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The branching characteristic of the spherulites of poly(ether ether ketone)

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The branching characteristic of the spherulites of poly(ether ether ketone) (PEEK) has been studied. The spherulitic branching texture was apparent under optical microscope when the PEEK films were very thin, when PEEK had been crosslinked to some extent, or when another amorphous polymer was added to PEEK. Various branching angles are possible in the fibrillar branching growth of the spherulites.

(Keywords: poly(ether ether ketone); spherulite; branching characteristic; optical microscope)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-performance and semicrystalline polymer which is generating much interest for applications such as reinforced composites[1], coatings, electronic connectors and many others[2]. There have been detailed studies on the crystalline morphology, especially, the spherulitic morphology of PEEK. It was found that the spherulites of PEEK could show radiating morphology with positive[3] or negative birefrigence[4,5]; the lamellae in the spherulites grow with the *b* crystallographic axis in the radial direction[4]. In our works[6], a banded spherulitic morphology of PEEK was observed when the radiating spherulites were heated in the heating stage of an optical microscope. The banded morphology was revealed to be interchangeable with the radiating morphology in thermal processes. Based on these results, the lamellae in the spherulites of PEEK were suggested to be twisted, in contrast to the lamellar growth with flat morphology reported previously[4]. In this paper, the branching characteristic of the spherulites of PEEK was studied.

EXPERIMENTAL

Commercially available PEEK powder (grade 450P, Imperial Chemical Industries (ICI), Wilton, UK) was used. With this powder, cast films of PEEK were obtained by dissolving it in α-chloronaphthalene. After melting at 400°C in the absence of air for 15 min or in air for 2.5 h, the films were quickly transferred to an oven held at 315°C for isothermal crystallization for 6 h, and then quenched to room temperature. Crystallized films of the blend of PEEK with phenolphthalein poly(ether ether sulfone) (PES-C) were obtained by dissolving 40 wt% PEEK with 60 wt% PES-C in α-chloronaphthalene, then casting and treating them in the same way. The PEEK films which were used for observation by scanning electron microscopy (SEM) had been initially etched in a solution consisting of 2 wt% potassium permanganate in a mixture of five parts by volume of concentrated sulfuric acid, two parts of orthophosphoric acid and two parts of distilled water for 10 min.

A Leitz Othoplan optical microscope was used to observe the crystalline morphology of the films, while a Hitachi S-520 scanning electron microscope was used for surface investigation.

RESULTS AND DISCUSSION

Figure 1a shows the spherulitic morphology of PEEK grown in very thin film. The usual Maltese cross is not so perfect as the reported spherulites of PEEK, and there is considerable local birefringence even within the cross. This makes the branching texture observable under optical microscope. When the film is thinner, the branching nature of spherulite growth is more apparent, as shown in *Figure 1b*, especially at the edges. Due to the depletion of nucleus and material, the spherulites tend to grow unhindered in a specific direction.

Figure 2 shows the morphology of PEEK, after melting at 400°C for 2.5 h in air followed by isothermal crystallization. Though the films are much thicker than those in *Figure 1*, the branching texture can still be seen. In this case, it is observed that the spherulite is growing in fibrils and forming branching dendrites. There are few side branches to the parent fibrils and the branching angles are relatively large. This is different to the texture in *Figure 1* and makes the branches more distinct.

Branching texture is also observable in the spherulites that grow in the blend of PEEK with another specific polymer. As seen in *Figure 3*, when PES-C, an amorphous and high-performance polymer[7], is included in the interfibrillar structure, the spherulites consist of branched fibrillar crystals. The texture is similar to that of pure PEEK in very thin films in spite of the much thicker film of the blend. It was revealed that such dispersion of PES-C in the spherulites is related to the partial miscibility of PEEK with PES-C[8].

These results indicate that the spherulites of PEEK grow in fibrillar branches. The branching texture can be observed under optical microscope in the above cases because there are limited branching crystals in the spherulites, so the spherulites are incompletely filled.

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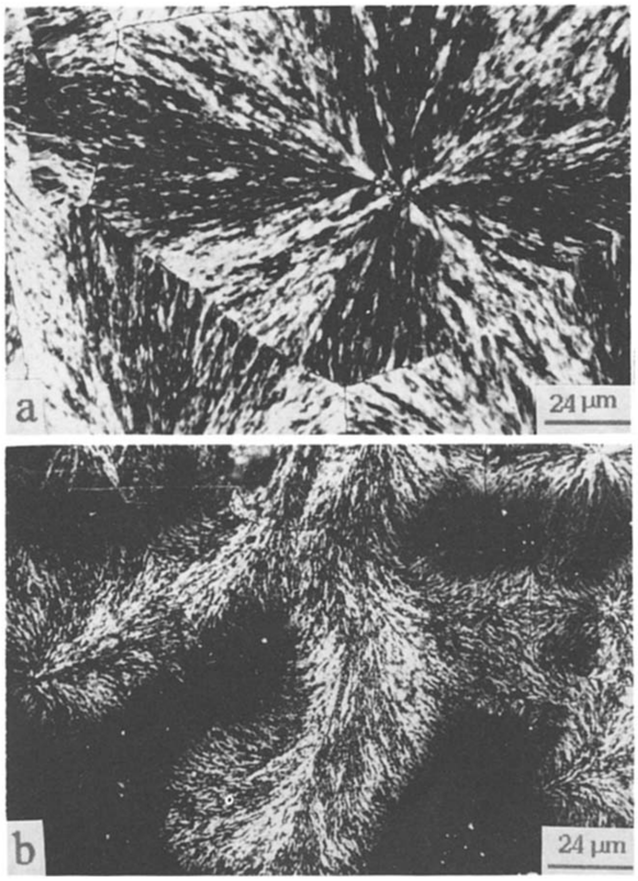

Figure 1 Morphology of PEEK in very thin films crystallized at 315°C; the film in (a) is thicker than that in (b)

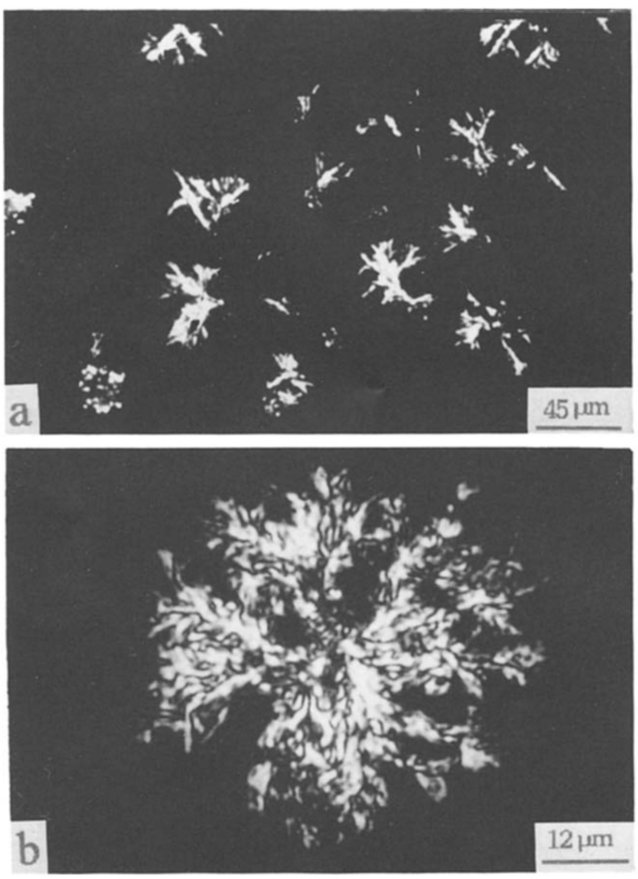

Figure 2 Morphology of PEEK after melting at 400°C for 2.5 h in air followed by isothermal crystallization at 315°C: (a) dendrites; (b) detail of the texture in an incomplete spherulite

When the film is very thin, the prior accretion of polymer chains to fibrils may lead to the depletion of PEEK in some areas. When PEEK is melted in air, crosslinking occurs and may retard the crystallization of PEEK[9]. At this time, the uncrystallizable chains dispersed in the films should be responsible for the morphology. When a lot of amorphous PES-C is added to PEEK, the dilution and phase separation will also cause the local depletion of PEEK. It is emphasized that the branching growth is

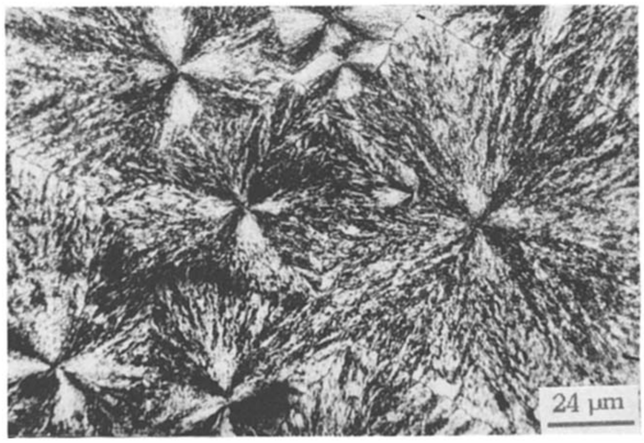

Figure 3 Morphology of PEEK/PES-C (40/60) blend crystallized at 315°C

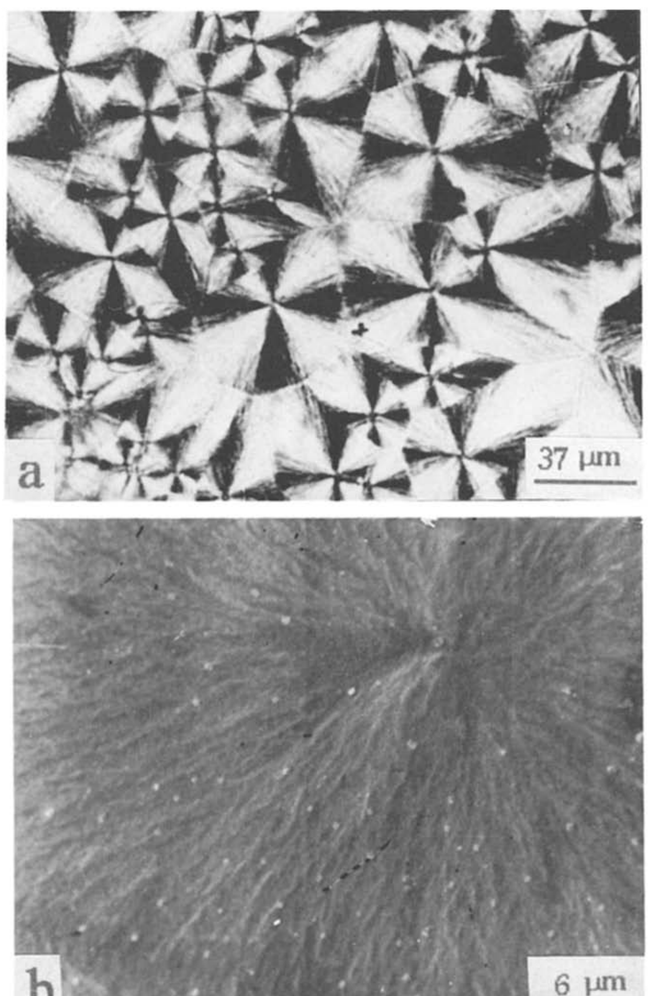

Figure 4 Spherulites of PEEK crystallized at 315°C: (a) optical micrograph; (b) scanning electron micrograph after etching

Figure 5 Preferentially developed edges of PEEK crystallized at 315°C

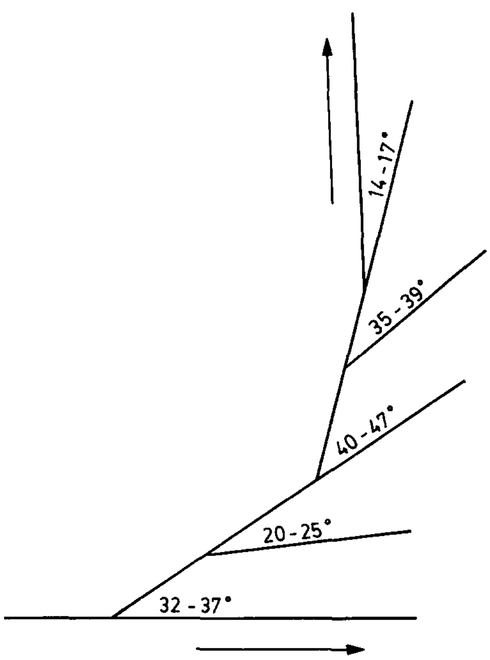

Figure 6 Sketch to illustrate the branching growth shown in *Figure 5*. The straight lines and their crossing angles represent the branches and branching angles, respectively, while the arrows indicate the main growth direction of the edge

the spherulitic characteristic of PEEK, although it cannot usually be detected directly under optical microscope except in the three specific cases described here. With other techniques, the texture can still be observed in the normal case. As shown in *Figure 4*, the branching texture, which is invisible under optical microscope, is apparent by observing the etched spherulitic surface by SEM.

The spherulitic branching texture of PEEK is characterized to some extent by the model of fibrillar branching growth from a central nucleus, in which a pair of circular cavities may form[9,10]. This is seen in *Figure 4b*, where two pits have been left after etching due to fewer crystals in these spaces. The spherulitic morphology revealed by Lovinger and Davis with transmission electron microscopy[4] has given a more direct impression of such a texture. Since circular cavities are only obtained by simplifying the branching angle to a constant value, the irregular pits in *Figure 4b* indicate that there might be various acute branching angles in the spherulite growth of PEEK. The branching growth may make PEEK form unusual spherulitic morphology. *Figure 5* shows the preferentially developed edges of the spherulite, which possess similar optical properties to the spherulite when the object stage is rotated. One of the edges grew almost straight at first, then made a turn and continued growing in a new direction. To reveal the detail at the turn, the branching angles at each branch point were determined. In *Figure 6*, several representative branches and their related angles are chosen to illustrate the growth simply. It is seen that the main growth direction of the edge is changed after a series of branching, and the branching angles of these branches are different from each other. It is emphasized that there are other branching angles in the texture shown in *Figure 5*. Their values fall between 14° and 47°, but are more probably in the range of 20–37°. Further investigation has shown that the branching angles in the spherulites shown in *Figure 1b* and *Figure 3* are in a similar range, but the maximum angle in the spherulites of in-air melted PEEK, shown in *Figure 2*, may reach 78°. The increase in the branching angle after the melting of PEEK indicates that the crosslinking in PEEK may change its spherulitic branching characteristic.

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REFERENCES

1 Seferis, J. C. *Polym. Composites* 1986, **7**, 158
2 Steining, T. C., Smith, C. P. and Kimber, P. J. *Modern Plastics* 1981, **11**, 86
3 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953
4 Lovinger, A. J. and Davis, D. D. *J. Appl. Phys.* 1985, **58**, 2843
5 Kumar, S., Anderson, D. P. and Adams, W. W. *Polymer* 1986, **27**, 329
6 Zhang, Z. Y. and Zeng, H. M. *Die Makromol. Chem.* 1992, **193**, 1745
7 Liu, K. J., Zhang, H. C. and Chen, T. L. Chinese Patent no. 85 101 721, 1985
8 Zhang, Z. Y. and Zeng, H. M. *Polymer* submitted for publication
9 Zhang, Z. Y. and Zeng, H. M. *Astronautic Mater. Technol.* 1989, (2), 24
10 *Keller, A. and Waring, J. R. S. J. Polym. Sci.* 1955, **17**, 447
11 Hearle, J. W. S. *J. Appl. Polym. Sci.* 1963, **7**, 1193