JOURNAL OF MATERIALS SCIENCE 26 (1991) 5915–5920

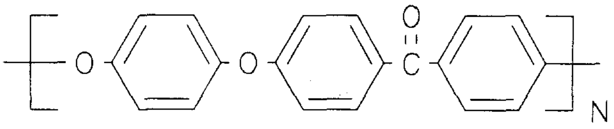
Studies on interface structure and crystal texture of poly(ether–ether–ketone)–carbon fibre composite

WEI WANG, ZONGNENG QI
Institute of Chemistry, Chinese Academy of Sciences, Beijing, PRC
G. JERONIMIDIS
Department of Engineering, The University of Reading, Whiteknight, RG62AY, UK

The interface structure of poly(ether–ether–ketone) (PEEK)–carbon fibre composite and the crystal texture of PEEK matrix have been studied by scanning electron microscopy (SEM) after the samples were properly etched by argon plasma. We find that most of the PEEK's crystals are induced by nucleating carbon fibre and then they developed the transcrystalline or spherulite shape, depending on the crystallization conditions. Because the volume fraction of the carbon fibre is 60%, and the space distance between two adjacent carbon fibres is about 10 μm–20 μm, the crystal size of PEEK matrix is mainly controlled by the space distance between adjacent carbon fibres, and the crystallization temperature has little effect on it. The detail of the oriented crystal growth of the PEEK relative to carbon fibre was first observed by SEM. Our results show that the nucleation process of PEEK–carbon fibre composite is as follows: The first lamella is formed orientationally in the carbon fibre surface in the way that the *a* crystallographic direction is parallel to the radial direction of carbon fibre, the *b* direction parallel to the tangent line of cross section of carbon fibre, and the *c* direction parallel to the axis of the carbon fibre. Therefore, the crystals finally formed are oriented.

1. Introduction

Poly(ether–ether–ketone) (PEEK) is a relatively new aromatic, high performance, and semicrystalline engineering plastic. The repeating unit of PEEK is



Semicrystalline PEEK has a glass transition temperature, T_g, near 145 °C and a melting temperature of about 350 °C, depending on sample history and on degree of crystallization [1–3]. The morphology, structure and crystallization behaviour of PEEK has been reported [2–14].

Currently, PEEK is being used as a matrix for advanced composites, such as PEEK–carbon fibre composite. For PEEK–carbon fibre composite, the strength of the fibre–matrix interface plays an important role in the mechanical properties as well as other properties. The interfacial strength primarily depends on the interfacial structure between matrix and fibre. Some literatures have reported that the carbon fibre surface could induce the crystallization of PEEK matrix, forming a transcrystalline matrix along the carbon fibre surface [16–20]. Those experimental results showed only nucleation on a carbon fibre surface for PEEK matrix. However, studies on interfacial structure on a fine and detailed scale have not yet been reported. Therefore, the inducing nucleation mechanism of PEEK or other polymers [21–24] on a carbon fibre surface has not yet been fully understood.

In this study we used SEM to investigate the morphology of PEEK–carbon fibre composite. After the composite was etched in the proper conditions the spherulite or transcrystalline PEEK matrix formed along the carbon fibre surface and the oriented PEEK spherulite nucleus on the carbon fibre surface were observed by SEM. The experimental results have shown that during the crystallization process the nucleus of the PEEK crystal was first oriented by the carbon fibre, therefore, the spherulite PEEK matrix exhibited an orientation relative to the carbon fibre. Furthermore, the orientation mechanism of PEEK crystals in composite has been explained on the basis of our experimental results.

2. Experimental procedure

2.1. Materials

The sample used in this study was APC-2 produced by Imperial Chemical Industry (ICI). APC-2 composite is based on continuous, unidirectional carbon fibres (Hercules AS4) embedded in a PEEK matrix. The content of carbon fibre was measured by thermogravimetry (TG) is about 66% by weight, near to the value of 68% reported in the literature [19].

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2.2. Specimen preparation

For studying the influence of the different crystallization conditions on the structure or morphology of PEEK–carbon fibre composites, before samples were etched, the small laminates of APC–2 were treated according to conditions shown in Fig. 1. The crystallization conditions A and B show that APC–2 samples are crystallized from melt. Samples were first heated at a rate of 40 °C min^{-1} to 400 °C and held for 2 min in order to erase the thermal history of the samples, and then cooled to the crystallization temperature, T_c, 310 °C (crystallization condition A) and 250 °C (crystallization condition B). In these crystallization temperatures, samples were kept for 30 min and allowed to crystallize. The crystallization condition C shows that the sample was crystallized from a rubbery state. In this case the sample was held for 2 min at 400 °C, and then quenched with ice water. The quenched sample was heated to 170 °C and held for 30 min in order to allow crystallization to occur.

2.3. Etching technique

In order to obtain useful morphological information of APC–2 composite from scanning electron microscopy (SEM), the argon plasma etching technique was used in this study to improve the contrast of different structure levels. The proper etching conditions are also very important. The etching chamber is shown in Fig. 2. The etching power is 3 W and etching time is 20–60 min. In order to avoid the temperature rising (in high temperature the morphology of samples will be changed), the sample stage was cooled by the sealed cooled water system and, after etching for 10 min the etching was halted for 5 min for cooling of the samples. In all of the etching processes the sample temperature did not exceed 80 °C, that is lower than the glass transition temperature and melting temperature of PEEK. After etching the sample surface was coated by platinum under a pressure of 6.66 Pa.

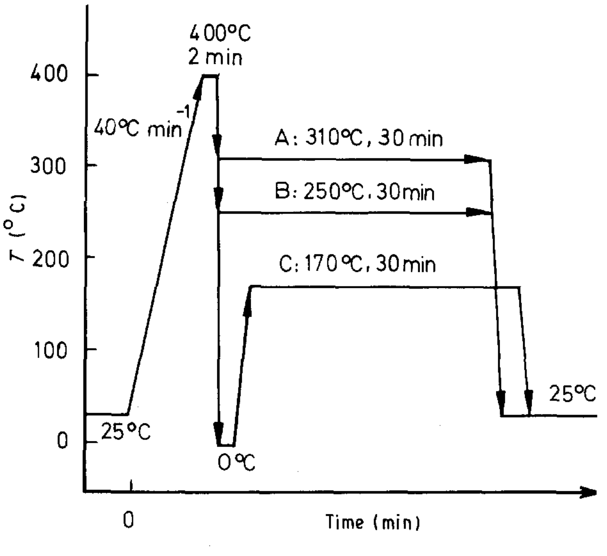


Figure 1 The crystallization conditions for APC–2 samples used in this study.

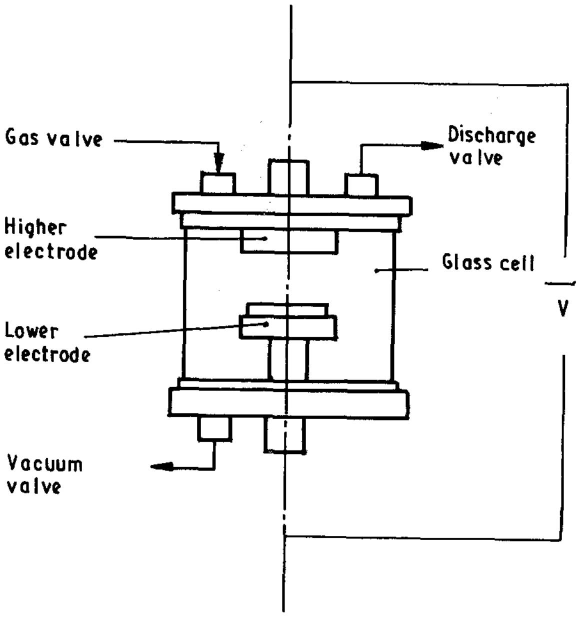


Figure 2 Schematic diagram of the Eiko IB–3 ion coater.

2.4. Electron microscope

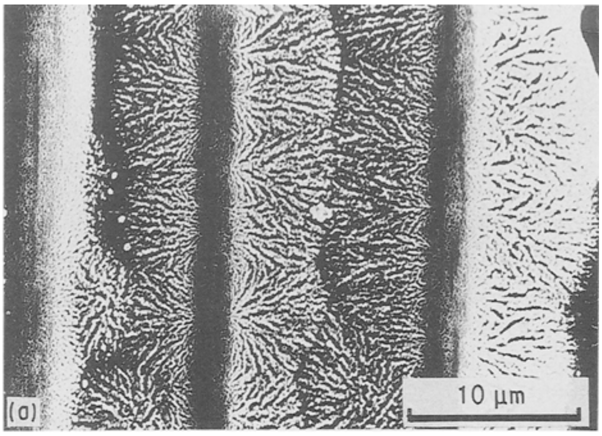
A Hitachi S-530 scanning electron microscope was used to observed the etched and coated surface of APC–2 laminate in an accelerating voltage of 25 kV.

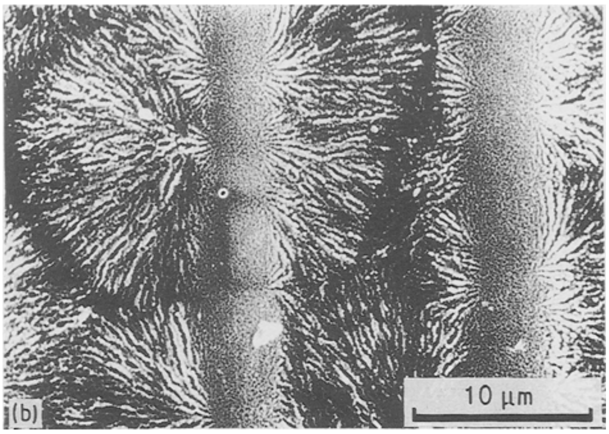
3. Results and discussion

3.1. The morphology of PEEK–carbon fibre composite

During the argon plasma etching process, owing to the chemical and physical structure difference between the carbon fibre and PEEK matrix, their ability to resist etching is also different. After etching the structural contrast between the PEEK matrix and carbon fibre in APC–2 composite was, therefore, improved. For the semicrystalline PEEK matrix, the physical structure and properties, such as the order of molecular chain, density and so on, in the region of crystal and non-crystal is clearly different, therefore the structure contrast between the crystal and non-crystal can also be improved with the argon plasma etching method. In a word, the APC–2 composite surface etched properly by argon plasma is favourable to the investigation of scanning electron microscope.

The SEM micrographs of APC–2 composite samples that were prepared and etched according to the methods mentioned above are shown in Fig. 3. It is well known that the carbon fibre is made up of many crystallites with a perfect structure and when compared with PEEK matrix, it has a stronger ability to resist the argon plasma etching. After etching the surface layer of PEEK matrix in APC–2 composite was totally eradicated. In Fig. 3 the long and narrow white pieces are clearly the carbon fibres. For PEEK matrix, due to the fact that the crystal structure is more perfect than that of non-crystal, the crystal region has a stronger ability to resist etching than the non-crystal region. It is very clear that the radial stripes shown in Fig. 3 are the laminae that make up





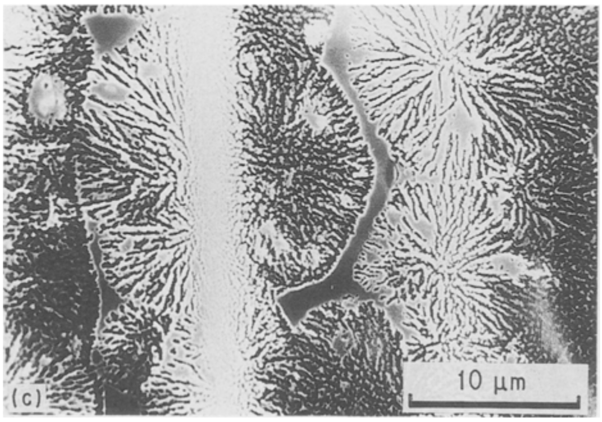


Figure 3 The SEM micrographs of APC–2 samples etched by argon plasma. The crystallization conditions were: (a), 310 °C and 30 min, crystallized from the melt; (b), 250 °C and 30 min, crystallized from the melt; (c), 170 °C and mins, crystallized from the rubbery state.

PEEK crystal and the region between laminae or crystals is the non-crystal region.

Comparing the three SEM photographs in Fig. 3, we can find that the morphology or crystal texture of APC–2 composite seriously depends on the crystallization conditions and the carbon fibre. When APC–2 composite was crystallized from the melt at a high crystallization temperature, for example, at 310 °C, a typical transcrystalline is observed, seen in Fig. 3a. This experimental result is fundamentally different to the result reported by Blundell *et al.* [20]. The morphology feature shown in Fig. 3 was enlarged 3000 times. Therefore, we can probe the fine structure of transcrystalline or crystal induced by carbon fibre. It is very clear that the transcrystallines are grown from the carbon fibre surface and is formed by a lot of long and narrow spherulite. During the high temperature crystallization process, a lot of nucleation sites in the carbon fibre surface can induce PEEK matrix to crystallize, thus a large number of small spherulites are formed. During the continuous growth process, the growing spherulites come into collision with each other in the axis direction and the development in axis direction is limited, but the development in radial direction is unlimited and growing spherulites grow continuously until a typical transcrystalline is formed.

Fig. 3b shows the SEM micrograph of the etched surface of APC–2 composite crystallized from the melt at 250 °C. The crystal texture has two characteristics, some crystals are transcrystallines, and others are spherulites. The transcrystalline and spherulite nuclei are on the carbon fibre surface, when APC–2 composite is crystallized from melt at 250 °C, and the nucleation sites on the carbon fibre surface are less than that of APC–2 composite crystallized at 310 °C. But in etching the whole APC–2 surface, we did not observe any crystals nucleated from self-seeding in bulk. The results mentioned above indicate that when APC–2 composite is crystallized from melt the crystals, no matter whether spherulite or transcrystalline, are still induced by the carbon fibre surface, but the inducing nucleation ability of carbon fibre is weakened.

When APC–2 composite was crystallized from a rubbery state at 170 °C, the spherulites nucleated on the carbon fibre surface were still observed by SEM, shown in Fig. 3c, but the transcrystalline was not observed. From Fig. 3c we can also see the non-crystal region between two spherulites. In some APC–2 sample surfaces, we observed spherulites that had their nucleation sites within the matrix. This result continuously indicates that when the crystallization temperature further decreases, the inducing nucleation ability of carbon fibre surface is further weakened. In a word, the crystal texture of PEEK matrix in APC–2 composite depends primarily on the crystallization condition. When the crystallization temperature is reduced, the influence of the carbon fibre on the nucleation of PEEK matrix is correspondingly weakened and the crystal texture of PEEK matrix transfers from the typical transcrystalline to the typical spherulite. During crystallization processes at lower temperatures (for instance at 170 °C), nucleation of PEEK matrix also occurred within the matrix.

As we know, crystallization in pure polymers is restricted to temperatures between the glass transition temperature (T_g) and the equilibrium melting point (T_m), and crystallization or spherulite rate reflect the competition between nucleation rate and the rate of transport or diffusion in the melt. Nucleation rate decreases with increasing temperature and dominates the overall growth rate at temperatures approaching T_m. Rates of transport in the melt increase with temperature and dominate near T_g. Between these extremes, the crystallization rate passes through a maximum [25]. For this reason, when APC–2 composite crystallizes from the melt at higher temperatures the nucleation rate within the matrix is very slow. At this time the carbon fibre surface supplies a vast amount of nucleation sites for PEEK matrix. In other words, carbon fibre is acting as a nucleating agent for the crystallization of PEEK matrix. When APC–2 was crystallized from the melt at the higher temperature, a typical transcrystalline is observed (Fig. 3 a). When APC–2 was crystallized from the rubbery state at the lower temperature and PEEK matrix is in the super-cooling state, there is a trend for PEEK matrix to nucleate within the matrix. In these conditions the inducing nucleation ability of carbon fibre is weak and nucleation of PEEK matrix can occur within the matrix or on the carbon fibre surface. Therefore, we can observe the crystal texture feature shown in Fig. 3c. Between these extremes, of course, the crystal texture shown in Fig. 3b is observed.

In the literature [7, 8] it has been reported that the spherulite size of pure PEEK resin depends primarily on the crystallization temperature. But for APC–2 composite the factors that determine the crystal size are temperature and the distance between two adjacent carbon fibres, and the latter is a key factor. It is very important to note that in APC–2 composite the volume fraction of carbon fibre is about 60% [19] and the diameter of carbon fibre is about 8 μm. The mean distance between two adjacent carbon fibres is about 10 μm. In this case, if nucleation of PEEK matrix occurs mainly on the carbon fibre surface in the crystallization process, the distance of two adjacent fibres is a key factor in determining the size of a crystal.

3.2. The nucleation mechanism induced by carbon fibre

Fig. 4 shows a typical PEEK spherulite micrograph that was taken from an etched APC–2 specimen. From the SEM micrograph we can see that after etching the laminae formed along the fibre axis direction at the top of the carbon fibre have almost been damaged, but we can still see the laminae formed along the fibre radial direction. It is very interesting to note that in the direction of fibre axis, there are only a few laminae on the carbon fibre surface that we can see clearly in Fig. 4. It is very important to note that these laminae are the laminae that form the nuclei of spherulites. The reason, that after etching we can still see this structural feature—only a few laminae in the centre of the spherulite and all other laminae in the same level damaged—is that in crystallizing from the melt these laminae in the centre are formed first and have a more perfect structure than other laminae. These laminae are, therefore, not damaged to the same extent during the argon plasma etching process. Fig. 5 shows the SEM micrograph of a PEEK spherulite that was taken from APC–2 specimen like Fig. 4. The feature in Fig. 5 is the laminae sheaf forming the nuclei of spherulites is perpendicular to the observation plane. From Fig. 5 we can see that laminae grow radially from the nucleus of the spherulite and progressively wrap-up the carbon fibres that have been damaged.

According to the results shown in Figs 4 and 5, we have already noted that a few laminae that form the spherulite nucleus are perpendicular to the axis direction of carbon fibre. Lovinger and Davis [5, 6] have studied the crystal structure of PEEK. Their results have shown that when PEEK ultra thin films were crystallized from the melt, the spherulites attain an extraordinary cylindrical symmetry and spherulites of PEEK are grown with a unique orientation: the *b* axis is radial, the molecular *c* axis is tangential to the plane of the film, and the *a* axis is tangential normal to the spherulite plane and nucleation plane on the substrate is on the *bc* plane. According to the results obtained by Lovinger and Davis and us, the first lamina orientation formed during the crystallization of PEEK matrix from melt is diagrammatically shown in Fig. 6. The orientation form of the first lamina is as follows: the *a* crystallographic direction is parallel to the radial direction of fibre, the *c* crystallographic direction to the axis direction, and the *b* crystallographic direction to the tangential line direction of cross section of carbon fibre. The nucleation plane on the carbon fibre surface is still on the *bc* plane.

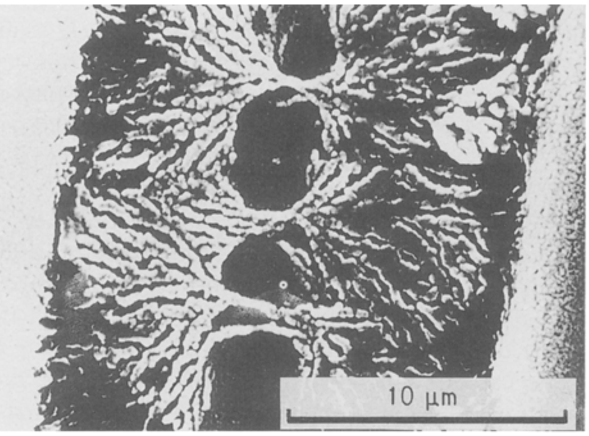


Figure 4 The SEM micrograph of spherulite nuclei of PEEK matrix in the carbon fibre surface. The direction of laminae that form the spherulite nucleus is perpendicular to the observed direction.

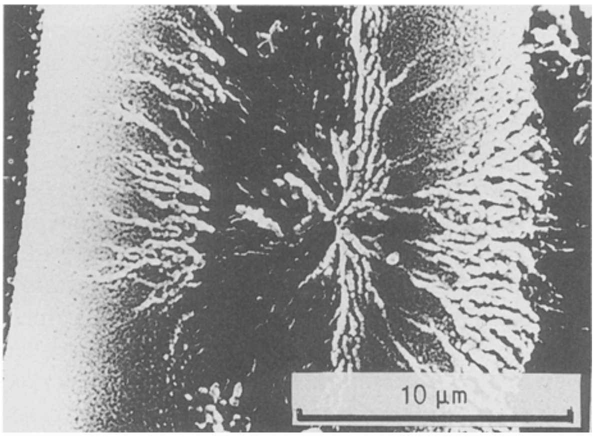


Figure 5 The SEM micrograph of a spherulite nucleus of PEEK matrix in the carbon fibre surface. The direction of laminae that form the spherulite nucleus is parallel to the observed direction.

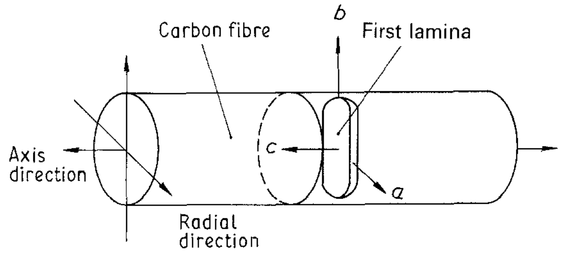


Figure 6 Schematic diagram of the first lamina oriented by the carbon fibre surface in the crystallization process.

The fine structural feature on the carbon fibre surface clearly affects the crystallization behaviour and crystal texture of polymeric matrix. The research results of Hobbs [24] have shown that if the dimension of fine crystallites plane on the carbon fibre surface are larger than 10 nm and these crystallites are oriented along the fibre axis direction, the carbon fibre has a very strong nucleation ability towards the polymer matrix. In the usual case, the lamina thickness of PEEK spherulite is between one and ten nanometres. It has been reported that unit cell dimensions are $a = 0.775$, $b = 0.586$ and $c = 1.00$ nm [8, 10, 26]. If we suppose that the thickness of lamina is formed by 20 unit cells, the dimensions of crystallite in fibre axis direction on the carbon fibre surface that is equal to the thickness of lamina is about 20 nm. Therefore, the result indicates that Hercules AS4 carbon fibre surface in APC–2 composite has the typical structural feature that can induce PEEK matrix to crystallize, like results reported by Hobbs [24]. We believe that solely because of this structural feature on the carbon fibre the transcrystalline is formed when APC–2 composite is crystallized from melt.

According to the model shown in Fig. 6 the first lamina is nucleated orientationally on the carbon fibre surface and the spherulite nucleation and growth model suggested by Keith and Padden [27], we can further infer the spherulite nucleation and growth process of PEEK matrix in APC–2 composite, shown in Fig. 7. When PEEK matrix crystallizes from the melt, the first lamina is orientationally formed on the carbon fibre surface, and in continuous crystal growth process a typical lamina–sheaf structure is formed, therefore, the spherulites finally formed are also oriented. Fig. 8 shows, diagrammatically, the PEEK crystal texture in APC–2 composite. When the distance between two adjacent nucleation sites is small, Fig. 8 shows the transcrystalline texture feature; but when the distance is large, Fig. 8 shows the spherulite texture feature.

Blundell *et al.* [19] have investigated the crystal structure of PEEK matrix in APC–2 composite using wide angle X-ray diffraction. Their results have shown "that when the commercially available PEEK–carbon fibre composite APC–2 is crystallized by slowly cooling from the melt, the crystals in the PEEK matrix exhibit a slight orientation relative to the carbon fibres", and the orientation is that the crystallographic direction is perpendicular to the axis of carbon fibre. According to our results in this paper we believe that the slight orientation reported by Blundell *et al.* [19] are the orientation lamina, forming spherulite nuclei.

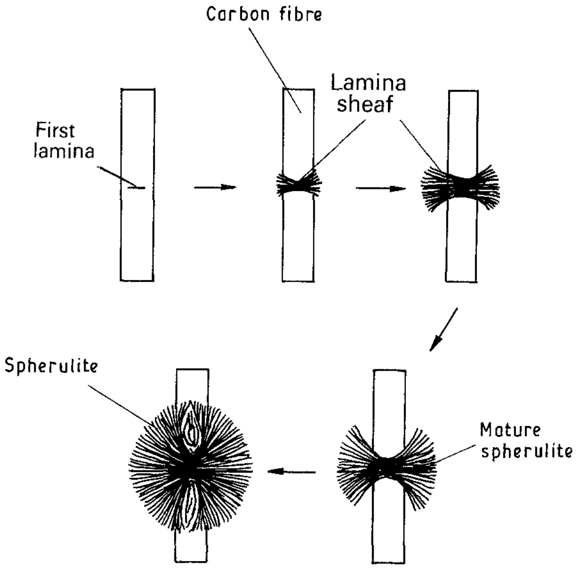


Figure 7 Schematic diagram of oriented growth process of PEEK spherulite in PEEK–carbon fibre composite.

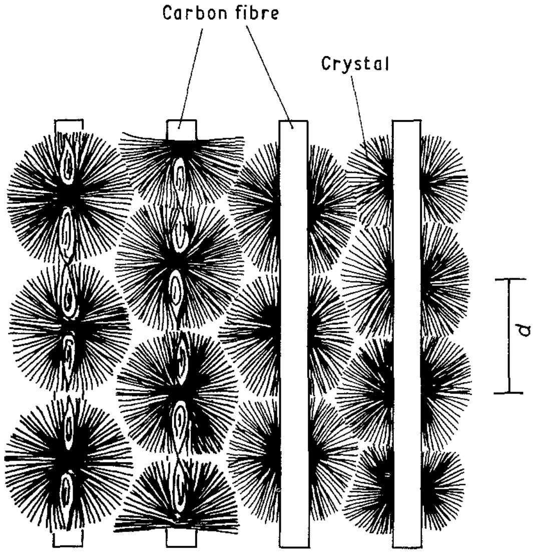


Figure 8. The suggested model of the oriented spherulite morphology for PEEK–carbon fibre composite.

3.3. The properties of PEEK–carbon fibre composite

Finally, the question of the relevance of the above observations to the understanding of the properties of composites must be addressed. Presently, composites containing long carbon fibres, such as APC–2 composite that was used in this research, are receiving attention in the aerospace industry for structural applications. Therefore, the mechanical properties of the composite for this type of utilization is very important. One of the important mechanical properties is the interlaminar fracture toughness. This is the energy necessary to separate layers of unidirectional fibre mats from a part composed of several layers. This property is mainly dependent on the polymer matrix and on the polymer–fibre interaction. In the literature, Ma *et al.* [29] studied the interlaminar fracture toughness of four uniaxial carbon fibre composites based on the four polymer matrices, PEEK, poly (*p*–phenylene sulphide) (PPS), polysulphone and epoxy. It is very important to note that PEEK and PPS are typical semicrystalline polymers, polysulphone is a typical amorphous polymer and epoxy is a typical crosslinked amorphous polymer. Their experimental results show that the critical strain energy lease rate, G_{IC}, of PEEK– and PPS–carbon fibre composites are 8.0 and 7.8 in lb/in^2, but the G_{IC} of polysulphone– and epoxy–carbon fibre composites are 3.8 and 0.6 in·lb/in^2, respectively. The comparison of PEEK and PPS with epoxy and polysulphone matrices indicates the superior interlaminar fracture toughness of the PEEK– and PPS– based composites laminates. It has been reported that carbon fibre can also induce PPS to crystallize in proper conditions [30]. The results that are mentioned in this present paper and in the literature [16–20, 29] have clearly indicated that these good interlaminar fracture toughnesses have been attributed to the formation of good bonding of semicrystalline polymers to the carbon fibres, that is, to the inducing crystallization on the carbon fibre surface. It is very important to realize that the morphological features of composites based on the semicrystalline polymers are extremely dependent on the processing conditions and fibre characteristics, like results presented in this paper, But, how the oriented crystal texture within the interface region affects the mechanical properties of composites has not been reported. However, we believe that this is a key factor.

4. Conclusions

After argon plasma etching the crystal texture and interfacial structure of PEEK–carbon fibre composite, APC–2, that has very high volume fraction of carbon fibre (60%), has been investigated by scanning electron microscopy. The results have shown that crystal texture and interfacial structure of PEEK matrix are sensitive to crystallization conditions and processes, with significant differences observed in the nucleation mechanism and morphology feature, but play small differences in the crystallite size. Samples crystallized from melt at high crystallization temperatures have a typical transcrystalline features, indicating that PEEK matrix nucleation occurred mainly on the carbon fibre surface. Along with the decrease of crystallization temperature crystal texture transfers to a typical spherulite feature and the spherulite nuclei are still on the carbon fibre surface, but the number of these nucleation sites decreases, indicating that the effect of carbon fibre on crystallization process is weakened. In the crystallization process the first lamina was orientationally formed on the carbon fibre surface in the way that the *a* crystallographic direction of lamina is parallel to the radial direction of fibre, the *c* crystallographic direction to the axis direction of fibre, and the *b* crystallographic direction to the tangential line direction of cross section of fibre. Therefore, the spherulite finally formed is, also orientation.

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Received 30 August 1990
and accepted 28 February 1991