# Morphology in PEEK–carbon fibre composites observed in transmission electron microscopy

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*(Received 10 November 1992; revised 4 February 1993)*

Transmission electron microscopy in dark field mode was used to visualize the crystalline morphology in poly(ether ether ketone) (PEEK)–carbon fibre composites both in the PEEK matrix and at the interface. The morphology is particularly sensitive to the temperature at which the polymer is held above the melt.

**(Keywords: thermoplastic polymer composite; morphology of crystalline entities; transmission electron microscopy; thermal process; interface)**

*Introduction*

The poly(ether ether ketone) (PEEK)–carbon fibre composite belongs to a class of high performance materials, the matrix of which is composed of thermoplastic aromatic polymers. PEEK exhibits very good thermal, chemical and mechanical properties. The mechanical properties of the composite depend on the nature and density of the reinforcing fibres and also on the semicrystalline morphology of the PEEK matrix, especially in the vicinity of the carbon fibre (interphase). The morphological features are, in turn, affected by variations in the processing conditions. Most papers devoted to the characterization of texture and morphology of PEEK have used polarized light microscopy or scanning electron microscopy (SEM)[1,2]. Transmission electron microscopy (TEM) is a powerful instrument, but has rarely been used in bright field[3–5] and only occasionally in dark field mode[3].

The thermal processing generally consists of bringing the material to a high dwell temperature $T_m$ for a short time $t_m$ in order to ensure a good wettability of PEEK onto the fibres. The material is then crystallized isothermally at a temperature $T_c$ for a time $t_c$, then quenched to room temperature. It is well known that a higher $T_c$ induces better crystallization, with larger and fewer crystalline entities; in contrast, the role of $T_m$ has seldom been considered[1,3]. In the case of poly(phenylene sulfide) (PPS) we showed[6] that the choice of $T_m$ has a great influence on the morphology since it controls the density of nuclei existing in the matrix before crystallization. A high $T_m$ deletes the thermal history of the polymer and favours nucleation from the carbon fibre. This sometimes leads to the appearance of a transcrystalline phase.

We have undertaken a study on the influence of the temperatures $T_m$ and $T_c$ on the morphology and texture of the PPEK–fibre interface.

*Experimental*

Before the thermal processing, the composite specimens were moulded by melting two PEEK plates (provided by ICI) at 380°C for 10 min under 5 MPa, in the presence of parallel carbon fibres. The fibre density was low (about 5%) in order to obtain large enough intervals between the fibres to be observed in TEM. The carbon fibres (AS4 fibres from Hercules without sizing) had previously received oxidative treatment to the surface. Small pellets were cut from the plates and were placed in an oven where they underwent four different thermal processes, which are specified in *Table 1*. Specimens of type A and B have low $T_m$, $T_c$ and $t_c$, which should not favour crystallization. On the contrary, types C and D should be far more easily crystallized, having higher $T_m$, $T_c$ and $t_c$. Small cubes were cut from the pellets and included in epoxy resin. Slices of thickness 200 and 300 nm, suitable for electron microscopy, were then obtained by ultramicrotomy. More details will be given in an extensive paper[7].

We have systematically used dark field TEM because it has proved to be an excellent way of imaging the spherulites and any crystalline entity, and therefore visualizing the detailed crystallization morphology in the matrix and at the surface. The images in TEM were obtained with a 3 MV microscope (CEMES) operated at 2 MV. At this voltage, most polymers have a much better resistance to radiation damage[8,9]. The 'life-time' of the PEEK, defined as the time at which the intensity of the diffraction spots starts to decrease, is about four times larger than at 200 kV. The magnification of the micrographs was chosen so that the exposure time is

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0032-3861/93/122668-02

**Table 1** Thermal processing of specimens A–D

| Specimen | $T_m$ (°C) | $t_m$ (min) | $T_c$ (°C) | $t_c$ (h) |
|---|---|---|---|---|
| A | 360 | 3 | 310 | 0.25 |
| B | 390 | 3 | 310 | 0.25 |
| C | 410 | 3 | 330 | 3 |
| D | 410 | 3 | 330 | 15 |

lower than this life-time. The specimen thickness can also be higher and specimens 400 nm thick were also observed. The images of the same specimens observed at 200 kV are much more faint because of the higher inelastic diffusion.

*Morphology and texture*

The texture of the PEEK far from the fibre in all four specimens consists of numerous spherulites all over the specimen. They are comprised of fan-shaped bundles, diverging from points which are likely the growth nuclei. In C and D specimens, these fans are most often laid out in a circular symmetry so that the spherulites are well formed and rather regular. On the contrary, the bundles in A and B specimens are developed in a more irregular fashion, so that the spherulites are not fully developed, and are interwoven or overlap. The sizes of the spherulites increase from specimens of type A to those of type D (*Figures 1* and *2*). Measurements on numerous pictures provide the following values of the mean diameter of the spherulites: A specimens, 0.5–1 $\mu$m; B, 2–5 $\mu$m; C, 4–8 $\mu$m; D, 4–10 $\mu$m. This is in agreement with our expectation since the thermal processing of D specimens (high crystallization temperature $T_c$ and long crystallization time $t_c$) favours crystallization. Selected diffraction patterns were recorded from small parts along the radius of the spherulites; they display small intense arcs that reveal good crystallinity. Their small angular extension is due to a very small divergence of the crystallites inside the selected area. The orientation of the $\vec{b}$ axis (0 2 0) is parallel to the direction of the lamellar growth along the radius of the spherulite.

Along the fibre surface, the spherulites are more or less disturbed with respect to the bulk matrix. In A specimens (*Figure 1*), the morphology seems to be the same as without fibre. The spherulites are numerous and small, and their nuclei lie inside the matrix. However, a closer inspection shows that some of them could start growing at the surface. Diffraction patterns are similar to that of the matrix and depict random orientations along the fibre. In B specimens, the general features of the morphology are the same at the interface as in the matrix. Spherulites along the interface appear as rather irregular shapes that grow in a disordered manner, impinging on each other and interweaving. The morphology at the interface of C and D specimens looks far more ordered (*Figure 2*). The matrix itself is fairly well organized with large spherulites, from which extensions reach up to the fibre without disturbance. Long bundles can be seen close to the fibre surface, most often laid out in diverging forms constituting spherulites, and sometimes with almost parallel growth. Along the fibres, dark areas of amorphous material are sometimes seen between well contrasted bundles. Parallel crystallization forms are sometimes seen. Locally, these resemble the characteristic form of transcrystallinity which takes place when the growth nuclei are dense and lie on the surface. The

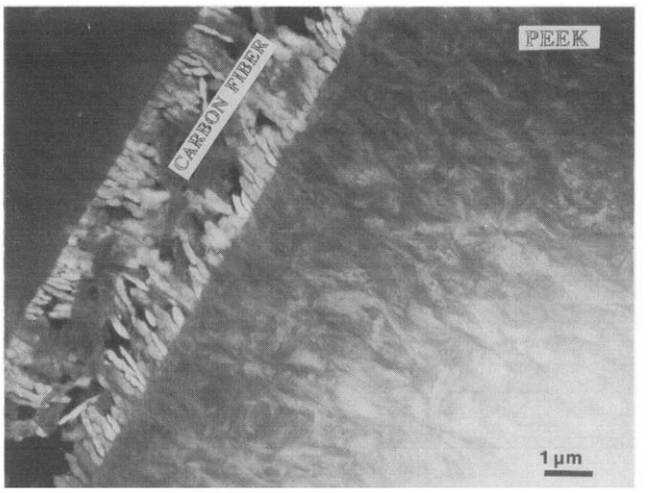


**Figure 1** Spherulites at the interface in an A specimen ($T_m$=360°C, $T_c$=310°C). Transmission electron microscopy, dark field image

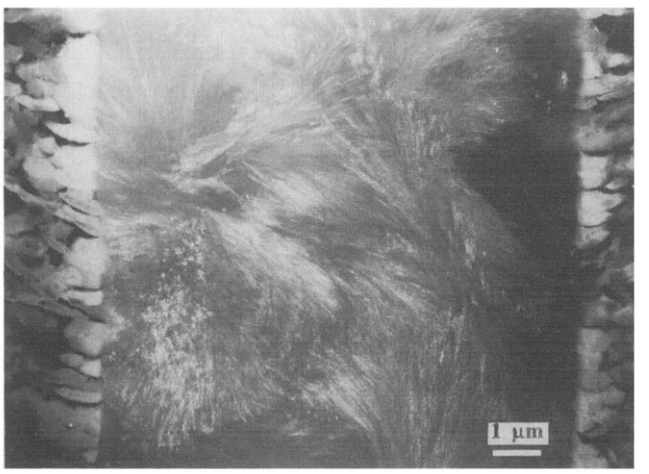


**Figure 2** Spherulites at the interface in a D specimen ($T_m$=410°C, $T_c$=330°C). Transmission electron microscopy, dark field image

diffraction pattern shows that the $\vec{b}$ axis is perpendicular to the surface. However, there is no evidence that the growth nuclei lie on the surface. On the contrary, they seem to be inside the matrix.

Dark field images in TEM provide a very good representation of the spherulites inside the matrix and along the interface. In this first set of experiments, we wanted to obtain the best crystallization so that both $T_m$ and $T_c$ have been varied. In the next set of observations, only $T_m$ will be varied in order to investigate the role of this parameter. Parameters such as the oxidative treatment and the size applied to the fibre can also play an important role, and these are under investigation.

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