JOURNAL OF MATERIALS SCIENCE 27 (1992) 5108–5112

# Evaluation of interfacial properties between carbon fibres and semicrystalline thermoplastic matrices in single-fibre composites

N. OGATA, H. YASUMOTO, K. YAMASAKI, HU YU, T. OGIHARA,
T. YANAGAWA, K. YOSHIDA
*Department of Materials Science and Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910, Japan*

Y. YAMADA
*Central Research Laboratories, Idemitsu Kosan Co., 1280 Kami-Izumi, Sodegaura, Chiba 299-02, Japan*

The interfacial properties between pitch-based carbon fibre and semicrystalline thermoplastic matrices have been investigated by using the fragmentation test on single-fibre composites. For this purpose, fibres with seven different degrees of surface oxidation were prepared. From the fragmentation test, it was found that oxidization of carbon fibre reduces the fibre fragment length. Further, the length is also influenced by the nature of resin used as matrix. The morphology of crystallites formed on the fibres has been studied. Based on these results, the interfacial properties of carbon fibre and thermoplastic resins are discussed.

## 1. Introduction

The thermosetting polymers such as epoxy and unsaturated polyester resins have been used as matrices in polymeric composites. Recently, high-heat-resistant semicrystalline thermoplastic resins, such as polyphenylene sulphide (PPS), polyetheretherketone (PEEK) have been developed. These high-quality thermoplastics are expected to be used as matrices in polymeric composites for further generation of aerospace and engineering materials because of their high processability and good mechanical properties. A review of the development of thermoplastic composites and processing methods used to fabricate the fibre-reinforced composites has been given by Chang and Lees [1].

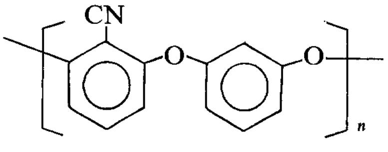
In any fibre-reinforced resin, tensile stresses applied to the composites are transmitted to the fibre through the fibre–matrix interface. Consequently, the condition of the interface plays an important role in controlling the mechanical properties of composites. Many attempts have been made previously to evaluate the stress transfer [2–11]. One of these studies is based on the measurements of fibre pull-out lengths or the fibre fragment lengths of a stressed specimen, which consists of a single fibre embedded in a thermosetting resin. Although the latter method is potentially less complex and less ambiguous in the interpretations, the method have been little applied to the high-quality thermoplastic composites, compared to thermosetting composites.

The aim of this study was to discuss qualitatively the influence of surface oxidized treatment of pitch-based carbon on fragment length of fibre in semicrystalline thermoplastic composites and to investigate the effects of the chemical structure of resins on the interfacial properties between carbon fibre and thermoplastic matrices, using the single-fibre composites.

## 2. Experimental procedure

Seven types of pitch-based carbon fibres with different degrees of surface treatment were prepared. The degree of oxidization was evaluated with the aid of X-ray photoelectron spectroscopy (XSP) [12]. Surface oxygen concentrations of these fibres were estimated from the areas of the peak attributed to $C_{1s}$ and $O_{1s}$, correcting for the elemental sensitivities, that is, the degree of oxidation was estimated by the value of $O_{1s}/C_{1s}$; this value will be referred to simply as O/C. In the following discussion, Samples S1 and S7 indicate the untreated carbon fibre (O/C = 0.08) and the maximally treated carbon fibre (O/C = 0.32), respectively. The mechanical properties of the fibres were also measured on monofilaments at room temperature using a tensile machine (Tensilon UTM-II-20); the gauge length was 20 mm and the crosshead speed 2 mm min$^{-1}$.

The thermoplastic polymers used as matrix resin were PPS, PEEK (380P) and polyethernitrile (ID300), the chemical structure of ID300 is as follows [13]:



This ID300 resin is referred to simply as PEN in this work. Using a Seiko Densikogyo DSC200 differential scanning calorimeter (DSC), the thermal behaviour of polymers was studied at a heating rate of 10 °C $\text{min}^{-1}$. The interface between carbon fibre and resins was observed using a polarized microscope. For this purpose, PEEK and PEN samples containing carbon fibres were placed on a glass slide and then heated to 390 °C; PPS sample was heated to 350 °C, held at that temperature for 10 min, and then cooled at 0.5 °C $\text{min}^{-1}$.

A single-fibre axially embedded, dogbone-shaped specimen was prepared as follows. A single fibre was mounted in the moulding die shown in Fig. 1 and both ends of the fibre were fixed with rubber adhesive. Polymer pellets were placed on the fibre and then compression moulded. After holding the specimen at an elevated temperature for 10 min, it was slowly cooled. Then the specimens were heat treated at various temperatures for 1 h. The moulding and annealing conditions are shown in Table I. By using the above procedure, three types of composites were made from PPS, PEEK and PEN resins. The single-fibre dogbone specimens were then strained on a tension machine at a constant crosshead speed of 0.4 mm $\text{min}^{-1}$. The testing machine was equipped with an environmental chamber enabling temperatures to be varied. Because the composites were easily fractured under tension below the glass transition temperature, relatively high temperatures were used for a standard test. During straining of the composite, a single fibre in the composite should break into fragments up to a limiting fragment size. After fracture testing, the specimen was partially melted at an elevated temperature and then quenched. This specimen exhibited a nature so amorphous that transparency was obtained. The length of individual fragments was measured for the treated specimen using an optical microscope.

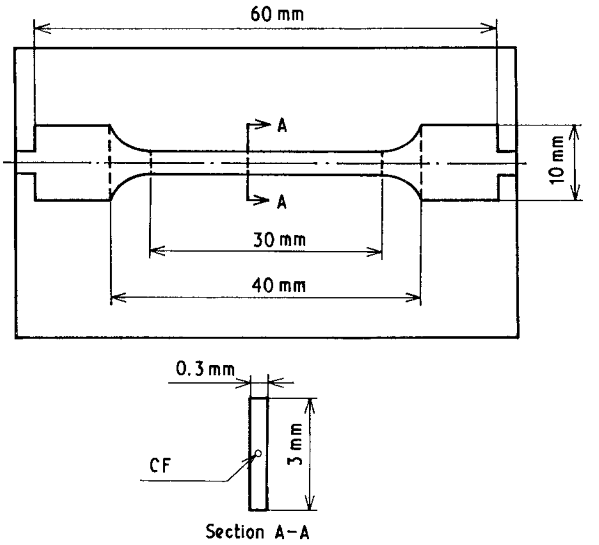


*Figure 1* Geometry of the single-fibre composite used.

TABLE I Conditions for preparation of samples used in this work

| Matrix | Moulding temperature (°C) | Annealing temperature (°C) |
|---|---|---|
| PPS | 330 | 180 |
| PEEK | 390 | 240 |
| PEN | 390 | 240 |

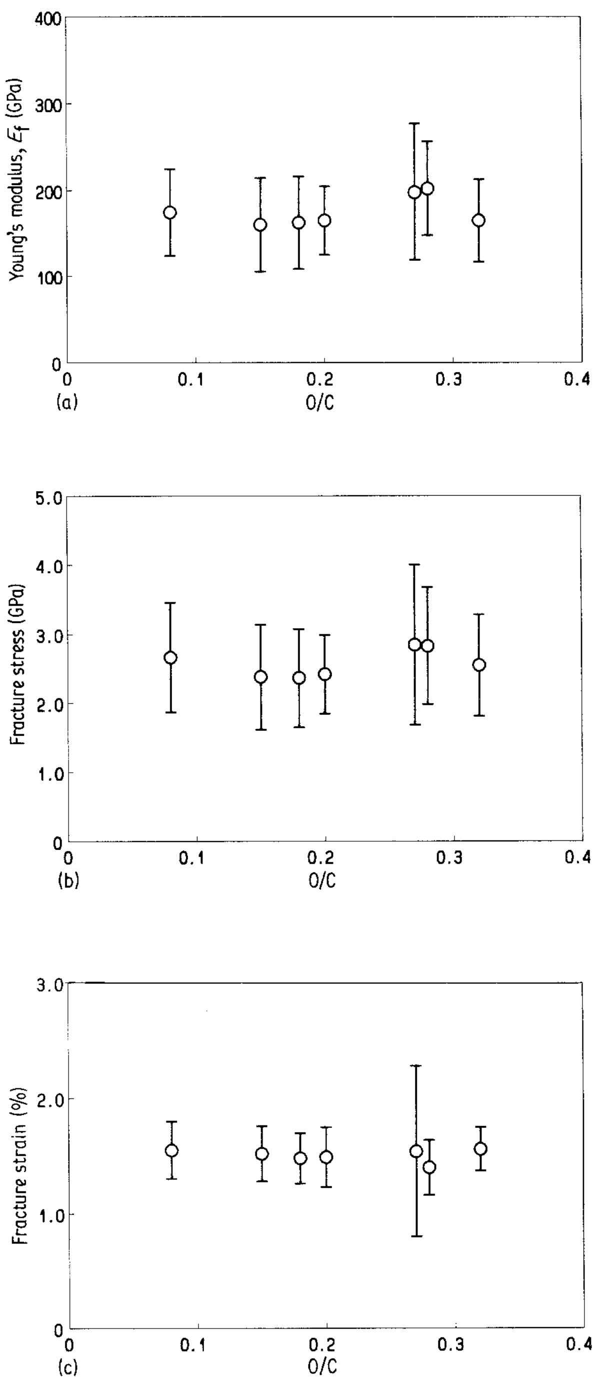


*Figure 2* Effect of oxidation of the carbon fibre on the mechanical properties measured at $T_e = 24$ °C: (a) Young's modulus; (b) fracture stress; (c) fracture strain.

## 3. Results and discussion

### 3.1. Characterization of fibres and resins

Fig. 2 shows the effects of oxidation of the surface of the carbon fibre on the mechanical properties. Within the range of O/C studied here, Young's modulus, the breaking stress and the breaking strain of the pitch-based carbon fibre are not largely influenced by the value of O/C. This means that the inner structure of the carbon fibre is not markedly changed by the oxidation. Fig. 3 shows the DSC curves of quenched PPS, PEEK and PEN samples used. The curves of these samples indicate the features of semicrystalline polymers, that is, there is a glass transition step, followed by an exothermic peak associated with crystallization, and then an endothermic peak associated with the melting of the crystallites. The melting point of the PEEK sample is similar to that of the PEN sample, although the crystallization temperature of the PEEK sample is somewhat higher than that of the PEN sample.

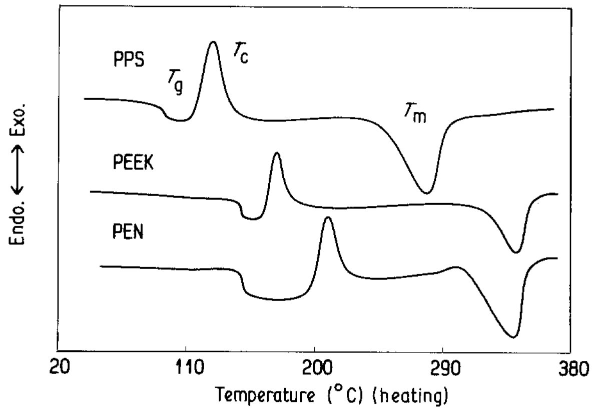


*Figure 3* DSC curves of quenched PEEK, PEN and PPS samples.

## 3.2. Fragmentation test

The effect of the strain of a specimen, $\varepsilon$, on the fragment length of a fibre, $l_\mathrm{f}$, was investigated for PPS, PEEK and PEN composites. Fig. 4 shows the relation between $l_\mathrm{f}$ and $\varepsilon$. It can be seen that $l_\mathrm{f}$ decreases with increasing $\varepsilon$ and then finally indicates a constant value above $\varepsilon = 8\%$, regardless of the sample used. Because the value of $l_\mathrm{f}$ indicates a constant value above $\varepsilon = 8\%$, the fragment length, which will be discussed later, was measured for the specimens after straining at 8%. Because this strain level is about four times the tensile ultimate strains of the fibres, the critical fragment length of the fibre reaches a minimum value.

The effects of O/C on $l_\mathrm{f}$ were studied for PPS, PEEK and PEN composites. The results are shown in Fig. 5. Although there was some scatter of data, $l_\mathrm{f}$ of PPS composite slightly decreases with increasing O/C. A similar trend can be seen in PEEK and PEN composites. It should be noted that the value of $l_\mathrm{f}$ of PEEK composite is roughly larger than that of PEN composites over a wide range of O/C, although both tests were performed at the same environmental temperature. This means that the nature of the matrix resin plays a major role in the process of stress transfer through the interface. If the value of $l_\mathrm{f}$ simply represents the bonding strength between matrix and fibre, the strength of the PEN composites seems to be superior to that of the PEEK composites. The reason for this may be that many factors, such as the chemical structure of the resins and thermal expansion values, are considered. However, we cannot discuss this further in this work, because of lack of experimental data. However, it should be noted that the bonding strength increases with increasing degree of oxidation, because strong covalent bonding between the carbon fibre and the thermoplastics resin is not thought to occur. With increasing oxidation, the surface of the carbon fibre may be cleaned. This is one reason for the decrease in $l_\mathrm{f}$ with increasing O/C.

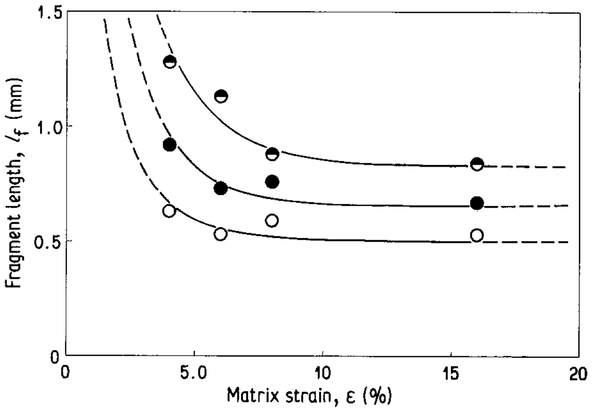


*Figure 4* Effect of sample strain, $\varepsilon$, on fragment length, $l_\mathrm{f}$. (○) CF (S1)/PPS, $T_\mathrm{e} = 120\,°\mathrm{C}$; (◓) CF (S1)/PEEK, $T_\mathrm{e} = 180\,°\mathrm{C}$; (●) CF (S1)/PEN, $T_\mathrm{e} = 180\,°\mathrm{C}$.

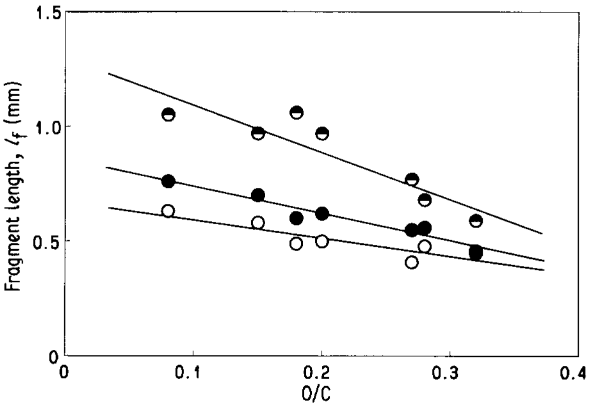


*Figure 5* Effect of O/C on $l_\mathrm{f}$ for different systems. (○) CF/PPS, $T_\mathrm{e} = 120\,°\mathrm{C}$; (◓) CF/PEEK, $T_\mathrm{e} = 180\,°\mathrm{C}$; (●) CF/PEN, $T_\mathrm{e} = 180\,°\mathrm{C}$.

In order to investigate the nature of the interface, a thin sample containing carbon fibres was crystallized. Fig. 6 shows polarizing light micrographs of the interface between carbon fibre and resins. PEEK and PPS samples show spherulitic structure and a transcrystalline layer in the interface between the fibre and matrix. However, the PEN sample does not show the existence of these structures. Because the crystalline structure of PEN is complex, large crystals may not be formed, and as the bonding strength of PEN sample is superior to that of PEEK sample as previously discussed, the bonding strength is not considered to be directly influenced by the formation of a transcrystalline layer.

Fig. 7 shows the effect of temperature on the values of $l_\mathrm{f}$ of PPS, PEEK and PEN composites, and Fig. 8 the effect of temperature on Young's moduli, $E_\mathrm{m}$, of PPS, PEEK and PEN samples. From Figs 7 and 8, it

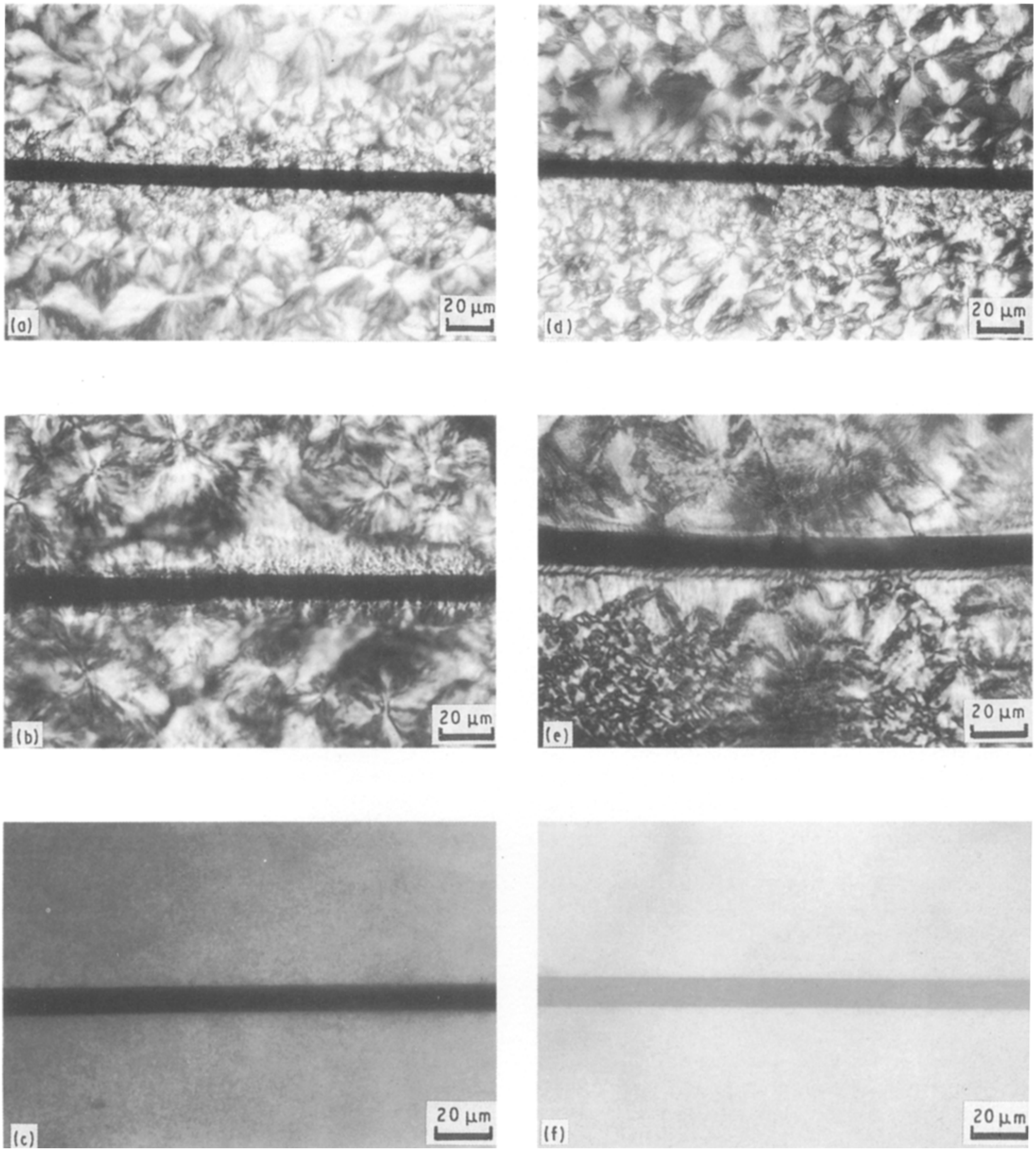


*Figure 6* Micrographs of the interface between carbon fibre and resins. CF (S1): (a) PPS, (b) PEEK, (c) PEN. CF (S7): (d) PPS, (e) PEEK (f) PEN.

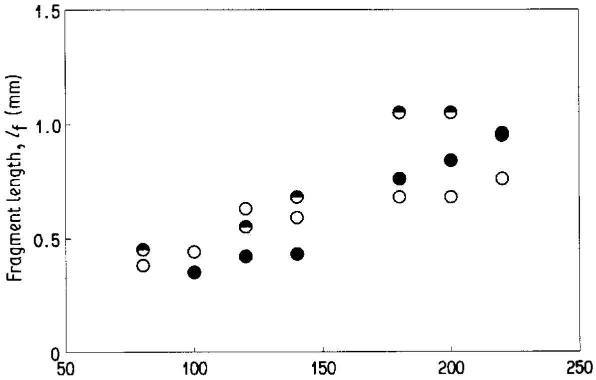


*Figure 7* Effects of temperature $T_e$ on $l_f$ for (○) CF (S1)/PPS, (◓) CF (S1)/PEEK, (●) CF (S1)/PEN.

can be seen that the value of $l_f$ of each sample slightly increases with increasing temperature, while $E_m$ is markedly decreased at the glass transition temperature, $T_g$. If $l_f$ is strongly influenced by $E_m$, $l_f$ is supposed to be largely changed at the glass transition temperature, $T_g$. Ohsawa *et al.* [14] have studied the interfacial properties between glass fibre and thermosetting resins. They reported that the critical aspect length, which was calculated from $l_f$, increases continuously with temperature, while the curves $E_m$ against temperature dropped steeply in the vicinity of $T_g$ of the matrix. By considering their report, we conclude that the fragment length measured in this work is not directly influenced by the value of $T_g$. This conclusion may imply that an interphase layer exists

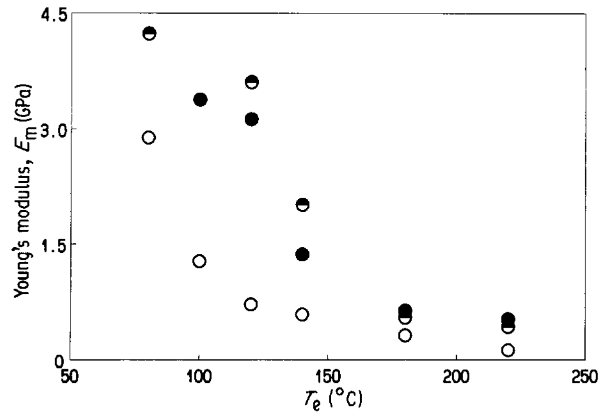


*Figure 8* Effect of $T_e$ on Young's modulus of resin, $E_m$. (○) PPS, (◓) PEEK, (●) PEN.

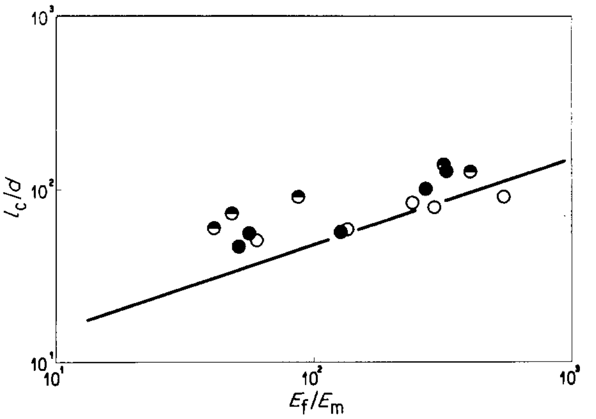


*Figure 9* Relation between $l_c/d$ and $E_f/E_m$: (———) theoretical prediction, for (○) CF (S1)/PPS, (◓) CF (S1)/PEEK, (●) CF (S1)/PEN.

between the fibre surface and the matrices used. However, the nature of its layer is not clear in this work. From the value of $l_f$, the critical fragment length, $l_c$, is evaluated by the equation $l_c = (4/3)\, l_f$. Fig. 9 shows the relation between log $l_c/d$ and log $E_f/E_m$, where $d$ is the diameter of the fibre, $E_m$ and $E_f$ are Young's modulus of matrix and fibre, respectively. It can be seen that the value of $\log(l_c/d)$ increases with increasing $\log(E_f/E_m)$. Asloun *et al.* [15] have studied the mechanism of stress transfer in single-fibre composites on the basis of Cox's model [16] and Termonia's analysis [17]. They have shown that the relation between log $(l_c/d)$ and $\log(E_f/E_m)$ for many polymer–fibre systems can be experimentally represented by Cox's theoretical equation

$$l_c/d = 4.7\,(E_f/E_m)^{1/2} \qquad (1)$$

A linear relation between $\log(l_c/d)$ and $\log(E_f/E_m)$ having a slope equal to about 0.5, can be seen for the engineering plastic matrices used in this work. This means that Equation 1 can also be applied to represent our data. However, it should be noted that our data are located above Cox's theoretical line. This means that the interfacial bonding between engineering plastics and carbon fibre is not perfect in comparison with the case where epoxy and unsaturated polyester resins are used as matrix.

## Acknowledgements

The authors thank Dr Y. Nakanishi, Government Industrial Research Institute of Osaka. Part of the study was supported by a Grant-in-Aid for Scientific Research presented by Hokuriku Industrial Advancement Centre and Fukui Sangyo Sinkou Zaidan.

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*Received 3 June*
*and accepted 22 October 1991*