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Spherulitic morphology of the matrix of thermoplastic PEEK/carbon fibre aromatic polymer composites

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PEEK/carbon fibre composites (derived from APC-2) have been examined with a permanganic etching technique in order to reveal the crystalline, spherulitic morphology of the thermoplastic PEEK polymer matrix. The locations of the nucleation sites for spherulite growth have been categorized. Nucleation can occur both within the matrix and from the carbon fibres. Crystallization at lower temperatures favours matrix nucleation. Nucleation from fibres is dominated by sites associated with fibre–fibre contact. There is no evidence of "transcrystalline" growth. The study also identifies two types of crystal orientation effect in the polymer matrix. The first is a slight orientation that can occur in standard mouldings and is the result of the fibres constraining the shape of the volume into which spherulite growth can occur. The second effect produces abnormally high crystal orientation and is the result of improper processing at too low a melt temperature. Such conditions cause self-seeding during consolidation of laminates which, coupled with flow-induced orientation, can lead to directionally arranged spherulite precursors in different stages of morphological development.

1. Introduction

Aromatic polymer composites (APC) [1] are a new class of advanced structural material based on carbon fibre where the polymer matrix is a tough thermoplastic rather than a conventional thermoset polymer. This paper is concerned with CF/PEEK composites in which the thermoplastic matrix is the semicrystalline polymer Victrex PEEK and the reinforcement is from high-strength carbon fibres. Such laminated structures are consolidated from prepreg by heating at about 400° C which is above the melting point of PEEK. On subsequent cooling, crystallization links together the polymer chains and rigidifies the structure. An appreciation of the crystalline morphology of the matrix is therefore essential for understanding the structure and behaviour of these materials.

In common with other semicrystalline polymers there are two main hierarchical levels to the crystalline morphology of PEEK [2]. The largest entities are the spherulites which are of the order of 10 μm across and which represent the three-dimensional growth patterns of the much smaller, underlying crystals. These crystals consist of stacks of lamellae typically 5 nm thick which grow outward from the nucleation sites until they mutually impinge with themselves or intercept with any intervening carbon fibres. Previous studies [3–5] of the matrix morphology of CF/PEEK have been mainly concerned with characterizing the crystallinity at the lamellar level or with the kinetics of the crystallization process. In this present paper we wish to focus on the spherulite morphology as revealed by scanning electron microscopy after using a permanganic etching technique [6]. The paper also brings together the results of several associated investigations in order to show how the spherulites are influenced by the embedded carbon fibres.

There are two main issues to be discussed. The first is to establish whether the carbon fibres in the composites are able to influence the nucleation processes of the spherulites. In the literature on fibre-reinforced crystalline polymers there have been several observations of prolific nucleation at the fibre/matrix interface giving rise to so-called transcrystallinity in which the growth pattern is predominantly perpendicular to the fibre surface [7–9]. Hot-stage microscopy studies of single carbon fibres embedded in a PEEK film sandwiched between glass slides have already noted this effect. Such specimens are, however, not representative of ICI's APC-2 grade of CF/PEEK laminates, where the fibre content is very high. To discover the reality of the situation it is necessary to use a microscopic technique that can probe the structure in the middle of a real composite specimen.

The second objective of the paper is to provide explanations for our previous observations [3] of a preferred orientation of the PEEK crystals relative to the direction of the carbon fibres. The early studies showed that, depending on the preparation conditions, there is sometimes a preference for the crystallographic *a*-axis to be aligned perpendicular to the

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fibres. At that time it was speculated that it could be ascribed to a preference in the direction of the crystal growth, possibly related to enhanced nucleation from the fibre surface, in the manner discussed above. As a result of our observation of the spherulitic morphology we are now able to offer a fuller explanation of the orientation effects. There are, in fact, two orientation phenomena associated with the crystal growth habits. The first is a very minor effect and occurs in APC-2 fabricated under normal recommended conditions. The second effect is more pronounced and can occur when consolidation is carried out at too low a temperature. The explanation of this latter effect depends on recent advances in knowledge of the basic growth habits of PEEK [10, 11].

2. Experimental details

2.1. Materials

Laminates were prepared from ICI's APC-2 prepreg consisting of 61% by volume of continuous, unidirectional, Hercules AS4 carbon fibres in a matrix of Victrex PEEK poly-ether-ether-ketone.

Unidirectional laminates were prepared using the recommended procedure for APC-2 by stacking layers of prepreg in a matched metal mould, consolidating at 400° C and then cooling in the mould at about 10° C min^{-1}. Previous studies [4] have shown that laminates prepared in this way crystallize in the region of 300° C. A further sample was prepared by taking a 20-ply consolidated laminate, heating to 400° C for 10 min and then rapidly transferring to a cold press to quench. At this stage X-ray examination showed that the polymer matrix was amorphous. The laminate was then crystallized by lightly clamping in a press preheated to 250° C. This sample simulates the thermal history experienced during rapid cooling fabrication methods where it can be necessary to post-anneal to achieve the necessary crystallinity in the matrix.

Subsidiary experiments described in the text were made in order to explore the origins of the pronounced orientation phenomenon.

2.2. Etching technique

The laminates were sectioned either perpendicular or longitudinal relative to the fibres and then polished. The pieces were then immersed in a stirred solution of 1% potassium permanganate in a 5 : 2 : 2 solution of sulphuric acid, orthophosphoric acid and distilled water for 5 min. After careful washing in a 7 : 2 solution of sulphuric acid and distilled water followed by a 30% hydrogen peroxide solution and then distilled water, the specimens were lightly gold coated for examination in a scanning electron microscope.

3. Spherulite morphology of standard laminates

Figs 1 and 2 show typical scanning electron micrographs of etched transverse sections from laminates that have been cooled after consolidating with the recommended APC-2 procedure. The etchant has removed a thin layer of PEEK leaving the ends of the carbon fibres standing about 1 μm above the matrix. The preferential etching of the amorphous regions in the polymer produce radiating patterns which reveal the spherulitic growth habit. Fig. 3 shows corresponding micrographs for the laminate that has been crystallized by post annealing after quenching from the melt temperature. The size of the spherulites is clearly smaller in this case indicating that the lower crystallization temperature has caused an increase in overall nucleation density. The fine detail is also less distinct and requires the SEM contrast to be enhanced in order to make them more visible. Poorer definition when crystallized at lower temperatures was also found in earlier etching studies on pure polymer [6].

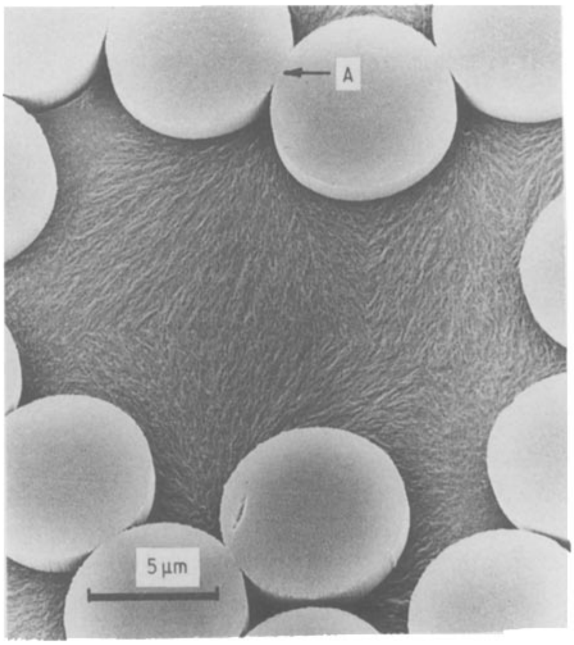

Figure 1 Scanning electron micrograph of etched transverse section of a standard laminate that has been slowly cooled from the melt. "A" indicates a typical nucleation event at a fibre–fibre contact point.

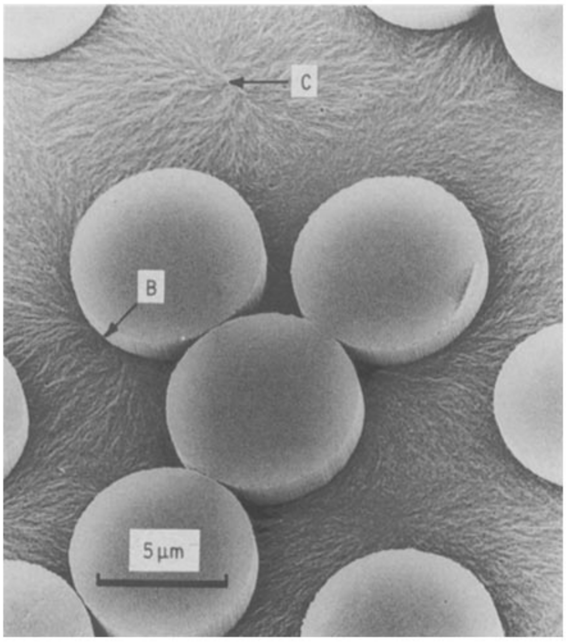

Figure 2 Scanning electron micrograph of etched transverse section of a standard laminate that has been slowly cooled from the melt. "B" indicates nucleation from a fibre surface and "C" indicates nucleation from within the matrix.

A survey of such micrographs from a range of specimens shows that the nucleation sites can be divided into three types.

1. Nucleation from contact points between fibres or regions where the fibres are almost in contact. Good examples are shown in Fig. 1. These events could be the result of local shearing at the contact points enhancing the chances of nucleation either by orienting the polymer chains or by exposing specific nucleation sites at the surface of the fibres. Alternatively they could be the outcome of differential contraction stresses being exacerbated at the contact points. The fact that extra stresses are present in the polymer matrix at the interface is possibly indicated by the fact that the etchant is often observed to preferentially penetrate at the interface with the carbon fibres.

2. Nucleation at a free fibre–polymer interface. An example is illustrated in Fig. 2. Our earlier studies of PEEK composites made from highly graphitized, high-modulus carbon fibre did in fact show prolific nucleation at the interface [12]. It is a possibility therefore that surface nucleation in APC-2/AS4 is also due to small graphitic crystals at the fibre surface. Again differential contraction stresses could have a part to play in these events.

3. Nucleation from within the matrix. There are several examples visible in Fig. 3. These events are assumed to be identical to those occurring in a normal bulk polymer sample.

The relative abundance of these three types of nucleation event varies with the preparation conditions. When crystallization occurs at lower temperatures, such as in Fig. 3, the nucleation from within the matrix increases in importance relative to the two types of site associated with the carbon fibre. Of the fibre-associated sites, the majority of the observed nucleation events appear to occur at the fibre–fibre contact points. Unlike our previous observations on high modulus carbon fibre-reinforced PEEK composites [12], nucleation from free fibre surfaces was rarely seen in these APC-2/AS4 laminates. There was certainly no evidence in APC-2 of cases of prolific surface nucleation giving transcrystallinity effects. It is our belief that the reported transcrystallinity effects sometimes seen from fibres embedded in thin PEEK films are related in origin to the fibre–fibre contact sites in APC-2 and occur where the carbon fibre comes into close contact with the glass slides sandwiching the film.

The packing of carbon fibres in composites is inhomogeneous. The above generalizations and trends of the relative abundance of nucleation sites are based on observations from regions of relatively low packing density where the regions of matrix are large enough to define the spherulite formations. They are not necessarily representative of the regions of high fibre packing which account for the majority of the volume of the laminate and where the matrix structure is not clearly visible with the etching technique on transverse sections. Longitudinal sections are more revealing but it is difficult to achieve an ideal cut that will coincide with the plane that passes through the contact line of two touching fibres. One such lucky cut in a standard

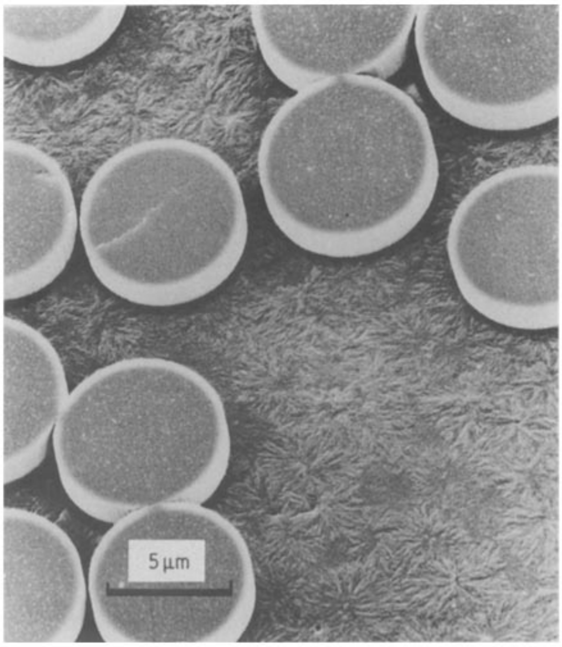

Figure 3 Scanning electron micrograph of etched transverse section of a laminate that has been post-annealed after quenching from the melt, showing significant nucleation within the matrix.

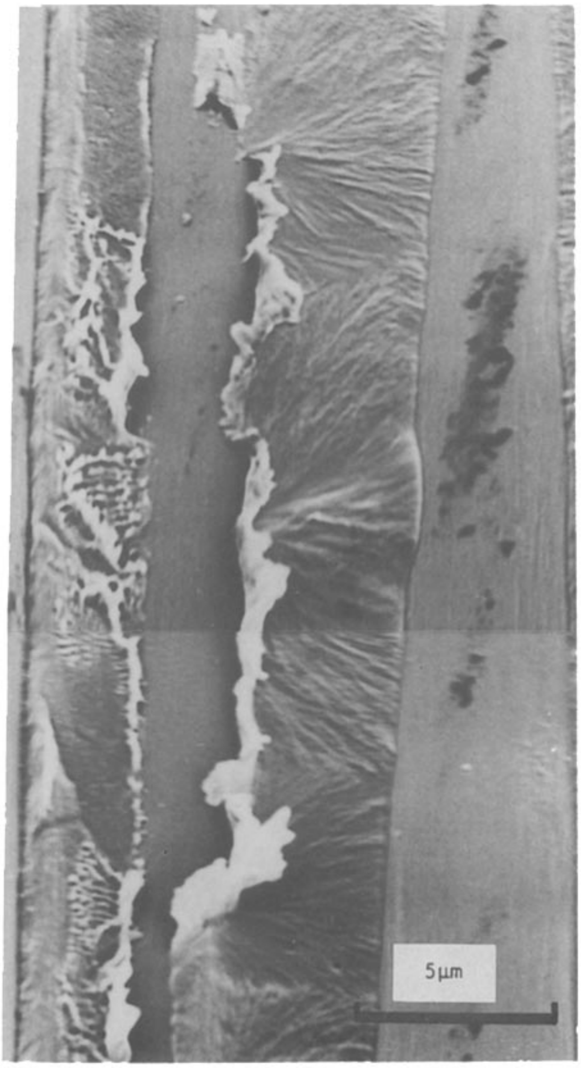

Figure 4 Montage of scanning electron micrographs of an etched longitudinal section showing a region of high fibre packing in a slowly cooled laminate.

cooled laminate, is illustrated by the montage of micrographs in Fig. 4 which show views at different positions along the same fibre strand. In Fig. 4 the hollow nest of the absent fibre is clearly visible. Also seen is the emergence of a second fibre underneath the hollow demonstrating that one is here witnessing the matrix polymer in the region of a fibre–fibre contact. The etching reveals a series radiating growth patterns emanating from well-spaced nucleation sites located along the line of contact. There is no sign of other competing nucleation events in this field of view. There is further corroborative evidence from recent SEM studies of fracture surfaces where the patterns associated with matrix ductility suggest rows of spherulitic growth correlating with the ridges of underlying fibres.

From the point of view of the following discussions it is important to emphasize that no evidence has been found where the nucleation density along the line of such fibre–fibre contact is high enough to constrain the crystalline growth to occur predominantly perpendicular to the fibres as can occur in "transcrystalline" growth situations.

4. Orientation effects in standard prepared samples

Our earlier X-ray diffraction studies [3] showed that to a first approximation the crystallites in the PEEK matrix are essentially randomly oriented. This infers that the overall growth habits of the spherulitic structures are relatively unimpeded by the intervening carbon fibres. However, more detailed diffractometer studies of the relative heights of the crystalline reflections demonstrated that when a laminate is cooled more slowly there is a tendency for the (2 0 0) reflection to intensify in directions perpendicular to the carbon fibre axes. This indicated a slight preference for the (2 0 0) crystal planes of the PEEK lattice to be arranged parallel to the carbon fibres, i.e. the *a* lattice vector has a preference to lie perpendicular to the fibre directions.

The slight orientation effect in question occurs in laminates prepared under normal recommended consolidation conditions and becomes evident when laminates are cooled very slowly from the melt ($\ll 10^\circ$C min^{-1}, which is below the recommended cooling rate). SEM observations in such cases reveal spherulitic developments very similar to that in Figs 1 and 2, except that the spherulites tend to be larger due to an overall reduction in nucleation density.

At the time of the early work mentioned above, details of the growth habit of PEEK crystals had not been established and the present SEM etching techniques for observing spherulite structures had not been developed. In the absence of other evidence speculation was therefore made that the crystal *a*-axis was probably the preferred growth direction and that the preferred orientation was the result of enhanced growth perpendicular from the carbon fibres from nucleation sites on the fibre surface. Both those speculations have since been proved incorrect. Subsequent work of our own [11] and other workers [10, 13] has established that the preferred growth direction of PEEK crystals is along the *b*-axis. Furthermore the microscopical studies discussed above now show that in standard prepared APC-2 samples there is no evidence of the transcrystalline growth effect perpendicular to the fibres.

We now believe these slight orientation effects can be explained in terms of the interplay between the disposition of nucleation sites and the shapes of the recesses between fibres into which the spherulites are constrained to grow. The ideas were developed in detail in a previous paper [11] where we describe our studies on model samples made with embedded fibres. Here we will summarize the main principles. It is proposed that the nucleating sites are arranged such that the space available for spherulitic development between fibres is elongated in the fibre direction. The natural growth habit of PEEK into these constrained regions will therefore create an enhancement of the *b*-axis in the direction of the fibres. This will be accompanied by an enhancement of the *a*-axis perpendicular to the fibre axes, consistent with the observed enhancement in the intensity of the (2 0 0) reflection.

It is difficult convincingly to substantiate this proposed mechanism because the regions in the composite where it is likely to be emphasized are in the regions of high fibre packing which remain relatively inaccessible to detailed observation by the SEM etching method. Nevertheless, the mechanism for producing the observed orientation effect has been demonstrated in the model fibre-embedded samples and is entirely consistent with the present SEM observations of spherulites and their mode of nucleation.

5. Abnormal orientation effects

In addition to the slight orientation effects discussed above, we have also reported observing an experimental laminate where the enhancement of the (2 0 0) reflection was particularly highly pronounced [3]. The orientation was high enough to be clearly visible in a transmission X-ray photograph of a small specimen of this material. This effect has since been observed occasionally in unidirectional laminates made from APC-2 prepreg. Fig. 5 shows two such photographs at different levels of exposure and Fig. 6 gives an explanatory key to the reflections. Microscopic examination using the etching techniques shows that both the morphology of the matrix and the origin of the orientation in these samples is entirely different from that of a normally consolidated laminate.

An etched view of a plane perpendicular to the fibres is shown in Fig. 7. The texture of the matrix is completely different from that of a normal APC-2 sample and indicates that the origin of the orientation effect must be totally different from that discussed above for normal samples. The normal spherulitic structure is absent. All that can be discerned is a smaller scale texture of randomly arranged sheaves about 1 to 2 μm long. Additional information can be obtained from longitudinal views of planes parallel to the fibre direction as in Fig. 8. At first sight the matrix structure is similar in size and texture to that seen in Fig. 7. Closer inspection, however, reveals that in many places the sheaves appear to be nucleated from

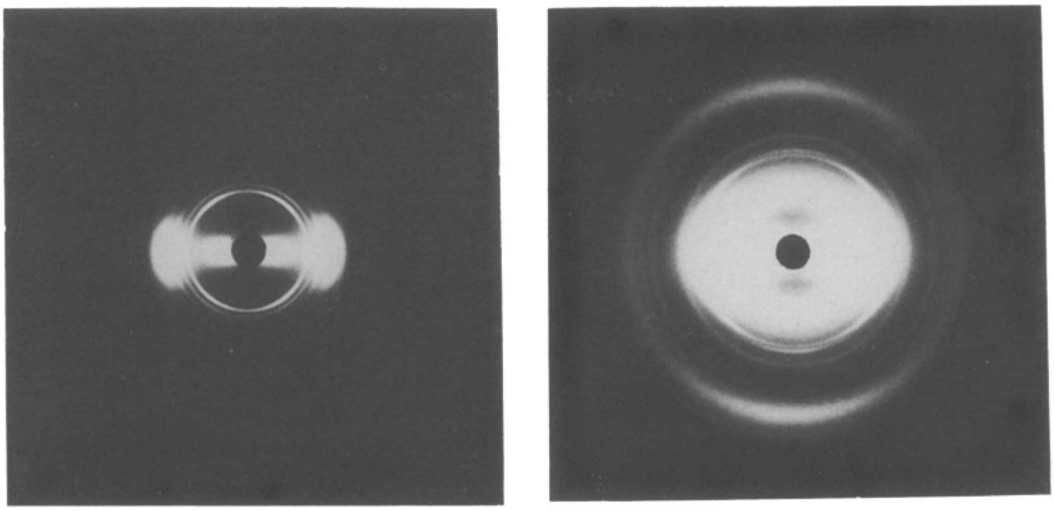

Figure 5 X-ray photographs of a uniaxial laminate with abnormal polymer orientation taken with different levels of exposure.

the same point, and form the appearance of small, primary radiating structures. The fact that the structure viewed perpendicular and parallel to the fibres is clearly distinguishable in this manner suggests that the crystallite orientation is related to a preferred orientation of the primary sheaf structures. It would appear that the basic crystallizing habit consists of sheaves which radiate in a two-dimensional manner. In this specimen the planes containing the two-dimensional growth are arranged preferentially parallel to the fibres. Thus in Fig. 8 one is able to see an occasional radiating habit, but in Fig. 7 all one can see are sections through the planes of growth.

These two-dimensional radiating structures closely resemble the two dimensional "spherulites" described by Lovinger and Davis [10] in their studies of PEEK which has been melt-crystallized from thin films. Their model for these structures is similar to the spokes of a cartwheel, where the spokes are crystal lamellae or stacks of such lamellae growing out from the centre. By careful electron diffraction studies they were able to demonstrate that the *a*-axes of all the crystals are preferentially directed along the axle direction of the cartwheel structure. This is similar to the radiating structures in the matrix of the above CF/PEEK sample and is a good starting model to explain the nature of the observed orientation effects, because the *a*-axes would then all be preferentially oriented perpendicular to the carbon fibre direction. It is therefore suggested that these two-dimensional sheaf structures are representative of the immature, early stages of growth of a PEEK spherulite from a bulk melt. The reason they are unable to reach maturity in this particular sample is that the nucleation density is so high that further growth is prevented by mutual impingement. If the nucleation density had been lower it is presumed that the growth habit would have been able to develop into larger three-dimensioned spherulitic entities such as those seen in Figs 1 to 4.

Two questions remain to be answered concerning this high orientation sample. (i) Why is the nucleation density so high? (ii) Why are these immature structures confined to grow preferentially in planes parallel to the carbon fibre axes? One well-known way of obtaining a high nucleation density is by the phenomenon of

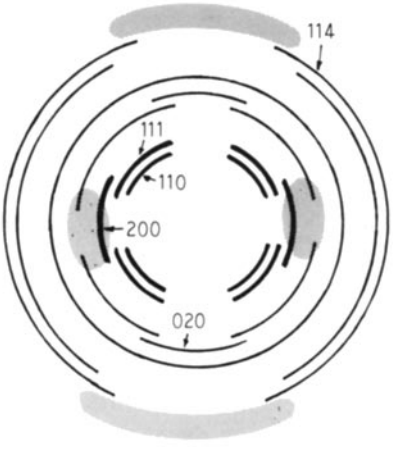

Figure 6 Schematic key for Fig. 5, showing the crystalline reflections from the polymer matrix. The diffuse scatter from the carbon fibres is indicated.

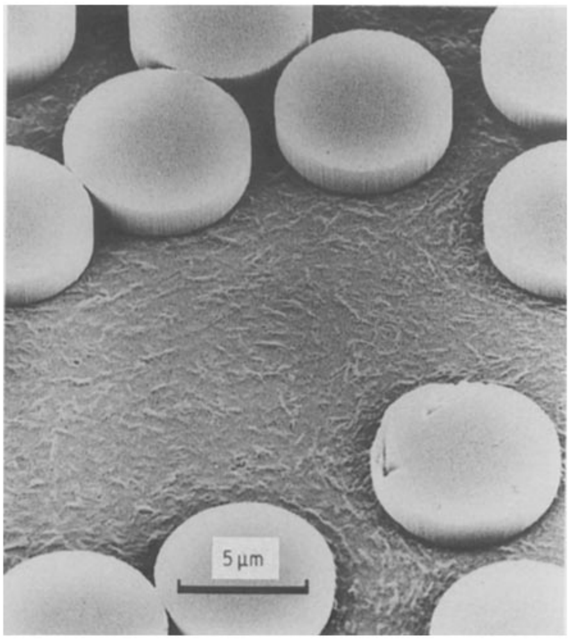

Figure 7 Scanning electron micrograph of etched transverse section of a laminate with abnormal orientation.

Figure 8 Scanning electron micrograph of etched longitudinal section of a laminate with abnormal orientation.

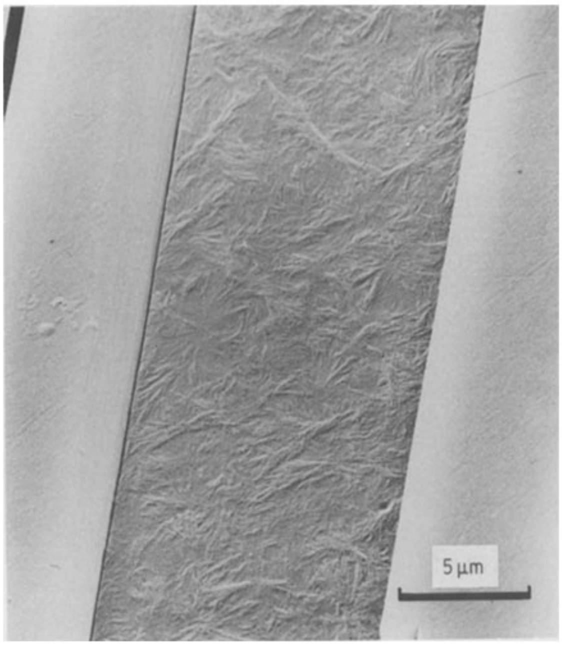

Figure 10 Scanning electron micrograph of etched longidutinal section of a pre-consolidated laminate that has been subsequently self-seeded.

self-seeding [14]. This occurs when the polymer is heated to a melt temperature which is above the main crystal melting temperature but which is not high enough to melt the last traces of crystallinity. On subsequent cooling the small remnant crystals are able to seed the crystallization process. Trial DSC studies were carried out on APC-2 prepeg to find an appropriate melting regime to promote self-seeding. It was found that when a sample of previously consolidated laminate was slowly heated in a DSC up to about 355° C the rate of crystallization on subsequent cooling was enhanced by a factor of about 10 due to the self-seeding effect. (355° C is about 15° C above the normal peak melting point in a DSC scan.) The same thermal history was applied to a pre-consolidated laminate while lightly clamped between the plattens of a press using an embedded thermocouple to monitor the temperature. After cooling to crystallize in the normal way, the laminate was examined by the etching technique.

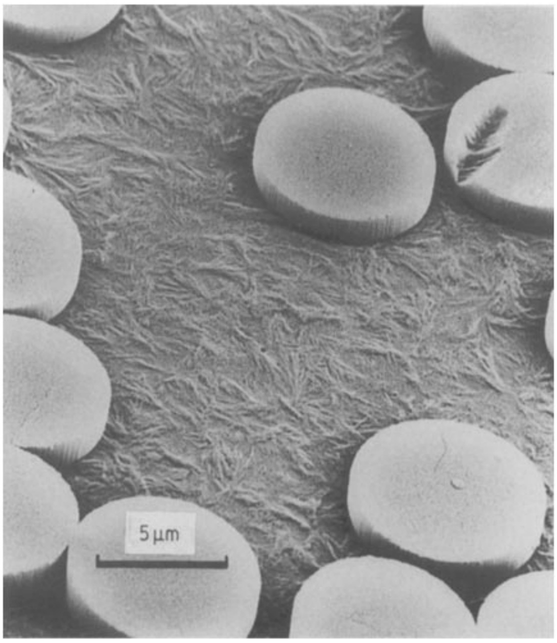

Figure 9 Scanning electron micrograph of etched transverse section of a pre-consolidated laminate that has been subsequently self-seeded.

The results from this sample are shown in Figs 9 and 10. The size scale and general appearance of the texture are very similar to that shown in Figs 7 and 8 indicating that self-seeding could satisfactorily explain the high nucleation density in the high orientation samples. However, closer examination shows that on this occasion the appearance of two-dimensional planar sheaf structures is clearly visible from both view points. There is no preferential orientation parallel to the carbon fibres. This observation was confirmed by X-ray examination which showed that the PEEK crystallites were randomly oriented in the sample. Thus, although the very small scale of the crystal texture can be simulated by self-seeding using low melt temperatures, an additional mechanism is needed to explain the orientation in this morphology. (It should be emphasized that the small spherulites in Figs 8 and 9 are obtained by crystallizing at high temperature using self-seeding to nucleate the spherulites. This is distinct from Fig. 3 where the enhanced nucleation is a consequence of crystallizing at lower temperature, where the normal nucleation rates are higher.)

The fabrication of this particular self-seeded sample was based on a preconsolidated plaque prepared according to recommended APC-2 conditions. During the melting process in the press, no excess pressure had been applied so that there would have been no significant flow of the matrix during the process. A further self-seeding experiment was therefore carried out to find whether flow of the molten matrix can have any effect on the morphology. A fresh plaque with unidirectional lay-up was therefore prepared in a

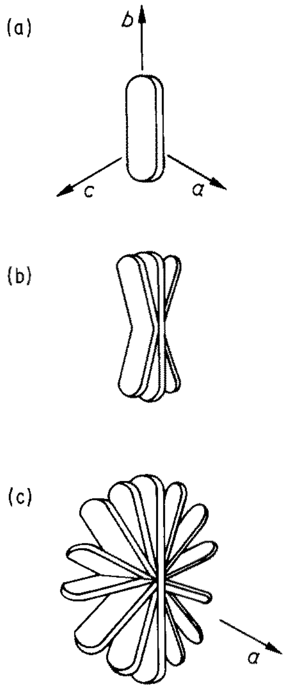

Figure 11 Development of a lamella (a), into a sheaf (b), and then into a "cartwheel" (c), where the "axle" is the crystallographic *a*-axis. Out of plane sheaving beyond (c) then leads to a spherulite.

matched metal mould using fresh prepreg sheet. The normal method of consolidation was used with the exception that the melt was restricted to the self-seeding temperature of about 355° C instead of the normal recommended temperature of 400° C. After etching, this sample revealed a texture identical to that shown in Figs 7 and 8. The planar sheaf structures were only clearly visible in the planes parallel to the carbon fibres. Furthermore, X-ray diffraction showed the *a*-axis had a very marked enhancement in the direction perpendicular to the fibres. This sample therefore clearly demonstrates that the small immature, planar sheaf structures are the result of crystallizing from a self-seeded melt and that the effect of compressing the pregreg during the fabrication causes the planes of the sheaf structures to be aligned parallel with the fibre direction.

One can therefore deduce that the previously reported examples of CF/PEEK with high orientation had been fabricated inadvertently at a low melt temperature in the region of 355° C. It should be emphasized that this temperature is well below the recommended processing range (380 to 400° C) for fabricating from APC-2 prepreg. Subsidiary DSC experiments show that the enhanced nucleation from self-seeding became negligible above 370° C.

The above ideas and explanations of crystal orientation in CF/PEEK were developed concurrently with studies of a similar orientation phenomenon in melt-drawn fibres of pure PEEK polymer. This other work, which involved extruding fibres of polymer at various temperatures in the range where self-seeding occurred, is described in a separate publication [15]. Detailed analysis using X-ray diffraction and SEM [16, 17] demonstrates that the planar "cartwheel" structure of Lovinger and Davis probably represents just one stage in the development of the growth habit from a primitive needle-shaped lamella through to a three-dimensional spherulite (Fig. 11). The precise structures and orientation present in a crystallizing melt fibre depend in a specific and interrelated way on the melt temperature, the extrusion rate and the cooling conditions. These factors determine the diversity of the crystal nuclei, the degree of maturity of the crystal habit and degree of orientation of the entities in the flowing melt. It has been shown that the degree of development between a lath shape and a "cartwheel" can to a certain extent be deduced from the intensity distribution around the diffraction rings. Despite difficulties from interference from the diffraction of the carbon fibres, a close scrutiny of PEEK diffraction rings in Fig. 6 shows a bias of the (1 1 4) around the equator and four discrete arcs in the (1 1 0) reflection; both these features suggest that the crystal habit is perhaps closer in character to axial sheaf structures rather than planar randomized "cartwheels".

These results have led to the proposal that when fibres are drawn from a seeded melt, the longitudinal flow interacts with the shape aspect of the developing crystal habits and rotates them in the flowing melt so that they preferentially align in the draw direction.

This orientation coupled with the appropriate stage of the morphological development within the consecutive sequence lamella → sheaf → cartwheel → spherulite (Fig. 11) can produce the orientations actually observed. By this scheme the cartwheel is not really a separate and novel entity but rather a stage of the usual sheaf development where sheaving is highly developed within the plane of the initial fanning but not, as yet, out of this plane. This particular stage, which seems more pronounced in PEEK than is usual in other polymers, provides yet another level on which orientation is possible in the morphological hierarchy. It is surmised that a situation similar to the above can exist when CF/PEEK is consolidated at self-seeding temperatures, and that there is a rotation of the sheaf structures due to melt flowing along between the carbon fibres.

The small size of the samples used in the above self-seeding experiments precluded any serious mechanical testing. However, it was still possible to carry out a few trans-flexural tests; these did not show any major deterioration from results on laminates fabricated using recommended conditions.

6. Conclusions

The use of the etching technique has revealed how the spherulitic growth habit of the crystals in the PEEK matrix develops inside an APC-2/AS4 composite and how the carbon reinforcing fibres interact with this process. Subject to being excluded by the volume already occupied by fibre, the growth habits in normally prepared composite specimens appear to be identical to the spherulites in pure polymer.

When fabricated under recommended conditions nucleation of crystal growth can occur both from within the matrix and from the carbon fibres, the relative abundance depending on the circumstances. Crystallization at lower temperatures favours matrix nucleation. Two types of nucleation events can originate from the fibres. The dominant events occur at fibre–fibre contact points. Nucleation from a free fibre–matrix interface is relatively rare. The level of fibre-originated nucleation is never high enough to give the appearance of a "transcrystalline" layer.

The observations have also helped in understanding the origin of preferred orientation effects of the crystallites. The slight orientation effect observed in normally prepared samples is probably due to the fibres constraining the shape of the volume into which growth can occur and thus favouring an excess of the *b*-axis growth direction along the line of the fibres.

The much greater orientation effect recorded in some occasional samples has been found to be associated with a high density of immature growth structures with a planar sheaf appearance which are organized with the planes of the structure parallel to the fibres. These structures originated from self-seeding of the matrix as a result of using a fabrication temperature that does not completely melt previous crystallinity. The preferred orientation of these structures appears to be the result of melt flow between the fibres during consolidation aligning the shape aspect of the planar sheaves along the line of flow. When fabricated under recommended processing conditions, articles made from APC-2 prepreg will not contain these self-seeded structures.

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