightly.

Fracture Toughness

Figures 7 and 8 show the values of fracture toughness and fracture energy K_{IC} and G_{IC} for unmodified epoxy resin and 20wt% PEI modified epoxy resin in relation to

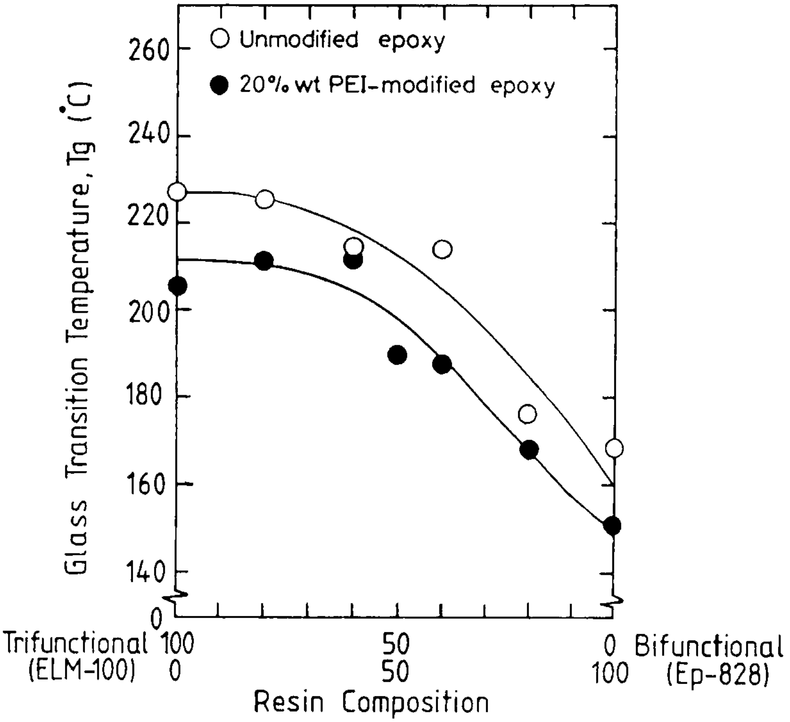


FIGURE 5 Effect of resin composition on temperature of tan δ peaks of unmodified and 20%wt PEI-modified epoxy resins.

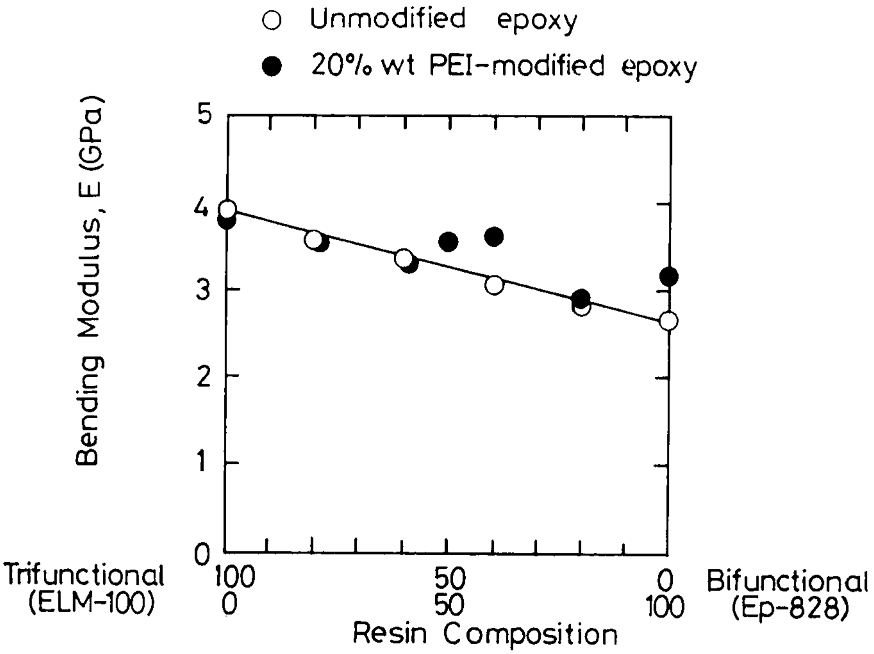


FIGURE 6 Effect of resin composition on Young's modulus of 20%wt PEI-modified epoxy resins.

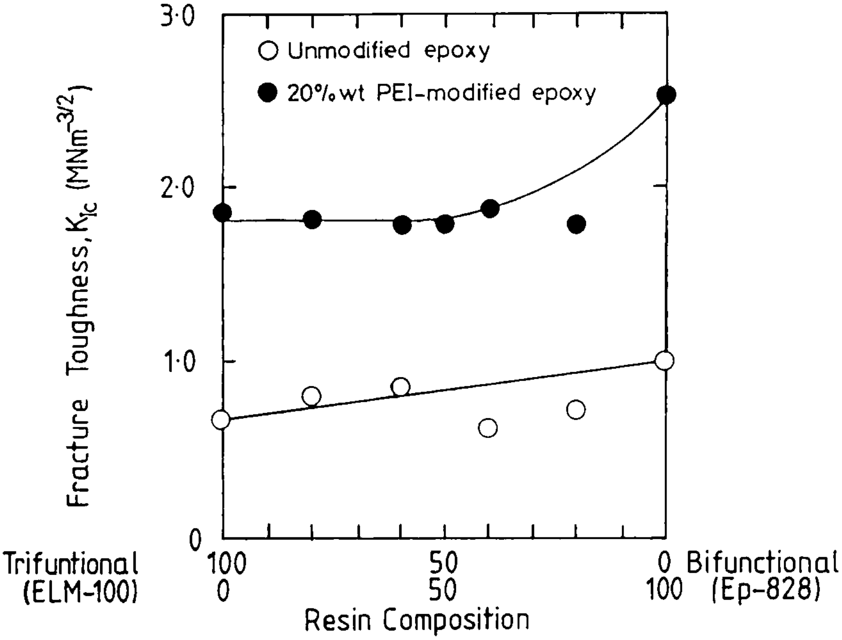


FIGURE 7 Effect of resin composition on K_{IC} of epoxy blends.

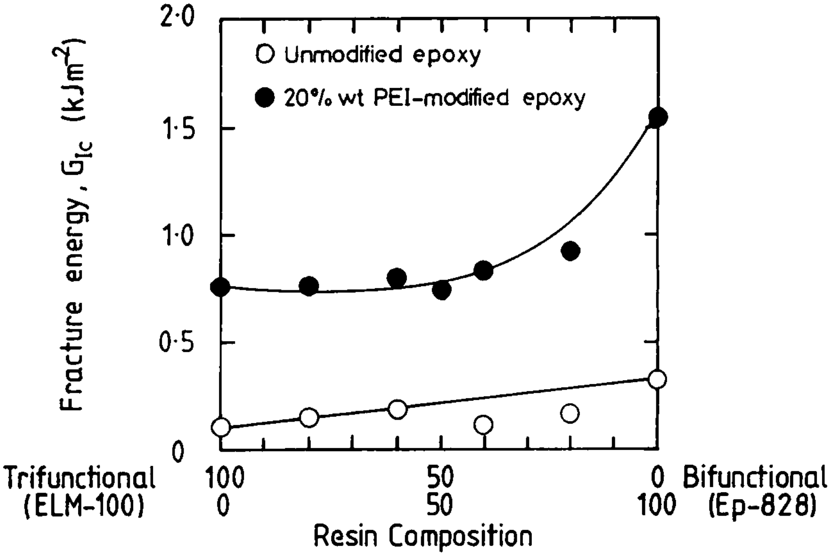


FIGURE 8 Effect of resin composition on G_{IC} of epoxy blends.

the proportion of bi-functional and tri-functional epoxy resin in the mixture. As a result of PEI modification, the fracture toughness K_{IC} is approximately four times that of unmodified resin, whilst fracture energy G_{IC} is about eight times higher, so a remarkable increase in toughness is possible using thermoplastic resins. An interesting point is that if we exclude the system with the lowest degree of cross-linking, K_{IC} is shown not to depend on the degree of cross-linking. Figure 9 shows the relationship between PEI content and K_{IC} in the system with the highest cross-link density. Where the PEI content is less than 10wt% there is almost no effect, but in 20wt% modified systems, the fracture toughness increases markedly. In 30wt% modified systems, there is a slight drop in fracture toughness compared with the 20wt% system, but no major difference. It is understood that the effect of modification will not be obtained unless PEI is added at 20wt% or greater.

Morphology

Figure 10 is a SEM micrograph of the fracture toughness test surfaces for 20wt% PEI modified epoxy resin containing different proportions of bi-functional and tri-functional epoxy resins. The micrographs on the right show the effects of etching with methylene chloride.

Epoxy resin does not dissolve in methylene chloride, but PEI does. According to these micrographs, it is clear that in the case of thermoplastic resin-modified epoxy resin, phase inversion occurs with the low weight ratio PEI forming the matrix level, and the high weight ratio epoxy resin forming the spherical domains.

Inoue and others report that they observed distinctive scattering maxima according to SD analysis when carrying out light scattering tests on polyether sulfone/

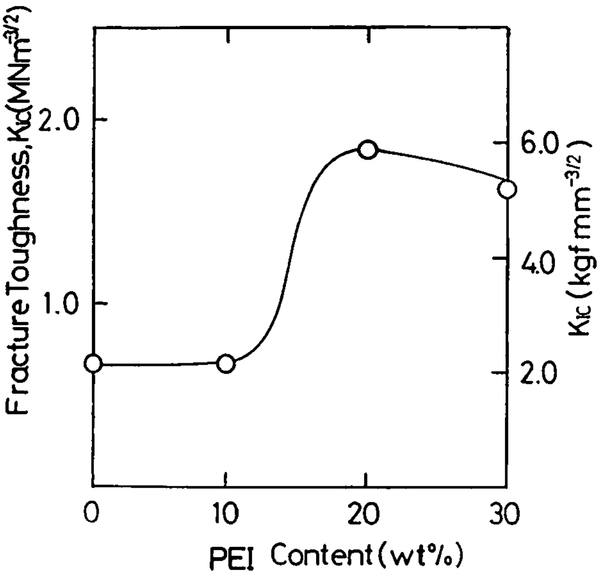


FIGURE 9 Effect of PEI content on K_{IC} of the epoxy blend 10/0.

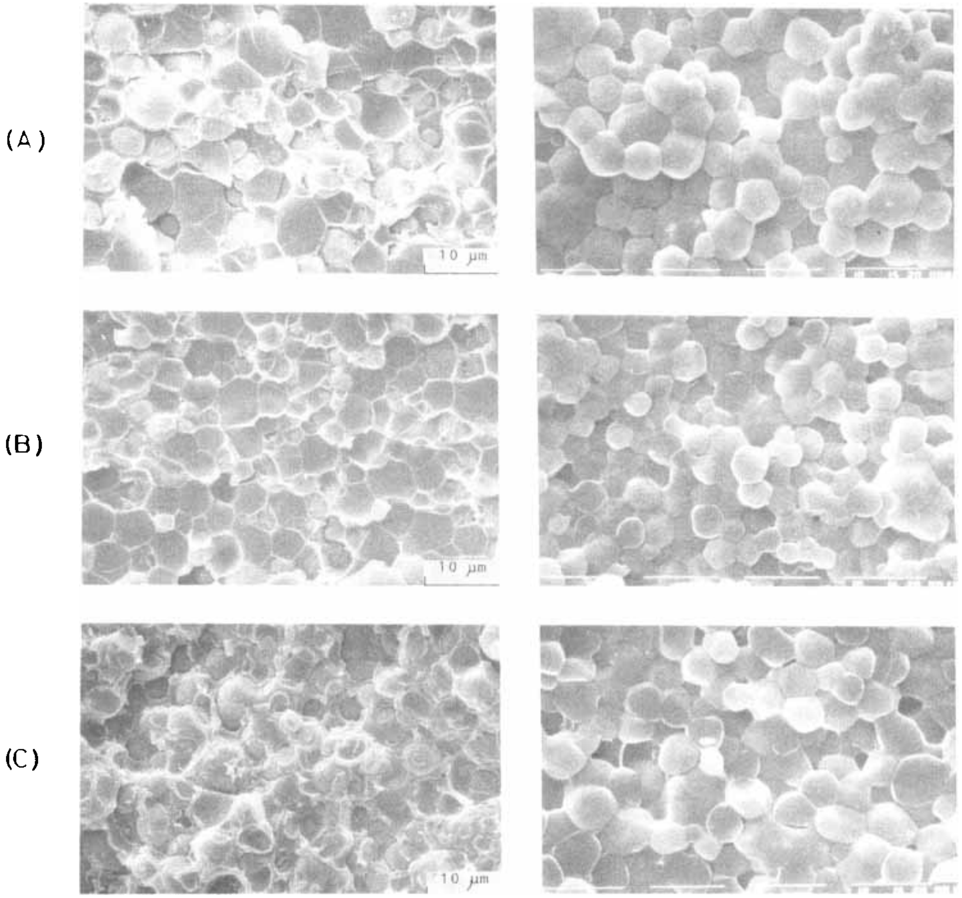


FIGURE 10 Scanning electron micrographs of fracture surfaces for 20wt% ULTEM-modified epoxy resins containing: (a) Trifunctional/Bifunctional = 10/0 (ELM-100) (EP828); (b) Trifunctional/Bifunctional = 5/5; (c) Trifunctional/Bifunctional = 0/10. Left hand side: no treatment. Right hand side: after immersion in methylene chloride.

epoxy systems, and that the epoxy spherical domains, with spheroids of uniform diameter, were interconnected, and distributed throughout the thermoplastic resin matrix in an extremely systematic arrangement.[8] It is clear that exactly the same phase separation is caused in PEI/epoxy systems too. In other words, in PEI/epoxy systems the ductile PEI forms the base material, and the toughening mechanism depends on the ductile drawing of the PEI.

As Figure 11 shows, it is clear that if the PEI does not exceed 20wt%, this phase inversion does not occur. The rapid increase in PEI systems of 20wt% (see Figure 9) can be said to be related to this. Additionally, the spheroids in the epoxy domains of 30wt% systems are slightly smaller than those of 20wt% systems.

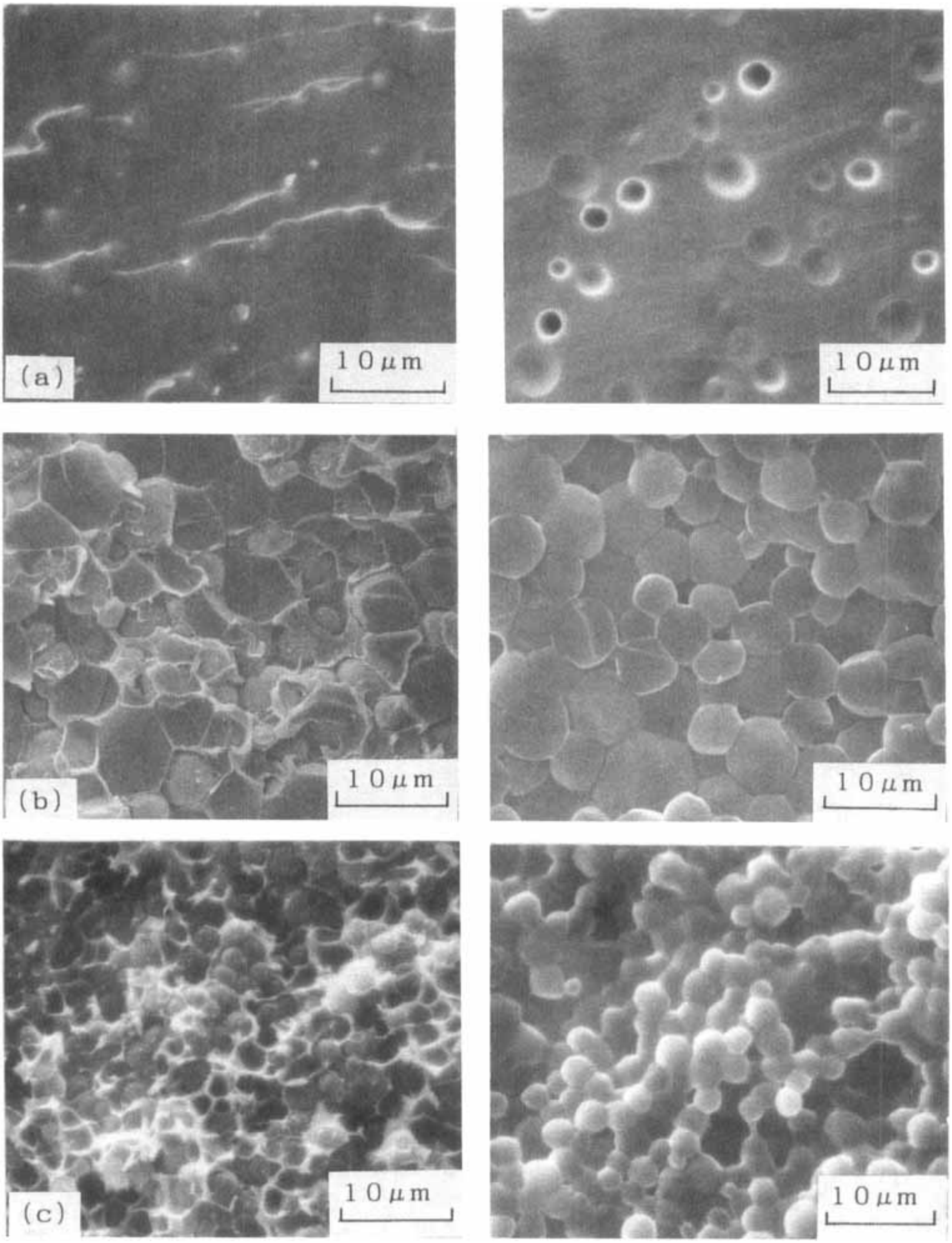


FIGURE 11 SEM of fracture surfaces for ULTEM modified epoxy resins with various ULTEM contents: (a) 10wt%, (b) 20wt%, (c) 30wt%. Left hand side: no treatment. Right hand side: after etching in methylene chloride.

Delamination Toughness of CFRP

Figure 12 shows the relationship between load (P) and aperture displacement deflection (δ) in delamination toughness tests. In unmodified CFRP the lowest separation load is shown. However for 20wt% and 30wt% modified epoxy systems, we find almost no difference. Figure 13 shows the log-log plot of the relationship between delamination length (a) and compliance, which in turn was derived from the relationship between P and δ. Both CFRP displayed linear relationships, and the gradients of these lines n, when substituted in Equation 3, allow G_{IC} to be derived.

Table I shows the results of interlaminar fracture toughness values G_{IC} and G_{IIC}. The G_{IC} of composite materials shows a value for PEI modification approximately 2.5 times that of unmodified systems. G_{IIC} on the other hand shows a fifty percent increase as a result of PEI modification. Even when the PEI modification was varied from 20wt% to 30wt%, G_{IC} and G_{IIC} show almost no change in value. This result correlates closely to the fracture toughness results of bulk resin (See Figure 9).

The interlaminar fracture toughness values for PEI modified resins obtained in these experiments are less than those of PEEK system CFRP, but in comparison with other CFRP used as base materials (Polysulfone, PEI) they are not much inferior.[10] Speaking from the point of view of mouldability, thermoplastic resin-

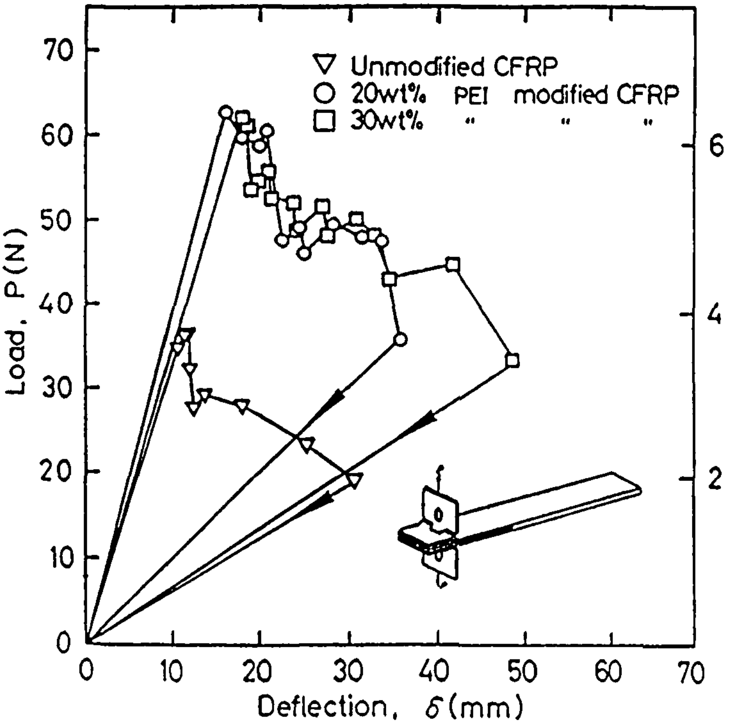


FIGURE 12 Typical load-deflection curves of unmodified and PEI-modified CFRP obtained from DCB tests.

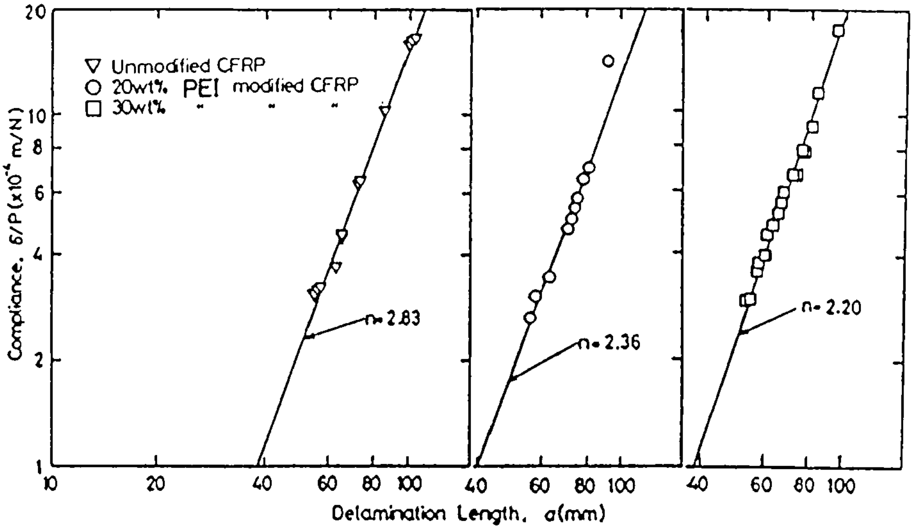


FIGURE 13 Typical relationships of compliance *vs* delamination length of unmodified and PEI-modified CFRP obtained from DCB tests.

TABLE I
Results of interlaminar fracture toughness tests

Materials	n	Separation force, Pc (N)	Delamination length, a (mm)	Compliance, C (mN^{-1})	G_{IC} (Jm^{-2})	G_{IIC} (Jm^{-2})
Unmodified Composite	2.83	34.8	55.0	3.10×10^{-4}	358.4	1632.7
20wt% PEI modified Composite	2.36	62.7	56.0	2.59×10^{-4}	820.3	2382.2
30wt% PEI modified Composite	2.20	61.8	53.7	2.96×10^{-4}	868.9	2249.8

modified epoxy is much better as a base material than CFRP using thermoplastic resin as the base material. From now on, research into the modification of epoxy with thermoplastic resin (polymer alloy) is likely to increase.

Perforation Strength of CFRP

Figure 14 shows examples of impact load and energy *versus* time plots. For each system, the load-time curve shows many load peaks. These load peaks correspond to the propagation and termination of fractures (interlaminar fracture, fibre breaks, etc.) within the CFRP.[9]

Table II shows a compilation of impact test results. The values for peak force and energy absorbed at peak force do not show any benefits from PEI modification. However, total energy absorbed does show good results as a result of PEI modification. Figure 15 shows a plot of total energy absorbed *versus* incident energy. In both

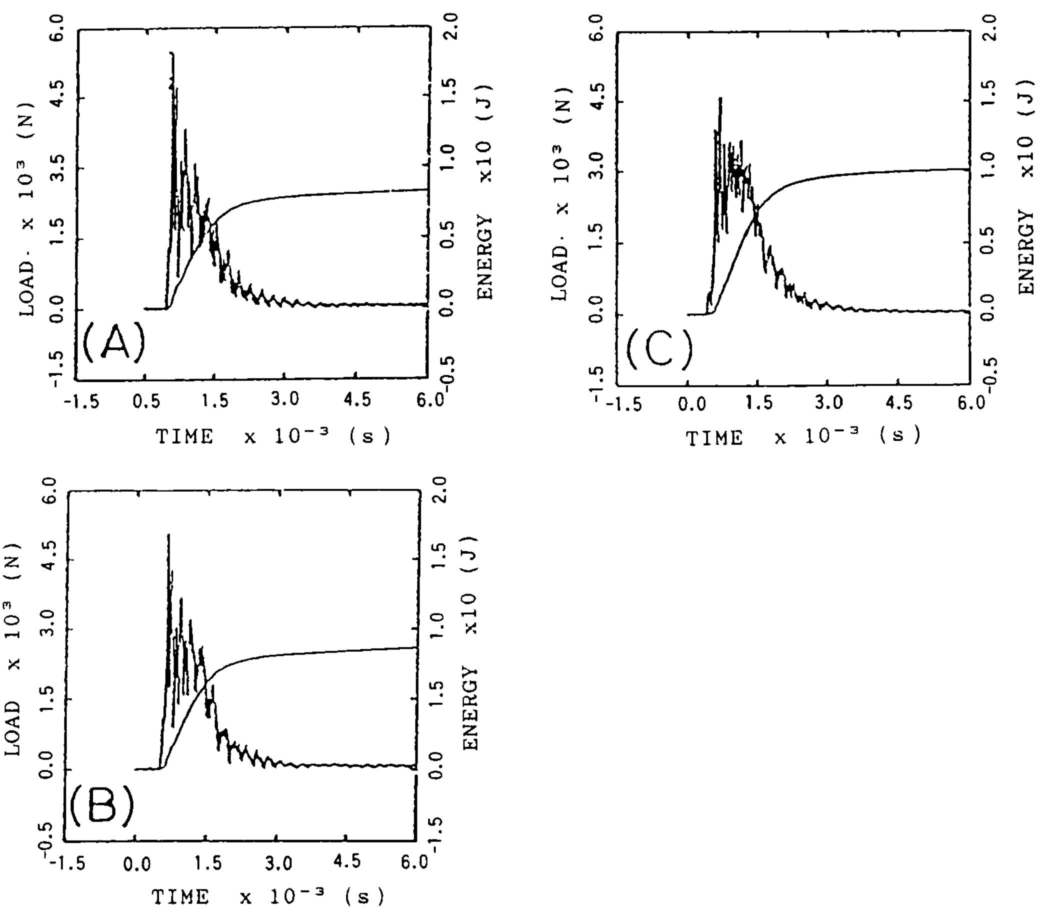


FIGURE 14 Typical load and energy *vs* time plots obtained from impact tests: (A) unmodified CFRP, (B) 20wt% PEI-modified CFRP and (C) 30wt% PEI-modified CFRP.

TABLE II
Impact test parameters for various CFRP impacted at 2.97 m/s

Materials	Average thickness (mm)	Mean peak force (N)	Energy at maximum force (J)	Total energy absorbed (J)
Unmodified Composite	3.14	5.09×10^3 (0.35)	0.467 (0.58)	8.04 (0.36)
20wt% PEI modified Composite	3.03	4.94×10^3 (0.16)	0.461 (0.04)	8.33 (0.63)
30wt% PEI modified Composite	2.99	4.45×10^3 (0.53)	0.486 (0.08)	10.19 (0.75)

(   ): Data reported as the standard deviation.

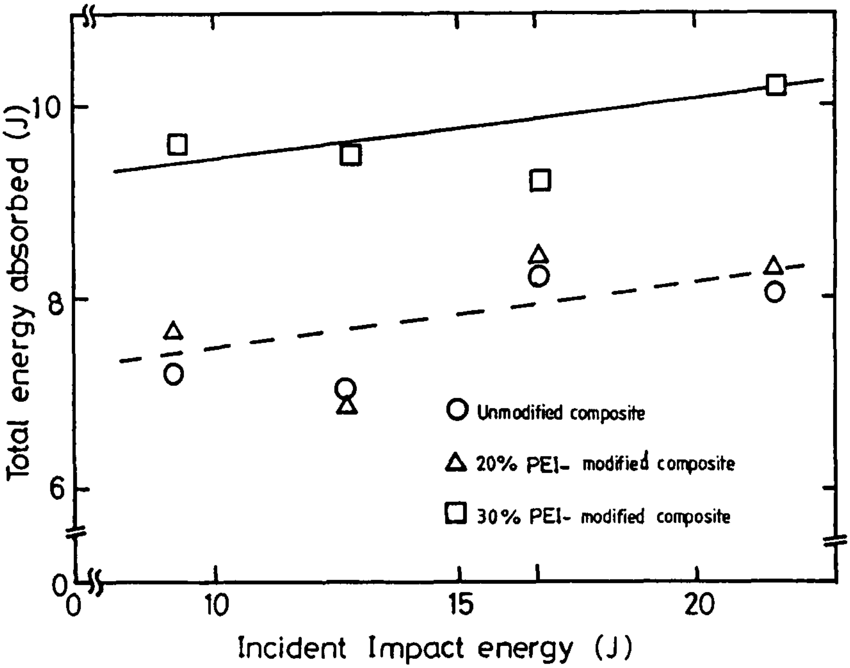


FIGURE 15 A plot of total energy absorbed *vs* incident energy for (a) unmodified CFRP, (b) 20wt% PEI-modified CFRP and (c) 30wt% PEI-modified CFRP.

CFRP there is a tendency for a drop in incident energy to be accompanied by a slight fall in the amount of total energy absorbed. Furthermore, when the PEI modification amount does not reach 30wt%, the benefits of PEI modification do not appear. At 20wt% modification and 30wt% modification the fracture toughness values for both bulk test material and composite material were much greater than those for unmodified material but, in this kind of impact testing, the fact that only 30wt% PEI modified systems showed any benefit is extremely noteworthy. Figure 16 shows the fracture surface configuration after interlaminar fracture testing. Whilst phase separation occurs topically in 20wt% PEI modified systems, in 30wt% modified systems phase separation can be seen to have occurred over the whole of the fracture surface. This kind of difference in phase separation configuration is thought to be the difference which arose in total absorbed energy in impact testing. The fact that the phase separation configuration of PEI/epoxy systems differs between bulk resin and CFRP is thought to be caused by the relative difficulty of bringing about phase separation by means of spinodal decomposition because of the small space between fibres in CFRP. However, as shown in bulk material, (see Figure 11) compared with 20wt% systems, 30wt% systems bring about phase separation in CFRP more easily because of the smaller particle diameter in the epoxy domain.

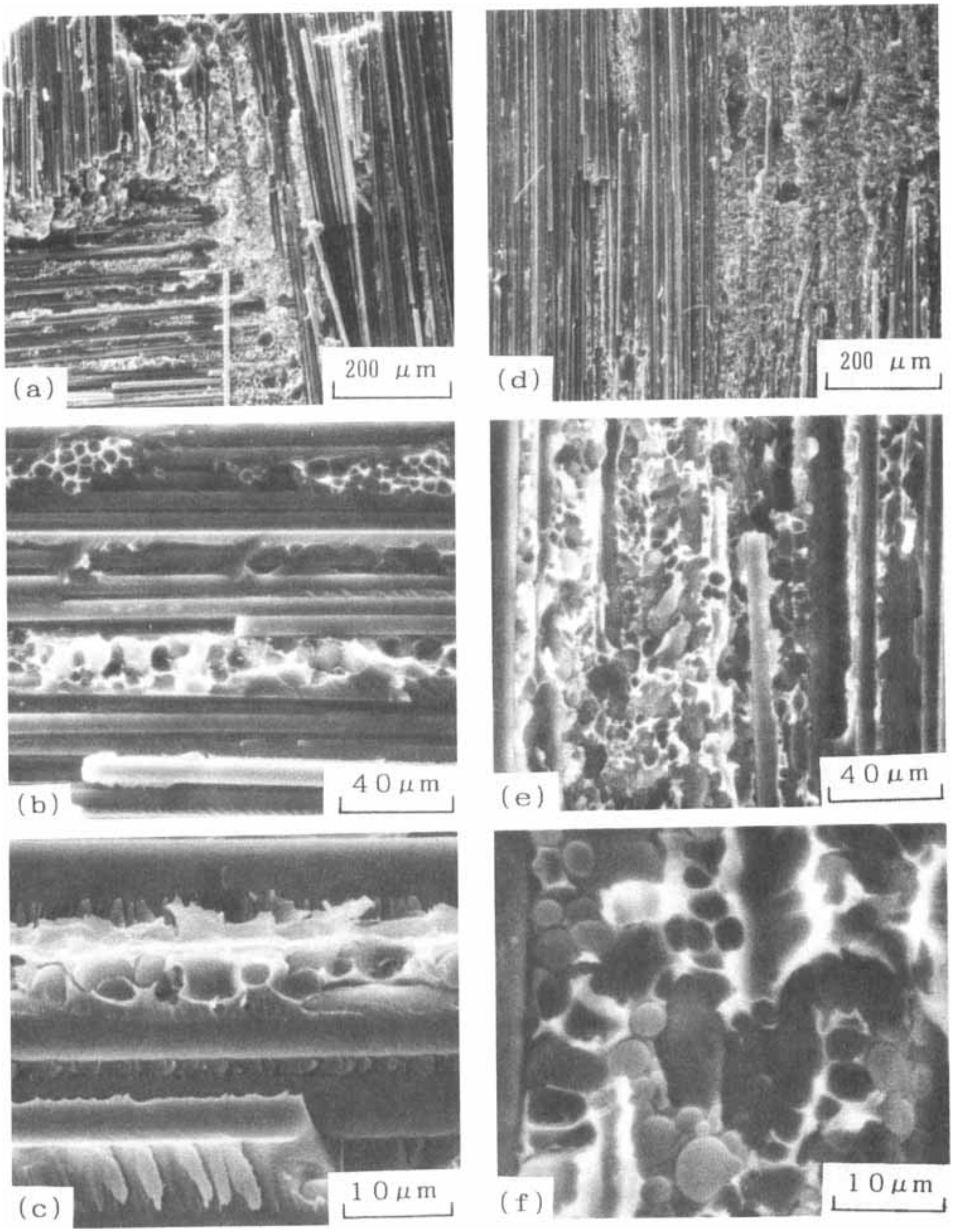


FIGURE 16 SEM of interlaminar fracture surfaces at different magnifications of CFRP containing (a)–(c) 20wt% ULTEM. (d)–(f) 30wt% ULTEM.

4 CONCLUSIONS

As a result of studying thermoplastic resin PEI (ULTEM) modified epoxy resin and its fracture behaviour in CFRP, the following results were obtained:

1. Modification with thermoplastic resin PEI is effective in toughening highly cross-linked epoxy resin, and the G_{IC} value can be increased by a factor of eight.
2. The toughening effect of PEI is caused by ductile PEI forming the matrix as a result of epoxy-rich domain particle deposition caused by phase inversion.
3. As a result of measuring interlaminar fracture toughness G_{IC} and G_{IIC} of CFRP, it was determined that PEI modification is effective for CFRP also, and it is possible to increase the value of G_{IC} by a factor of 2.5.
4. In CFRP impact testing PEI modification of less than 30wt% is ineffective. This is caused by differences in epoxy and PEI phase separation configuration in bulk resin and CFRP.

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References

1. W. D. Bascom, R. L. Cottington, R. L. Jones and P. Peyser, *J. Appl. Polym. Sci.* **19,** 2545 (1975).
2. S. C. Kunz, J. A. Sayre and R. A. Assink, *Polymer* **23,** 1897, (1982).
3. A. J. Kinloch, S. J. Shaw, D. A. Tod and D. I. Hunston, *Polymer* **24,** 1341 (1983).
4. A. Murakami, T. Ioku, D. Saunders and T. Yoshiki, *The Proceeding of Durability of Polymer Based Composites for Structural Application* (Elsevier Applied Sci., Belgium, 1990), p. 202.
5. R. A. Pearson and A. E. Yee, *Tough Compos. Mater. Recent Dev.* (Noyes Publishing, Park Ridge, NJ, USA, 1987), p. 157.
6. C. B. Bucknall and A. H. Gilbert, *Polymer* **30,** 213 (1989).
7. R. S. Bauer, H. D. Stenzenberger and W. Romer, *35th International SAMPE Symposium,* April 2–5, p. 395 (1990).
8. K. Yamada and T. Inoue, *Polymer,* **30,** 663 (1989).
9. C. K. L. Davies, S. Turner and K. H. Williamson, *Composites* **16,** 279 (1985).
10. D. L. Hunston, *Compos. Tech. Rev.* **6,** 176 (1984).