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Interface morphology of carbon fibre/PEEK composites

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The morphology of high-performance thermoplastic composites (APC-2) based on continuous carbon fibres embedded in a poly-ether-ether-ketone matrix is studied by means of scanning electron microscopy. Samples with different degrees of crystallinity obtained using different thermal treatments are investigated. The effect of the crystallinity content seems to be crucial for fibre/matrix adhesion, as can be detected by SEM analysis.

1. Introduction

High-performance thermoplastic composites have been developed in recent years as alternative composites to eliminate some disadvantages of thermosetting matrix composites. One particular composite (APC-2) is based on continuous carbon fibres embedded in a poly-ether-ether-ketone (PEEK) matrix. The characteristics of PEEK as a matrix for advanced composites and its application in aerospace structures have been reported in the literature [1–4]. PEEK is a semicrystalline polymer with a glass transition temperature of 144° C and a melting point of 342° C. The level of crystallinity is strongly dependent upon the processing conditions [5–7]. By cooling the melt at controlled rates it is possible to obtain a maximum level of crystallinity approaching 40%. By quenching the melted polymer at cooling rates higher than $1000^\circ\mathrm{C\,min^{-1}}$, an amorphous material is obtained. On heating the amorphous PEEK at controlled rates, at temperatures between the glass transition temperature and the melting point, a semicrystalline polymer with crystallinities between 15% and 35% is obtained.

The structure of PEEK–carbon fibre composites has been reported by Blundell *et al.* [8]. Commercial APC-2 consists of 125 μm thick plies of unidirectional impregnated tapes. The carbon fibres within each prepreg layer are about 7 μm diameter and typically occupy about 60% of the volume. The polymer matrix is formed by spherulitic entities embedded in the amorphous matrix. Spherulites represent the growth pattern of underlying crystals as they grow outwards in a three-dimensional manner from the nucleation sites. The main growth process continues around the fibres and terminates when the spherulites impinge on one another or an intervening fibre. Electron microscope etching studies on neat PEEK confirm that, in common with other crystalline thermoplastics, the crystals within the spherulites are in the form of stacks of lamellae which grow laterally outwards along the radial direction of the spherulites. Previous studies of pure PEEK polymer show that the thickness of the crystal lamellae is typically in the range 3 to 5 nm and increases with the crystallization temperature. The crystalline morphology of PEEK as a matrix of PEEK–carbon fibre polymer composites has been studied by several authors. Wide-angle X-ray scattering (WAXS) has been used by Blundell *et al.* [8] to estimate the crystallinity of the PEEK matrix in composites and to correlate the crystallinity level with the thermal history. The effect of the fibres on the crystallinity behaviour of PEEK has been studied by Lee and Porter [9] using calorimetry and microscopy. These authors did not observe significant differences in melting temperature for PEEK with and without carbon fibre, but they found that all PEEK samples with carbon fibres exhibit a higher nucleation density than PEEK itself at equivalent thermal histories. For samples held in the melt for long times, fewer spherulites are seen in the bulk and a more distinctive transcrystalline region is developed on the carbon fibre surface. It is generally known that a high density of nuclei at an interface promotes unidirectional growth of spherulites because of the proximity of nucleation sites. The nucleation of a polymer on substrates can be complex. Several different explanations have been offered including considerations of the surface energy of the substrate, possible temperature gradients, matching of unit cell structure, and shear stresses.

To measure the interfacial bond, tensile tests were carried out [9] in the transverse direction (perpendicular to the fibre direction). Samples showing transcrystallinity on the carbon fibre surface show

TABLE I Thermal treatment and crystalline characteristics of PEEK/carbon fibre samples

Sample	Isothermal temperature (° C)	Time (min)	Crystallinity (%)
1 (as-received)	–	–	< 5
2	180	60	16
3	400	60 +	
	+ 320	60	30
4 (as-received)			32

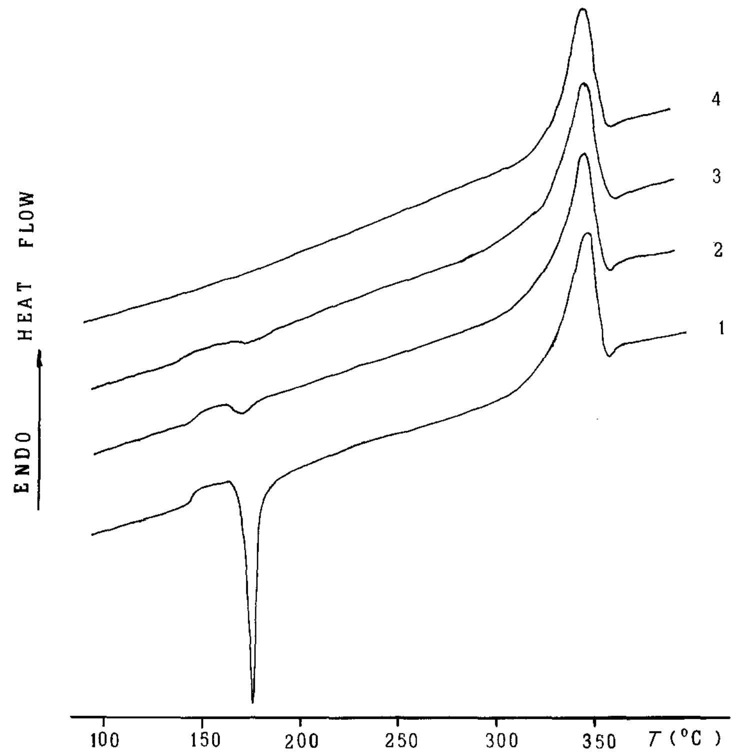

Figure 1 Thermograms of samples of PEEK/carbon fibre composites with different thermal treatments as indicated in Table I.

considerably higher values of strength than the matrix, indicating that they exhibit a strong interfacial bond between the carbon fibre and the PEEK. The thermal history above the melting point is the main reason for the difference in the transverse tensile strength.

Seferis [3] investigated the influence of the presence of fibres on the morphology of the semicrystalline polymer matrix from polarized microscopy observations of thin composite films.

The adhesion between carbon fibres and PEEK matrix has been studied by Di Landro and Pegoraro [10] by the "single filament composite" method. They observed that a sensible lower interfacial efficiency is achieved with respect to epoxy matrix composites where a stronger interfacial bond is probably established. However, they did not take into account the effect of the crystallinity on the interfacial adhesion between the thermoplastic matrix and the carbon fibres.

Crick *et al.* [11] have studied the interlaminar fracture morphology of carbon fibre/semicrystalline PEEK composites using scanning electron microscopy of fracture surfaces. The use of an etching technique revealed the spherulite texture. No attempt has been made to correlate the fracture behaviour with the crystalline structure.

In this paper we report some results obtained from the observation of fracture surfaces of carbon fibre/PEEK composites in relation to the crystalline morphology.

2. Results and discussion

Carbon fibre composites with amorphous and semicrystalline PEEK matrix, obtained from ICI, were used as raw materials for sample preparation. Different thermal treatments were performed on the samples in order to obtain different crystalline morphologies.

The samples are identified by numbers 1 to 4. The characteristics of each sample are reported in Table I. The crystalline contents were measured by calorimetry [1] and the corresponding thermograms are shown in Fig. 1. The composite with amorphous matrix (sample 1) shows a small difference between the area of the recrystallization peak and the area of the melting peak,

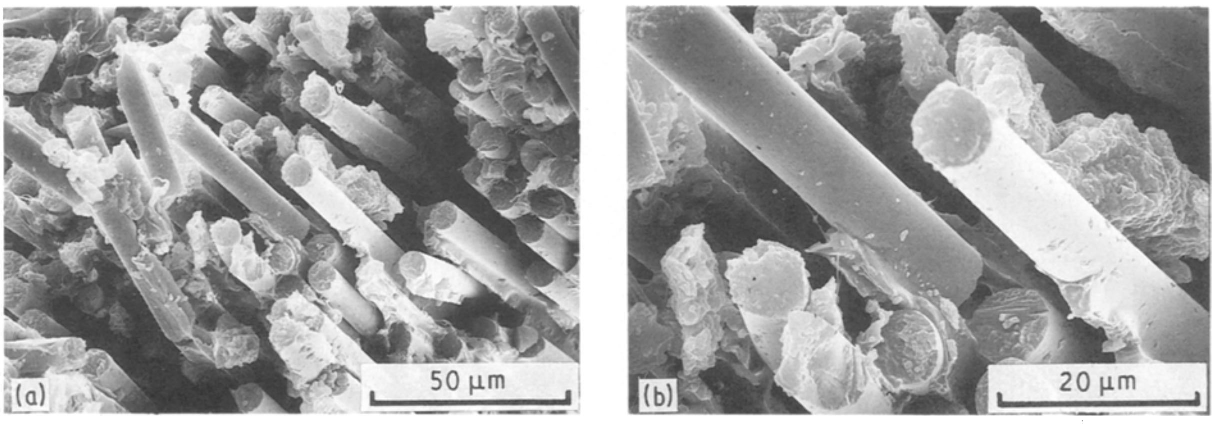

Figure 2 Scanning electron micrograph of sample 1.

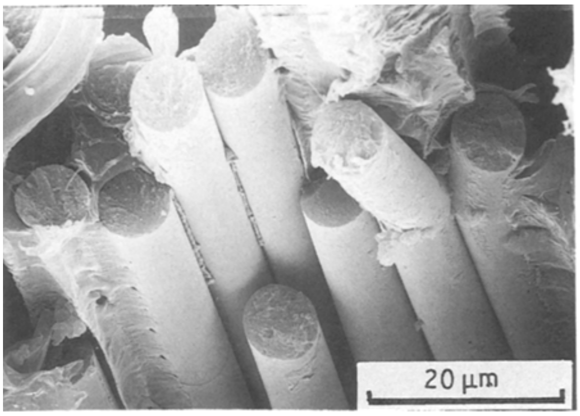

Figure 3 Scanning electron micrograph of sample 2.

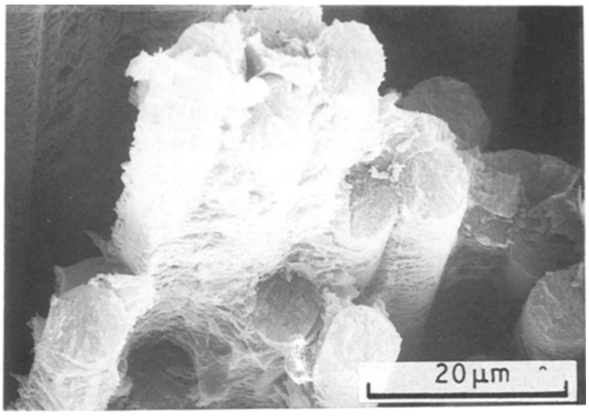

Figure 4 Scanning electron micrograph of sample 3.

indicating a level of crystallinity less than 5% (referred to the matrix content). Semicrystalline PEEK matrix composite (sample 4) shows a level of crystallinity of 32% (referred to the matrix content), near to the value reported in the literature. Sample 2 was obtained by heating the amorphous matrix composite up to 180° C and maintaining the material at this temperature for 1 h to allow the polymer matrix to crystallize. The level of crystallinity obtained in the matrix (16%) is similar to that reported in the literature for recrystallized matrices at temperatures just above the glass transition temperature. Finally, sample 3 was obtained by heating the original amorphous matrix composite up to 400° C. The material was kept at this temperature for 1 h in order to allow the matrix to melt and to limit the survival of crystallization nuclei. The system was then cooled to 320° C and the polymer was crystallized under isothermal conditions for 1 h. The final crystallinity level determined by calorimetry was 30%, similar to that of sample 4.

The crystalline structure of the PEEK matrix and the interfacial aspect was studied using a scanning electron microscope Hitachi model S2300. In order to obtain fracture surfaces that reveal the matrix morphology and the fibre/matrix interactions, the samples were fractured transversely to the fibre direction after stabilization in liquid nitrogen. Samples for microscopy were prepared by covering them with a thin gold deposit.

The results of SEM observations are presented in Figs 2 to 5. The original amorphous matrix composite (Fig. 2, sample 1, < 5% crystallinity) shows a fracture characterized by the presence of clean fibres protruding from the matrix. There is no resin on the fibre surface and where fibres have been pulled out from the matrix, no resin deformation or fracture is observed, clearly indicating a poor fibre/matrix adhesion. No ordered regions are observed in the matrix in this case.

In the original semicrystalline composite (sample 4, APC-2) shown in Fig. 5, ordered structures are observed around the fibres. These structures grow from the fibre surfaces impinging on other spherulites growing from other fibres, producing a continuous crystalline structure.

The effect of thermal treatment on the crystallinity is shown in Figs 3 and 4. Fig. 3 corresponds to the amorphous matrix composite after cold crystallization at 180° C (sample 2). Some ordered structures are observed in the matrix but, as in the amorphous matrix composite, clean fibres have been pulled out from the matrix indicating little interaction between fibres and PEEK matrix.

Fig. 4 refers to the original amorphous matrix composite where the polymeric matrix has been crystallized by cooling the melt and keeping the composite at 320° C (sample 3). In this case the material behaves like the semicrystalline matrix composite shown in Fig. 5. The presence of a crystalline phase is evident and the fibres are still covered by the matrix after the fracture. Only some differences in crystallite dimensions between both

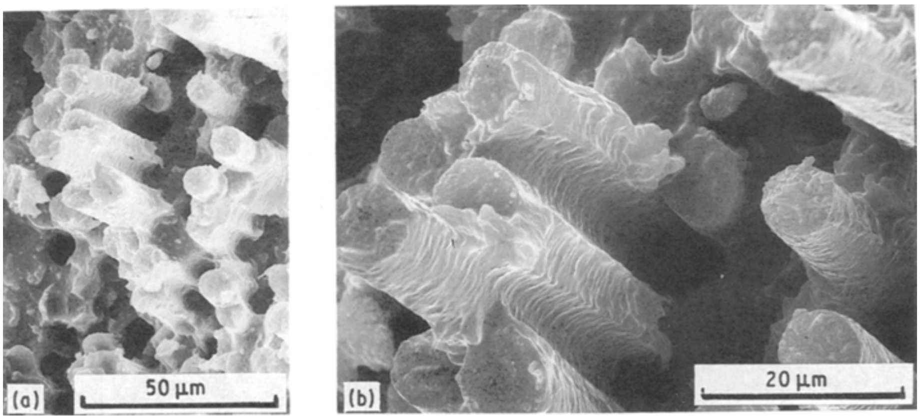

Figure 5 Scanning electron micrograph of sample 4.

materials are observed, but these differences can be attributed to the different thermal histories at high temperatures.

The differences observed in the fibre/matrix interaction between amorphous matrix or low crystalline matrix composites (Figs 2 and 3) and semicrystalline matrix composites (Figs 4 and 5) can be attributed to the reinforcing action of crystals as reported previously by Lee and Porter [9].

3. Conclusions

The fibre–matrix interactions and their relationship with the matrix crystalline morphology have been studied using scanning electron microscopy. The effect of the crystalline content obtained with different thermal treatments seems to determine the fibre/matrix adhesion. An amorphous matrix or low crystalline matrix obtained by cold crystallization show poor fibre/matrix adhesion. Semicrystalline matrix composites obtained by melt crystallization show a higher level of fibre/matrix interaction.

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