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Effect of transcrystallinity on tensile behaviour of discontinuous carbon fibre reinforced semicrystalline thermoplastic composites

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Short carbon fibre reinforced polyetheretherketone (PEEK) composites with and without transcrystalline interphase are prepared under different conditions, and are used to investigate the effect of transcrystalline interphase on the tensile behaviour of semicrystalline thermoplastic polymer based composites. Volume dilatometry and scanning electron microscopy (SEM) are also employed as supplementary means. It is found that the formation of transcrystalline interphase improves such important characteristics of the composites as tensile stiffness, strength and toughness. The transcrystalline interphase enhances fibre-matrix adhesion and reduces stress concentration and cavitation at the fibre ends. The predominant deformation mechanism of the composite is changed from cavitation to shearing process in the presence of transcrystalline interphase, and moreover, significant local plastic deformation that absorbs more energy occurs, resulting in cohesive failure of the composite instead of adhesive failure happening to the composite without transcrystalline interphase. Copyright © 1996 Elsevier Science Ltd.

(Keywords: transcrystalline interphase; PEEK; carbon fibre reinforced)

INTRODUCTION

It is well recognized that various properties of fibre reinforced composites are controlled by fibre-matrix interface or interphase[1]. With respect to the semicrystalline thermoplastic polymer matrix, a so-called transcrystalline layer developed in the resin phase adjacent to the fibre during cooling procedure of composite preparation plays the role of interphase, which exhibits morphology different to that of spherulites in the bulk (*Figure 1*), and has been observed in polyphenylene oxide (PPO)[2], isotactic polypropylene (PP)[2], polyphenylene sulfide (PPS)[3], polyethylene (PE)[4], polyetheretherketone (PEEK)[5], etc. Microstructural study indicates that both transcrystalline and spherulites are composed of lamellae and an amorphous zone. However, the lamellae in the former organization are oriented perpendicular to the fibre axis whereas lamellae in the latter are radially aligned[6].

From a practical point of view, the mechanical role of the fibre-matrix transcrystalline interphase is evidently more interesting. Although the transcrystallization kinetics, microscopic details of transcrystalline and their processing condition dependence are well documented[7], little information about the effect of transcrystalline interphase on the macroscopic performance and the mechanism involved in the semicrystalline polymer-based composite is now available. Due to the complexity of interfacial phenomena, the influences of the transcrystalline layer are a little ambiguous. Since the transcrystalline interphase has good affinity to the fibre surface that acts as nucleation sites for crystal growth, direct evidence has been illustrated by the protruding fibre being covered with resin film[8]. Some studies found that transcrystallinity improved interfacial bonding[9] as well as transverse strength of unidirectional composite[5], while Ogata and co-workers proved that the bonding strength was not directly influenced by the formation of a transcrystalline layer[10]. In the presence of transcrystallinity, both the static and dynamic adhesion strengths were enhanced, and the composite was provided with remarkable crack tension[11,12]. Incardona and co-workers demonstrated that a thicker transcrystalline layer led to lower thermal stresses in carbon fibre reinforced J-polymer[13], but Zeng and Ho suggested that residual thermal stress could be eliminated in the absence of the transcrystalline interphase in carbon fibre/PPS composite[14]. Thermal fatigue evaluation further revealed that transcrystallinity reduced composite engineering stability in the alternating temperature field[15]. In consideration of the fact that all of the above-mentioned contradictory results have their own sufficient supports, it might be called to mind that on the one hand, transcrystalline regions might be beneficial, detrimental or have no effect on composite properties[16], and on the other hand, we should avoid the case as the saying goes, where one cannot see the wood for the trees. Additional effort therefore must be paid to collect much more data concerning the role of transcrystallinity in different composites under a range of mechanical applications. This is also the aim of our study.

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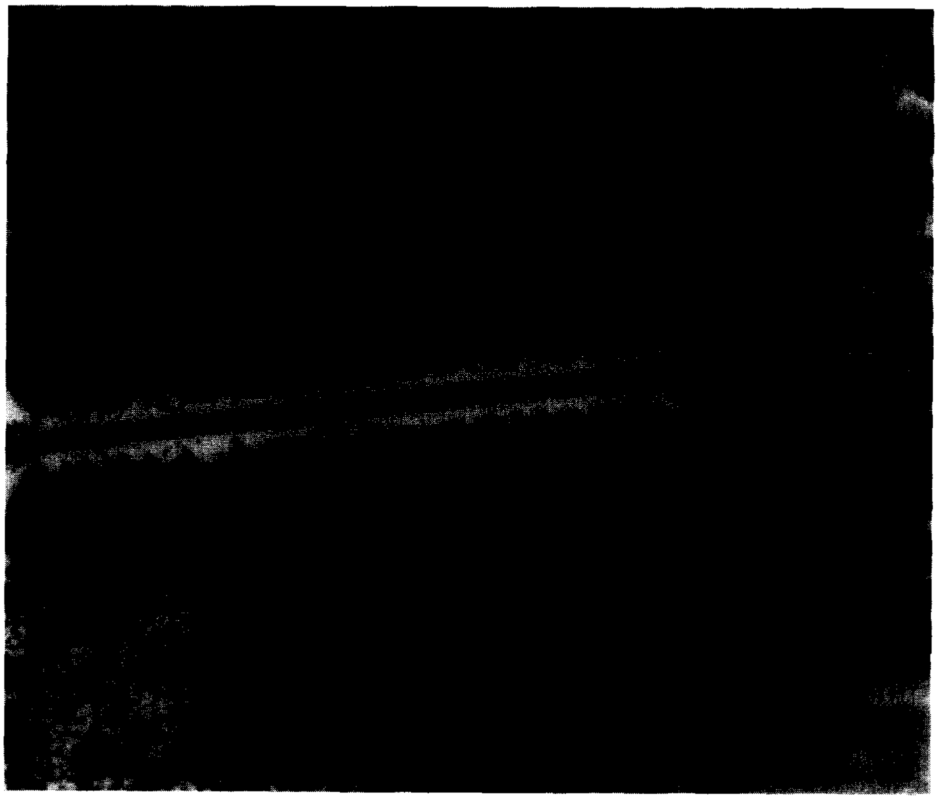

Figure 1 Crystalline morphology of carbon fibre/PEEK system

Table 1 Processing conditions of the short carbon fibre reinforced PEEK composites

Composites I.D.	10-CF/PEEK(395)	20-CF/PEEK(395)	10-CF/PEEK(375)	20-CF/PEEK(375)
Fibre content (wt%)	10	20	10	20
Hot pressing	Melted at 395°C for 15 min and then helded at 310°C for 1 h under 120 MPa		Melted at 375°C for 15 min and then cooled down naturally under 120 MPa	
Post-annealing	250°C, 12 h		250°C, 12 h	

In the present work, tensile behaviour of short carbon fibre reinforced PEEK composites with and without transcrystalline interphase is investigated. PEEK, a high-performance semicrystalline thermoplastic matrix resin for advanced composites, possesses combined high strength and modulus, excellent toughness, thermal stability with the advantages of easy processing by the techniques common to other thermoplastics, chemical inertness, wear and radiation resistance. In order to tailor PEEK composite, thorough crystallographic researches on its transcrystallinity are made[6,7]. Their results furnish the basis for the current study.

EXPERIMENTAL

Powdered PEEK kindly supplied by the Jilin University, China, was mixed with chopped Hercules AS-4 carbon fibres (CF) with an average length of 0.4 mm, and moulded into sheets by hot pressing. *Table 1* gives the processing and composites' identification. As shown in ref. 17, by using the X-ray diffraction monitoring method proposed by Blundell and co-workers[18], the transcrystalline layer is detected in the composite CF/PEEK(395), while only spherulites are detected in CF/PEEK(375).

Room temperature tensile measurement was carried out on dogbone type specimens (gauge section 30 mm × 5.5 mm × 4 mm) by a domestic WD-5A universal tester at various crosshead speeds: 50, 10, 2, 0.5, 0.1 and 0.05 mm min^{-1}, respectively. Volume dilatation was measured by simultaneously recording the longitudinal strain ε_L and the transverse strain ε_T with two strain gauges adhered to the specimens, and calculated from

$$\varepsilon_V = (1 + \varepsilon_L)(1 + \varepsilon_T)^2 - 1 \qquad (1)$$

where ε_V denotes the volume strain.

The fractured specimens were observed with a HITACHI S-520 scanning electron microscope (SEM), prior to which the surfaces were coated with a thin gold layer (~ 60 Å thick).

RESULTS AND DISCUSSION

Modulus and strength

Generally, Young's modulus reflects the capability of material to transfer elastic deformation in the case of small strain. As the transcrystalline interphase is a third and relatively stiff intermediary phase compared with the

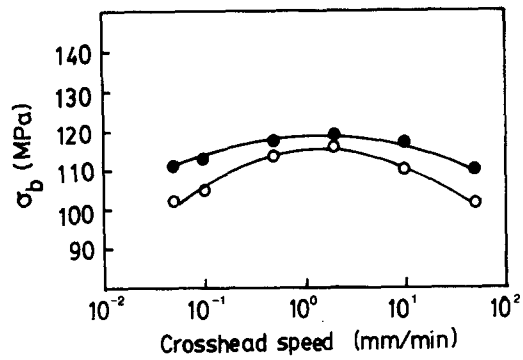

Figure 2 Variation of composite tensile strength, σ_b, with crosshead speed. (○) 20-CF/PEEK(375), (●) 20-CF/PEEK(395)

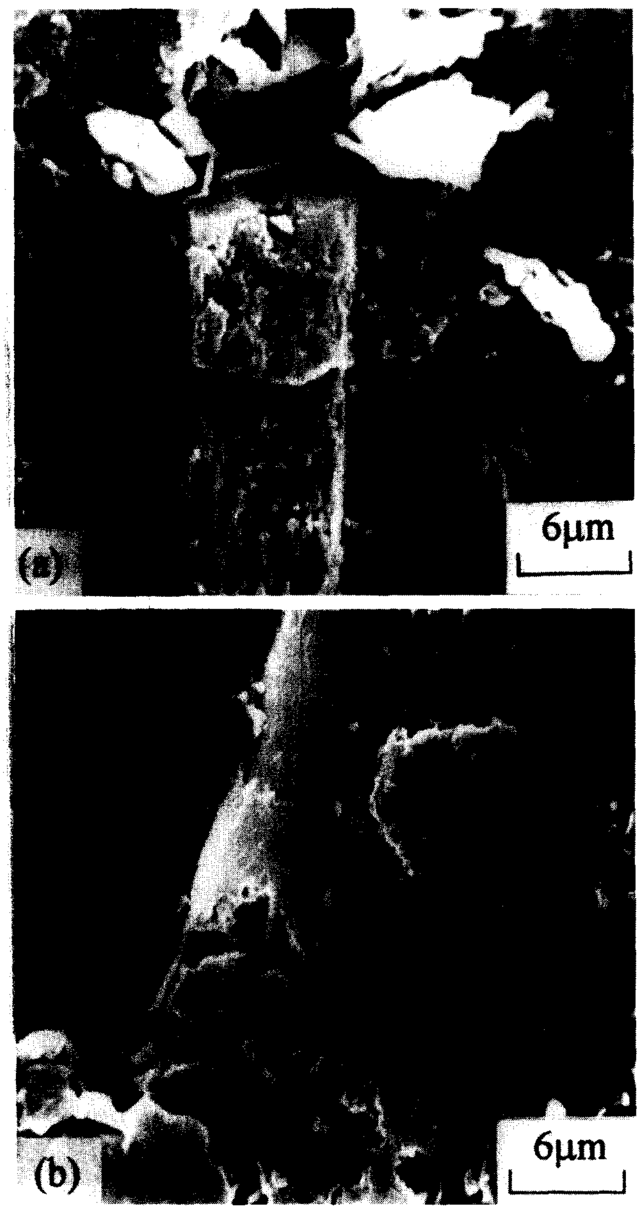

Figure 3 Typical SEM micrographs taken from the side faces of fractured (a) 20-CF/PEEK(375) and (b) 20-CF/PEEK(395). Crosshead speed: 2 mm min^{-1}

bulk resin phase[11,13], its appearance might result in a rise in Young's modulus of the composite. This is confirmed by the results that the modulus of 20-CF/PEEK(395) is higher than that of 20-CF/PEEK(375) in the whole range of crosshead speed. Also, the Young's moduli of the composites increase with increasing crosshead speed, which should be attributed to the common strain-rate dependent characteristics of polymers.

Bearing in mind that the load from matrix is mainly transferred across the interphase, a sufficient stress transfer ability is necessary to obtain higher strength of composite materials. Kroh and Bohse investigated theoretically the local stress field within a matrix under consideration of an interlayer, and suggested that the lowest stress concentration could be reached by using an interphase with modulus equal or higher than that of the matrix[19], meaning that a higher interphase modulus would lead to a higher composite strength. The result shown in *Figure 2* gives some support to the deduction. The tensile strengths σ_b of 20-CF/PEEK(395) are seen to be superior to those of 20-CF/PEEK(375).

Regarding that the fibre end usually acts as the site of a micro-crack source controlling the strength of a short fibre reinforced composite, it is interesting to clarify its behaviour in the present composites. *Figure 3* exhibits the SEM observation results of the side surfaces of the composites after tensile testing to failure. In 20-CF/PEEK(375) that lacks transcrystalline interphase, a cavity is found at the fibre end and the propagation of interfacial micro-cracks along the fibre sides due to shear stress concentration also leaves traces on the fractured specimen. In contrast, 20-CF/PEEK(395) has another appearance: debonding at the fibre end observed in 20-CF/PEEK(375) is replaced by the local ductile flow and the interphase between fibre and matrix remains intact. Evidently transcrystalline interphases growing at carbon fibre ends, referring to *Figure 1*, reduce the cavitation possibility. The greater matrix adhesion to the carbon fibre alleviates the concentrated stress and causes localized plastic deformation in the neighbouring resin, so that damage could not be induced at lower stress level. A similar phenomenon is also observed from the *in situ* SEM and acoustic emission study on glass fibre reinforced coupled PP[20].

On the other hand, with increasing crosshead speed tensile strength of the two composites increases at lower speed and decreases at higher speed, displaying a dynamic mechanical response feature. It might be related to some internal friction process of the matrix. Vu-Khanh and Denault speculated that during impact test resin relaxation could lead to an increase in temperature at the crack tip and hence cause a decrease in the dynamic fracture toughness with loading rate[21]. Although in the present case it is not clear whether the tensile fracture process is an energy-activated one, the different shapes of the curves in *Figure 2* imply that transcrystallines certainly exert influence on the response behaviour.

Failure strain and tensile dilatometry

The rupture behaviour of composites can be partially assessed by failure strain, an important parameter for engineering usage. The incorporation of short reinforcing fibres into thermoplastic resin usually results in a decrease in some properties including failure strain. However, the distinctive failure strains of the composites employed in the present test suggest there must be another factor influencing the final breakage. Whitehouse and Clyne proposed a geometrical model

Table 2 Tensile failure strains of the composites[a]

Composites I.D.	10-CF/PEEK(395)	10-CF/PEEK(375)	20-CF/PEEK(395)	20-CF/PEEK(375)
ε_b^{cal} (%)	3.99	3.40	3.29	2.12
ε_b^{obs} (%)	3.68	3.20	3.10	2.23

[a] Crosshead speed: $0.5\,\mathrm{mm\,min^{-1}}$

that allowed prediction of the failure strain for a given reinforcement volume fraction and aspect ratio[22]. This model is going to be used here in the hope of realizing the mechanical role of PEEK transcrystalline interphase in one aspect. They assumed that: (a) only the matrix was able to deform plastically; (b) cavity made a contribution to the composite strain; (c) some matrix was constrained by the reinforcement and cannot flow plastically; (d) all cavitation sites had been activated at the time that failure occurred. The failure strain of the composite, ε_b, can then be written as

$$\varepsilon_b = \varepsilon_{b0}(1 - V_f)(1 + \varepsilon_{cv})(1 - V_{con}) \tag{2}$$

where ε_{b0} stands for the failure strain of the matrix and V_{con} the volume fraction of the constrained matrix. Because the value of ε_{cv} is calculated from the relative axial length contribution of the hemispherical cavities in ref. 22, fibre orientation should be considered and equation (2) is slightly modified as

$$\varepsilon_b = \varepsilon_{b0}(1 - V_f)(1 + \eta_0\varepsilon_{cv})(1 - V_{con}) \tag{3}$$

According to the model geometry that takes the constrained region of the matrix as an isosceles triangular-section volume of revolution surrounding a fibre, equation (3) is expressed as

$$\varepsilon_b = \varepsilon_{b0}(1 - V_f)(1 + \eta_0 V_f^{3/4}/\xi)[1 - 2\xi(h/l)/(1/V_f - 1)] \tag{4}$$

where ξ is the aspect ratio of fibre, h is the height of the triangular constrained region and l is the length of both the isosceles triangle base and fibre.

Supposing l/h has the value of 80 for the specimens of CF/PEEK(395) and 30 for CF/PEEK(375), ε_b^{cal}, the failure strains predicted by equation (4), are listed in *Table 2* together with the experimental data, ε_b^{obs}. The good agreement shows that not only the model proposed by Whitehouse and Clyne can be applicable for the present composites after being slightly modified, but also the amount of the constrained resin is reduced when transcrystalline interphase comes into existence. An enlightenment is drawn that the PEEK interphase encourages more resin to be involved in plastic deformation.

Study of the stress dependence on strain indicates that there is an obvious difference in the tensile behaviour between the two composites. In order to distinguish the micro-mechanism involved that cannot be revealed from the stress–strain curves alone, a volume dilatometry technique is employed, the principle of which was first proposed by Bucknall and Clayton[23], and later developed by Heikens and co-workers[24]. According to their consideration, shear flow has no volume change during tensile test and the slope of the volume strain vs. longitudinal strain curve is zero for the pure shear flow process and unity for the pure voiding process. Other values of the slope are attributed to the mixed deformation processes. And moreover, with the help of a simple model that determines different contributions of several possible deformation mechanisms to the total deformation, quantitative information about the cavitation process might be gained[24,25].

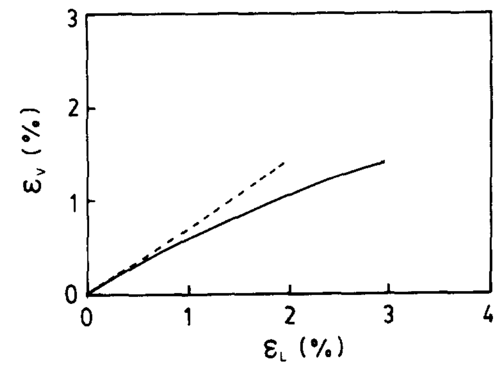

Figure 4 Typical volume strain ε_V vs. longitudinal strain ε_L at the crosshead speed of $10\,\mathrm{mm\,min^{-1}}$. (- - -) 20-CF/PEEK(375), (—) 20-CF/PEEK(395)

Figure 4 shows the results of the tensile dilatation test. After the initial linear volume increases due to homogeneous elastic deformation, the $\varepsilon_V \sim \varepsilon_L$ curves of the two composites exhibit different developing tendency. Assuming the linear additivity of volume strain and elongation strain is caused by elasticity, shearing and cavitation, the individual strain components are given as[24,25]

$$\varepsilon_{el} = \sigma_t/E \tag{5}$$

$$\varepsilon_{sh} = \varepsilon_L - \varepsilon_V - 2\nu\sigma_t/E \tag{6}$$

$$\varepsilon_{cv} = \varepsilon_V - (1 - 2\nu)\sigma_t/E \tag{7}$$

where σ_t is the true stress, ν the Poisson's ratio, and ε_{el}, ε_{sh}, ε_{cv} are the elastic, shear and cavitation strains, respectively. By using equations (5)–(7), every strain component is calculated using the experimental data determined at a crosshead speed of $0.5\,\mathrm{mm\,min^{-1}}$, and plotted against ε_L in *Figure 5*. In both cases, the deformation at the initial loading stage is definitely elastic. When the strain increases, onsets of deformation due to shearing and voiding appear at the strain corresponding to the first-cracking. These curves quantitatively reveal that the non-Hookean deformation for the two composites is dominated by different mechanisms: shear deformation for 20-CF/PEEK(395) and cavitation for 20-CF/PEEK(375), coinciding with the qualitative estimation in the last paragraph. Also, this conclusion is supported by the SEM investigation discussed below. It is seen that, although the shearing and voiding processes occur almost simultaneously, transcrystalline interphase affects the extent to which the cavitation process contributes to the total deformation, so remarkably that the predominant deformation mechanism is changed to the shearing process.

In fact, the shear deformation is produced by the stress concentration associated with fibre. A larger portion of neighbouring matrix resin might be involved in shear deformation owing to stress fields overlapping between the carbon fibres. In 20-CF/PEEK(375), cavitation at fibre ends and interfacial debonding can thus begin due to weaker fibre–matrix adhesion. When increasing the load, micro-cracks induced by the cavities might grow and propagate along fibre sides or coalesce with each other, leading to larger ε_{cv} in *Figure 5*. Then some fibres are pulled out and localized plastic deformation originates. The load bearing capacity is reduced gradually. Finally, fatal pass-through cracks result in the failure of the composite. In 20-CF/PEEK(395), the presence of transcrystalline interphase reduces the stress concentration at fibre ends. Cavitation is shown in rare cases and local plastic flow appears instead. As the load increases, surrounding shear plastic deformation becomes more and more significant and micro-cracks are formed in accordance with a rise in ε_{cv} as shown in *Figure 5*. In the case that the matrix cracks grow so severely that they link together, final failure occurs.

Now it becomes clear that the PEEK transcrystalline interphase is a somewhat ductile one (besides its higher modulus than the bulk spherulites) because the fibre–matrix interface almost remains intact during tensile testing and the interphase experiences plastic deformation. More energy is consumed and the composite toughness is increased as a result.

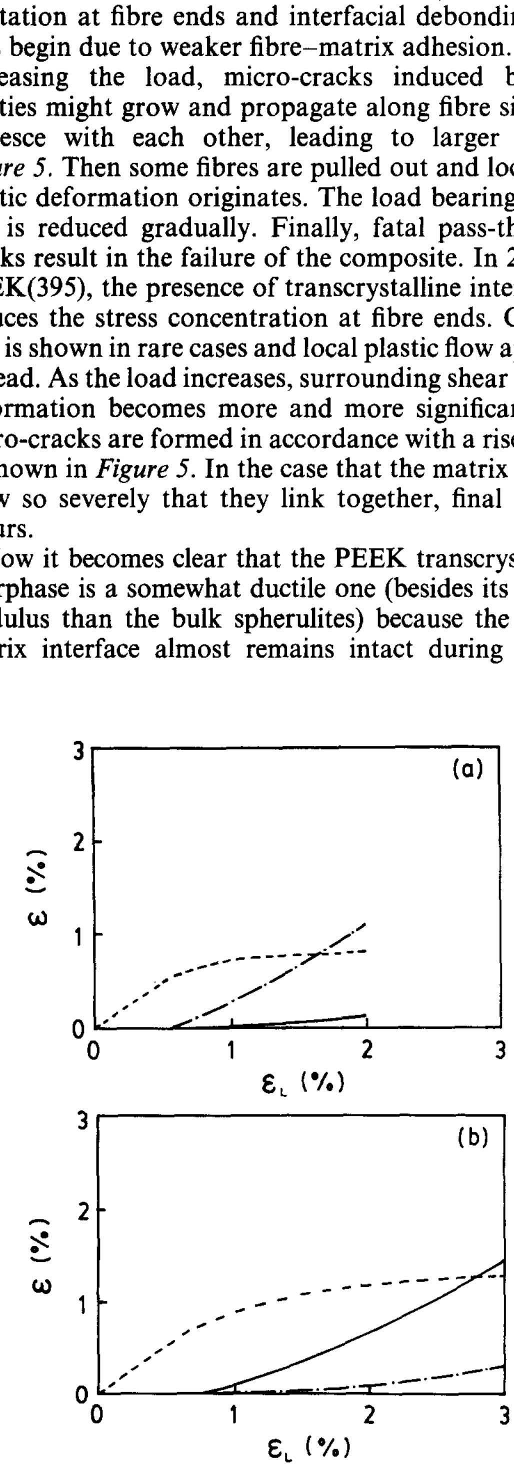

Figure 5 Estimation of the contribution of elastic (- - -), shear (—) and cavitation (-·-) deformation to the total elongation. (a) 20-CF/PEEK(375), (b) 20-CF/PEEK(395). Crosshead speed: 0.5 mm min^{-1}

Microscopic observation

Composite fractography has been the subject of a series of investigations[26]. The study of fractured surfaces enables the establishment of structure–property relationships dealing with material failure. A thorough fractographic survey of continuous carbon fibre reinforced PEEK laminate composites can be found in Purslow's works[27,28].

The SEM micrographs with low magnification of the fractured composites are shown in *Figures 6a* and *b*. Benched patterns resulting from the joining of various fractured planes as well as some tail-like patterns originated by the interaction of cracks with carbon fibres are exposed in both composites. These are the reflections of multiple cracking. Although the fractured surfaces of 20-CF/PEEK(395) and 20-CF/PEEK(375) look similar at low magnification, other close shots of *Figure 6* can tell the difference. In 20-CF/PEEK(375), see *Figure 6c*, when cracks have propagated along the fibre sides due to the low bond strength between fibre and matrix, the fibres are left smoothly, or more precisely, the matrix resin is cleanly peeled from the fibres[26]. Slight shear yielding traces can be found near the hollows produced by fibre pull-out and the dimensions of the hollows is obviously larger than the fibre diameter. All these indicate that local plastic deformation originating at the edges of the cavities continues when the tensile test proceeds, as shown in *Figure 5*. In 20-CF/PEEK(395), extensive river markings appear in the resin-rich phase, see *Figure 6d*. The end surfaces and side surfaces of the pulled-out fibres are all covered with resin. Micro-stretching of PEEK is observed in both the resins adhering to the pulled-out fibres (*Figure 6d*) and the resin remains due to cohesive damage (*Figure 6e*), suggesting good interfacial adhesion. The transcrystalline interphase seems to have undergone ductile deformation and provides greater resistance to crack propagation. In addition, hackle markings, with the so-called 'stacked lamellae' microstructure[29], are also observed on the surfaces of some fibres (*Figure 6f*). The formation of the undulatory contour of the river markings and the fresh surfaces of the hackle platelets is believed to dissipate more energy applied to the composite and thus enhance composite tensile toughness.

On the basis of the above investigation, the effect of transcrystalline interphase on the micro-failure processes is schematically drawn out in *Figure 7*, and may be used to interpret the macroscopic failure of the composite.

The strain-rate influence on the fracture morphology can be examined by *Figure 8*. Unlike the morphology obtained under lower rate (*Figure 6*), the proportion of shear deformation is remarkably reduced at higher rate, and the ends as well as the side surfaces near the ends of the pulled-out fibres are free of resin. It again demonstrates that higher strain rate inhibits shearing and facilitates cavitation, as discussed previously. On the other hand, it is worth noting that there is a resemblance to the result of the shear lag model in the pulled-out

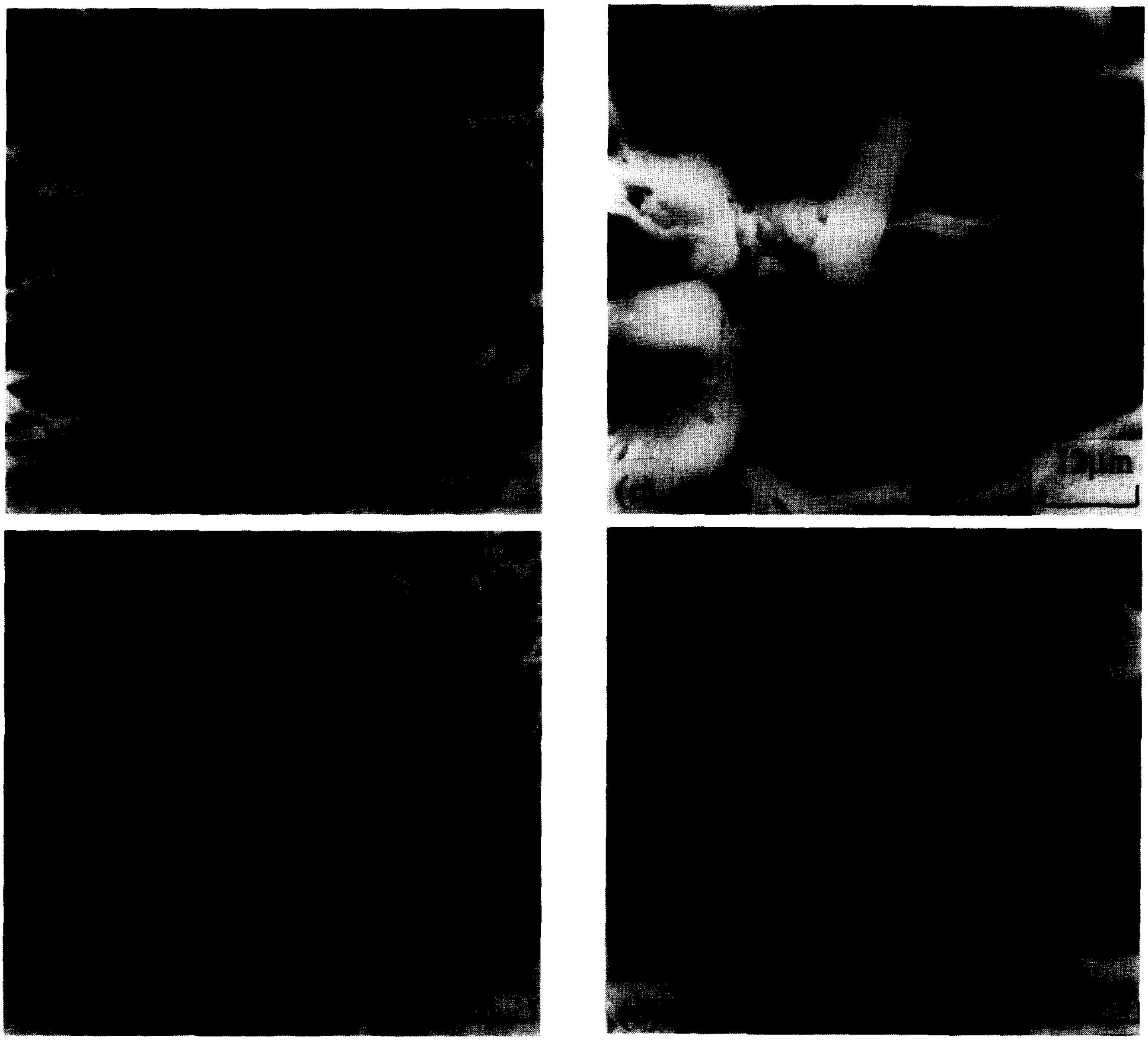

Figure 6 Typical SEM fractographs of the composites. (a) and (c) 20-CF/PEEK(375); (b), (d), (e) and (f) 20-CF/PEEK(395). Crosshead speed: 0.5 mm min^{-1}

fibres shown by *Figure 8*, i.e., shear stress reaches maximum at fibre end but minimum at the middle. Naturally, the question arises as to what should be responsible for the changes in the fractographic feature by comparing *Figures 6* and *8*. It is speculated that the following cases might be the cause: (a) the interfacial adhesive bonding decreases with increasing strain rate; (b) the shear stress component applied to the fibres increases with increasing strain rate; (c) the combination of (a) and (b). Since the tensile strength of 20-CF/PEEK(395) does not vary dramatically with crosshead speed (*Figure 2*), the first factor might play the secondary role.

CONCLUSIONS

In this paper, the effect of transcrystalline interphase on the tensile behaviour of short carbon fibre reinforced PEEK composites is studied with the help of volume dilatometry and SEM observation, in the hope of obtaining more information about its mechanical role in the composite macroscopic performance. The experimental results show that PEEK transcrystalline interphase is a very influential factor for the composite. In the light of engineering properties, the transcrystalline interphase promotes the elastic modulus, tensile strength and work of fracture of the composite. The stronger interfacial bonding and higher stiffness of the interphase reduces the modulus mismatching of the fibre and matrix, and facilitates stress transfer. When transcrystalline interphase is produced, the high stress concentration at the fibre ends is so eased that cavitation probability decreases dramatically. Shear deformation becomes the major deformation mechanism in the composite with transcrystalline interphase and more matrix resin is involved in plastic deformation leading to cohesive failure of the composite, whereas cavitation plays the leading role in the composite without transcrystalline interphase, which fails in an adhesive damage mode.

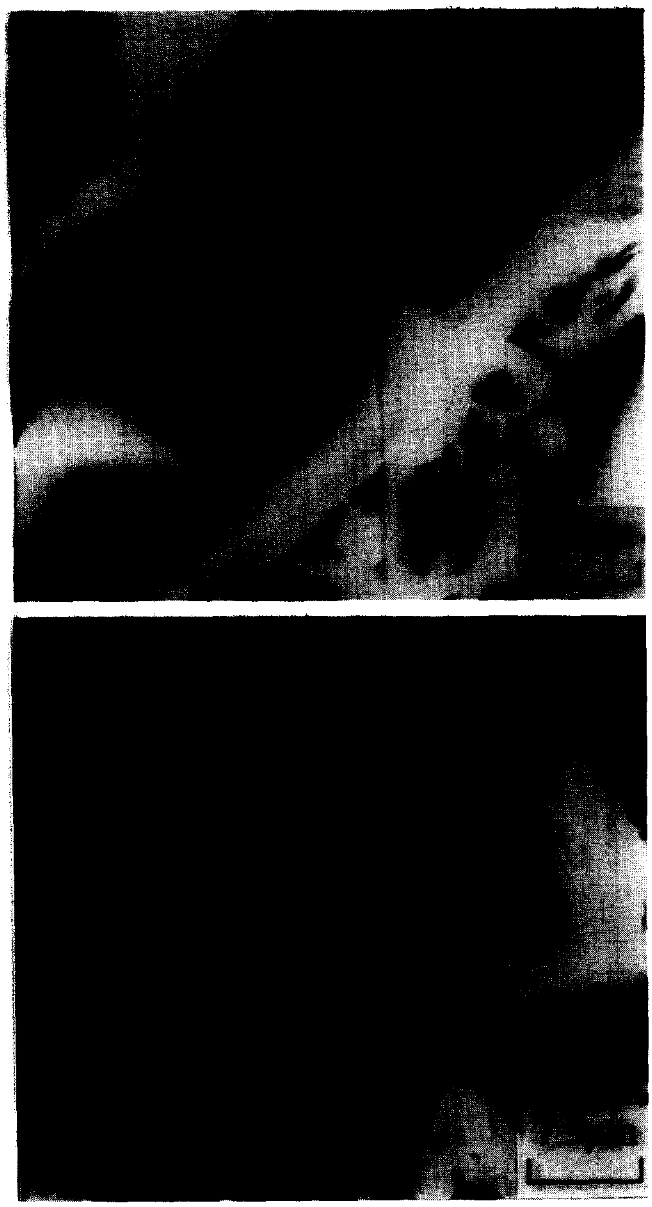

Figure 6 Continued

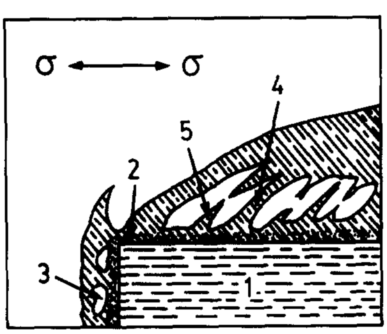

Figure 7 Schematic drawing of the micro damage processes in a CF/PEEK(395) specimen. 1: Carbon fibre; 2: transcrystalline interphase; 3: cavitation; 4: matrix shear flow; 5: cohesive failure between interphase and bulk resin

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Figure 8 Typical SEM fractograph of the 20-CF/PEEK(395) specimen tested at the crosshead speed of $50\,mm\,min^{-1}$

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