Polymer Bulletin 19, 297–304 (1988)

Polymer Bulletin

b Axis type orientations in melt drawn fibres of poly(ether-ether-ketone) (PEEK)

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SUMMARY

Melt drawn fibres of poly(ether-ether-ketone) (PEEK) have been investigated in which various textural effects occur, arising through alignment of self-seeding nuclei, rather than simple orientation on a molecular level. Growth of the seeds can be arrested at different stages, with associated changes in x-ray diffraction patterns.

INTRODUCTION

This note is a preliminary announcement of a more comprehensive work on morphological issues arising from studies of PEEK polymer but with implications of wider relevance(1). On the one hand the latter stretch back to works by one of us in 1956(2) and on the other it interacts with current works on PEEK/carbon fibre composites(3). The essence of our studies is macroscopic orientation effects arising, not through the conventional alignment of chains, but through larger scale entities in the morphological hierarchy.

EXPERIMENTAL

The subject matter is based on rather unusual orientation effects observed while pulling out threads or pressing mouldings from PEEK melts, solidification taking place during gentle flow. In the course of it, wide angle X-ray patterns (WAX) such as Figs. 1a) and 2a) were obtained with the respective small angle (SAX) patterns shown in Figs 1b) and 2b). The unusual nature of the patterns will be apparent from comparison with the conventionally drawn _c_ axis fibre pattern (Fig. 3). It will be stated here that Fig. 2 is not merely a more disoriented version of Fig. 1 but has distinctly different features of its own. These are the azimuthally different positions of the weak hkl reflections displayed e.g. by 114 which is broadly equatorial in fig 1a) and meridional in Fig. 2a). The same difference is displayed even more conspicuously by the SAX patterns with maxima on the equator (Fig. 1b)) and meridian respectively (Fig 2b)). The distinction between Figs. 1 and 2 is therefore basic to the underlying orientations which will be referred to as I and II respectively.

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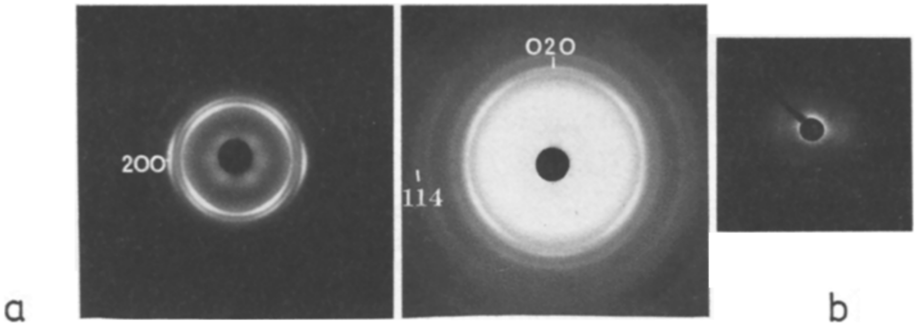

Fig. 1 Orientation I; drawn at 6 mms $^{-1}$; maximum melt temperature 356°C; a) WAX i) inner reflections, ii) outer reflections; b) SAX. Fibre axis vertical.

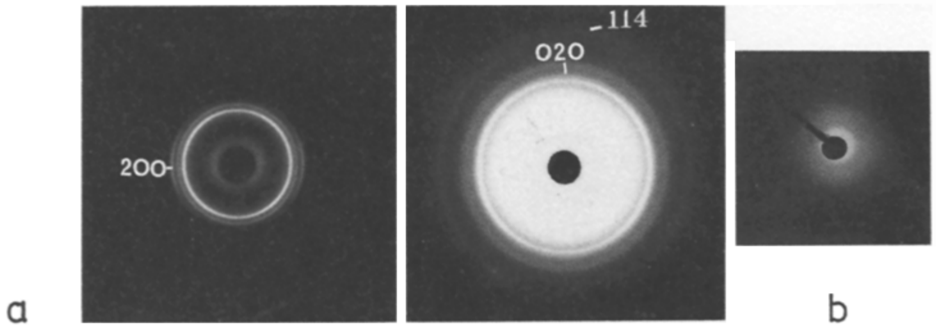

Fig. 2 Orientation II; drawn at 6 mms^{-1}; maximum melt temperature 368°C; a) WAX i) inner reflections, ii) outer reflections; b) SAX. Fibre axis vertical.

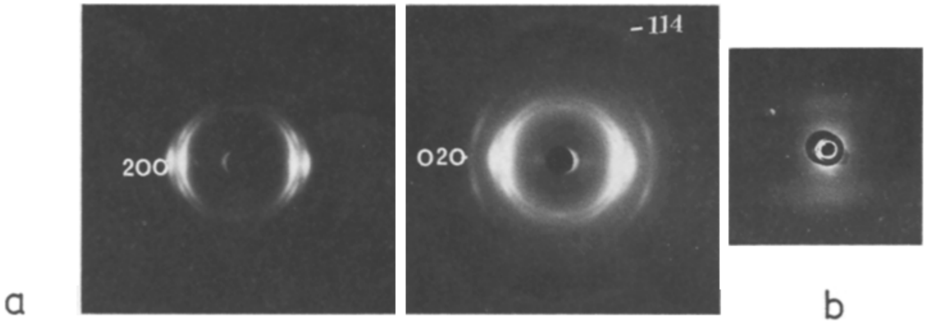

Fig. 3 *c* axis oriented fibre; a) WAX i) inner reflections, ii) outer reflections; b) SAX. Fibre axis vertical.

Three factors were instrumental in producing patterns such as Figs 1 and 2: i) orientation, ii) preceding maximum melt temperature and iii) degree to which crystallization is allowed to go to completion. The role ofi) is self evident: it should be sufficient but not too high. The natural melt strength seems to satisfy these requirements automatically, so as to yield orientations as in Figs. 1 and 2. Whether that in Fig. 1 or Fig. 2 pertains depends more on conditions ii) and iii) than on i) in the following way. The situation is clearest for high degrees of crystallinities (high for PEEK) which may be achieved, if necessary, by post orientation annealing. In the cases of figs 1 and 2 low melt temperature (356°C) yields orientation I and high melt temperature (368°C) orientation II for a common draw speed of 6 mms^{-1}. Without post orientation heat treatment the crystallinity may sometimes be low in which case much of the slowly crystallizing sample will be in the amorphous glassy state when solidifying during orientation. In some cases orientation I will prevail. This will transform into II in the case that the preceding melt temperature was high, but will stay as I, with enhanced definition of the reflections if the melt temperature was low. In another case (not shown) of high melt temperature, orientation II was apparent before heat treatment within a glassy matrix, with the texture being preserved on annealing but again with enhanced definition.

DISCUSSION

The above observations (together with some others to be quoted) are readily explained when considering the genesis of the morphology.

First take the WAX patterns. It is a basic truth, only too often ignored, that in general a texture cannot be uniquely defined from the pole distribution alone, even in the unrealistically favourable case when the latter is fully mapped. If mapping is highly incomplete, as in the present case, assumptions are needed for its construction and, following this, a model is required for representing it through a real texture.

In spite of sparsity of information we are greatly helped by the presence of an axis of cylindrical symmetry. With 020 maximum on the meridian and 200 and 114 on the equator (and others in appropriate intermediate azimuths) we believe that we are safe to asssume that Fig. 1, i.e. case I, corresponds to a _b_ axis fibre orientation. If so, this can be readily visualized using morphological information. We know that PEEK crystallizes with elongated acicular shaped chain folded lamellae with _c_ along the layer normal and _b_ being the long lamellar dimension (4,5,6). Further, _b_ will be the long direction of sheaves and the radius of spherulites developing from these lamellae (4,7,8). Now, if the initially forming lamellae became oriented in the flow field so that the lamellar planes _and_ the long lamellar directions become parallel to it the cylindrically averaged assembly of such lamellae will provide orientation I observed.

One can proceed to orientation II by considering the sheaving which arises from the above oriented initial lamellae. Here further morphological information due to Lovinger (7) can be invoked who observed, in thin PEEK films 'cartwheel' type structures as in Fig. 4. If we assume (to be justified below) that sheaf development in PEEK proceeds through such planar fanning even in the three dimensional sample interior, then the texture becomes an assembly of such 'cartwheels' with the axes of the 'wheels' normal to the flow, hence orientation direction. If we further assume that otherwise the 'cartwheels' are cylindrically averaged, pole figure construction (1) reveals that orientation II is achieved. Amongst others, the planar sheaving retains 100 pole (the 'wheel' axis) on the equator, the 010 pole (b axis) on the meridian (with a spread that is intrinsic to this texture and not due to disorientation) but moves the 001 pole (hence the 114 close to it) to the meridian from the equator. Similarly the lamellar normal (identifiable from SAX patterns) will move from its equatorial position in orientation I to the meridional in position II (see Figs. 1b and 2b), again readily demonstrable from pole figure construction (1). Thus,the orientation effects observed can be accounted for, and in fact follow from, the development of the morphology (Fig. 5). In this context the 'cartwheel' does not represent a basically new type of morphology; it is the usual sheaf formation where the initial planarity of the sheaves, always present to some extent, prevails.

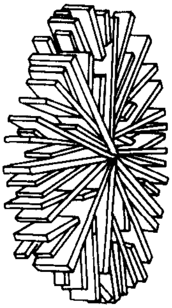

Fig. 4. Schematic representation of a 'cartwheel'; after Lovinger and Davis (7)

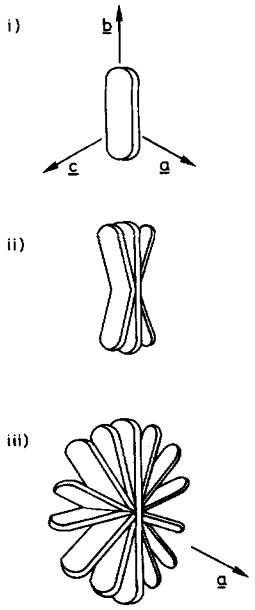

Fig. 5 Development of a lamella (i) into a sheaf (ii) and a 'cartwheel' (iii).

While the above accounts for the diffraction effects, we need to explain why the morphology does not develop into spherulites, known to exist in PEEK otherwise, thus removing all macroscopic orientation altogether. There are two separate reasons for this, both encountered in the present work.

The first is incomplete crystallization (relating to (iii) above) when the oriented morphologies (such as in Fig. 5) are arrested by cooling induced vitrification in their early stages. This explains the observation quoted above that in some poorly crystallized samples subsequent heat annealing transforms orientation I into II.

The second reason is confinement through impingment of the developing morphologies. Clearly, the state of the morphology at the stage of impingment will be determined by the crystal nucleation density. It is at this stage that the influence of the melting temperature becomes operative ((ii) above). In the case where this is low residual crystal nuclei will survive (self seeding), enhancing subsequent impingement, hence orientation I. At higher melt temperatures pre-existing nuclei are reduced and so is the subsequent impingement. This promotes orientation II and eventual randomness through fully developed spherulitic structures. All these cases differ from the ones in the preceding paragraph to the extent that here crystallinity will be as high as achievable morphologically, and subsequent heat treatments will not produce further changes (at least in the type of orientation) as indeed observed.

It will be noted that in orientation I the _c_ pole is equatorial; in contrast in II, while broadly spread, it is centred on the meridian. In terms of polarizability this means that the sign of birefringence from this source alone should be negative in I and positive in II. The observation is that the birefringence is usually positive but in samples where X-rays give the best defined orientation I, negative birefringence was in fact the case in some places. We consider the existence of negative birefringence in itself significant because the orienting influence will always introduce some chain orientation in the amorphous portions of the sample, which in the case of a low crystallinity polymer such as PEEK, can therefore easily dominate, hence imparting positive birefringence irrespective of crystal orientation.

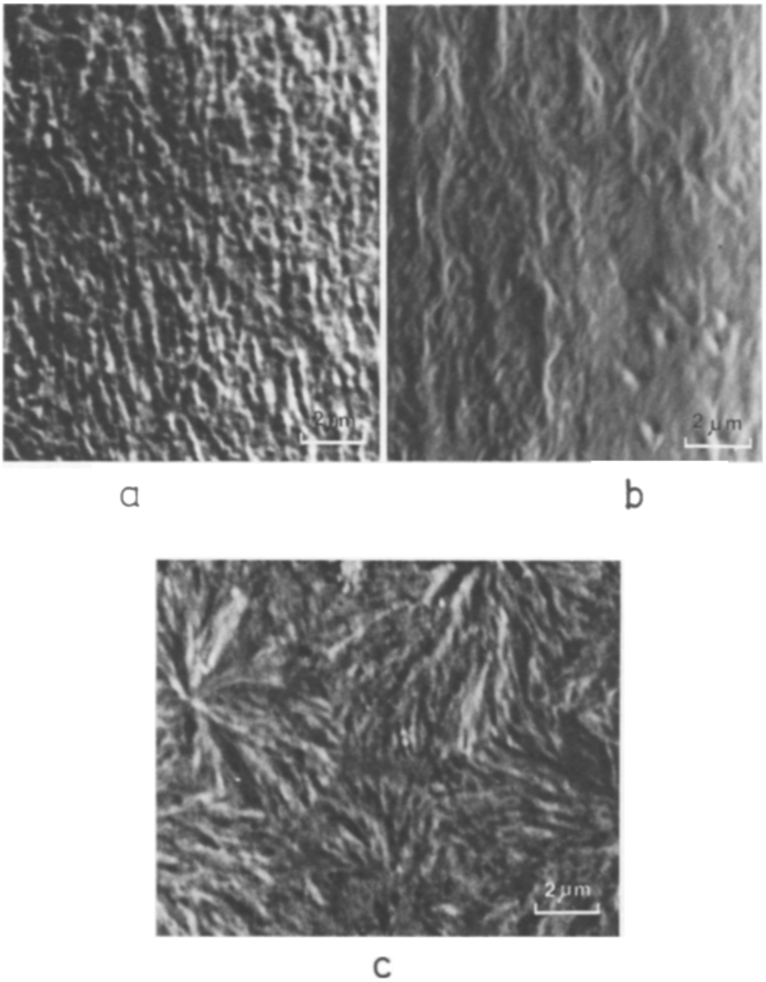

Fig. 6 Scanning electron micrographs of etched specimens; a) fibre with orientation I; b) fibre with orientation II (fibre axes vertical); c) usual spherulitic material.

Morphological information was obtained by scanning electron microscopy on fibre surfaces or exposed interior surfaces etched with a modified version of the permanganic acid etch of Olley, Bassett and Blundell (9) (see Fig. 6). As seen, within the resolution and definition of the images the fibrous structure in Fig. 6a is consistent with orientation I, which is regarded as an assembly of parallel structures that would usually form the radii of fully developed spherulites such as in Fig. 6c. Additionally, the in parts disc-like and in part fibrous features in fig. 6b are consistent with the largely planar sheaves or 'cartwheels' seen in all orientations, flat-on, edge-on and foreshortened in between. Thus the deduction from the diffraction patterns are corroborated by the visible morphology and by the birefringence as far as separable from other effects.

CONCLUSIONS

To sum up the main points: 1) Unusual orientations in the WAX patterns can be interpreted in terms of alignment and subsequent further development of morphological entities during crystallization in weakly flowing melts. This is consistent with SAX patterns, and is corroborated further by the visible morphologies. It is being emphasised that diffraction based analysis on its own, without any underlying morphological concept, could hardly have given meaningful results.
2) Conversely, in possession of the correct model the observed orientation effect can serve to identify the state of morphological development. In this respect PEEK is special only so far as it tends to retain the original sheaving plane up till later stages of spherulitic development than other substances known so far, so that the sheaf plane (or its normal, the 'wheel axis') takes on a role as oriented or orientable texture entity in itself. A further feature of PEEK in this scheme is that there is no appreciable lamellar twist (or other averaging of the lamellar normal around a growth axis (here $\underline{b}$) within a given sheaf). Namely, if it were otherwise, the equivalent change from Fig. 5i) to iii) would not give a recognisable degree of orientation for the $\underline{a}$ and $\underline{c}$ poles.
3) The density of the residual crystal seeds, i.e. melt memory can, through impingement, control the extent to which the morphological units develop, and through it the resultant orientation.

Spatial constraints such as produce macroscopic orientation effects can also be caused by heterogenities such as the particulate phase in composites. We recognized this in our previous works on PEEK/carbon fibre composites (4) where we identified two sources of orientation due to constrained development of morphological entities related to the presence of carbon fibres. This was even without invoking flow induced orientation and special features of PEEK such as the 'cartwheel'. The presence and consequences of self seeding have been identified since (separate paper on the composite to be published (3)) and the additional influence of flow, should such occur, can be readily conceived in the light of the above. All in all, the present considerations of morphologically induced orientation effects should be of general relevance for composites with crystallizable thermoplastic matrices. But even setting aside the topical issue of composites, it will be evident that the effects reported here need to be considered in the processing (e.g. injection moulding, extrusion etc.) of crystallizable thermoplastic polymers.

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Accepted December 4, 1987 C