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# Texture studies of carbon and graphite tapes by XRD texture goniometry

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Novel mesophase pitch-based carbon and graphite tapes have been developed, in which the graphite basal planes are aligned predominantly either parallel or perpendicular to the tape surface. The XRD texture goniometer has been used to quantifiably characterise the orientation of the graphite layers in these novel materials to provide a correlation between processing parameters, structural orientation and physical properties. The pole figures of the carbon and graphite tapes clearly show the arrangement of the graphitic crystalline structure within the tapes which can be directly correlated with the textures as observed in transverse cross-sections in the SEM. X-ray texture analyses of the as-spun mesophase pitch tapes indicate that they have better initial preferred orientation along the tapes compared to as-spun circular fibres. Additionally, the tapes can be made to have a texture in which the graphite layers are largely orientated parallel to the tape surface which may make them more graphitisable materials for thermal management applications.


## 1. Introduction

Mesophase pitch-based carbon fibres have found applications as thermal management materials due to their excellent thermal transport properties [1–4]. The most thermally conductive, commercially available mesophase pitch-based graphite fibre, K1100 (produced by BP-Amoco), has a nominal thermal conductivity value of 1000 $Wm^{-1}K^{-1}$. The production of such fibres requires an expensive thermal treatment at extremely high temperatures (well above 3000°C). The high value of thermal conductivity is a direct result of the highly crystalline graphitic structure and its high degree of orientation parallel to the fibre axis [2–5].

There are two distinct types of pitch-based carbon fibres available commercially. The "General Purpose" carbon fibres, which are produced from isotropic pitches, have low tensile strength (0.5–0.7 GPa) and modulus (30–60 GPa). The "High Performance" carbon fibres, which are produced from liquid crystalline mesophase pitches, have tensile strengths up to 4 GPa and modulii up to 960 GPa due to the graphitic structure being highly oriented along the fibre axis. It is known that the highly oriented graphitic structure of the mesophase pitch-based carbon fibres is inherited from the high degree of orientation of mesophase molecules in the precursor pitch fibres, which originates from the shear flow-induced orientation of the discotic mesophase molecules during melt-spinning [3]. It has also been known that fibres having a radial or flat-layer transverse textures, have higher graphitisability [3]. Thus, improvements in the degree of preferred orientation and transverse arrangement of discotic mesophase pitch molecules during fibre spinning may allow a more highly graphitic structure to develop at heat treatment temperatures below 3000°C. The corollary is that such an arrangement of mesophase molecules may yield even higher thermal conductivities than K1100 type fibres if heat-treated at an equivalent temperature, i.e., >3000°C.

It has already been shown that as-spun mesophase pitch fibres with larger diameters (>15 $\mu$m) have a higher degree of preferred orientation [6], but stabilisation of these fibres takes a longer time compared with those of smaller diameters and some randomisation of the preferred orientation also occurs [7]. The diameters of carbon fibres that can be achieved in commercial processes are restricted by the time-consuming stabilisation process; therefore carbon fibres with average diameters larger than 15 $\mu$m are rarely produced. It has been shown that ribbon-shaped carbon fibres with the graphite layer largely oriented perpendicular to the ribbon surface have higher graphitisability [3]. The speculation that the layer structure might be able to orientate *parallel* to the ribbon surface, resulting in higher graphitisability due to the more extended planar structure has been verified by the recent successful development of a novel form of graphitic material termed Highly Oriented Mesophase-based Graphite (HOMG) tape [8, 9]. HOMG tape can be made with a rectangular cross-section equivalent to the total cross-sectional areas of 100–200 conventional carbon fibres, and has a highly ordered structure with the basal plane layers oriented predominantly parallel to the tape surface. Typically, the tape can have a width up to 1–4 millimetres and the thickness (10–20 $\mu$m) of the tape enables a short stabilisation time. After such a stabilisation

TABLE I Samples studied by XRD texture goniometry

| Samples | Starting materials | Heat-treatment temperatures | $2\theta^\circ$ | Expected preferred orientation |
|---|---|---|---|---|
| Isotropic carbon tapes | Isotropic pitch A75 | 1500°C | 23.97 | None |
| P100 | Mesophase pitch from petroleum | ~3000°C | 26.30 | Strong orientation parallel to fibre axis |
| HOPG | Hydrocarbon gases | >3000°C | 26.51 | Strong orientation parallel to surface |
| Carbon tape (preHOMG) | Mesophase pitch ARA24 | 1500°C | 26.57 | Parallel orientation |
| Carbon tape | Mesophase pitch ARA24 | 1500°C | 26.57 | Vertical orientation |
| HOMG | Mesophase pitch ARA24 | 2700°C | 26.57 | Parallel orientation |
| Circular pitch fibres | Mesophase pitch ARA24 | As-spun | 25.24 | Axial |
| Pitch tapes | Mesophase pitch ARA24 | As-spun | 25.24 | Bi-directional |

treatment, the orientation is retained during subsequent pyrolysis and so gives rise to the highly ordered structure. Adjustment of processing variables enables control over the orientation of discotic mesophase pitch molecules, namely their arrangement either parallel or perpendicular to the planar surface of the tape (Details of how to control texture during processing will be presented elsewhere.). The textures are evident in transverse cross-sections from polarised light optical microscopy or scanning electron microscopy. The purpose of this study is to quantifiably characterise the orientations of the graphite layers in these novel materials by X-ray diffraction (texture goniometry) and therefore provide a firm basis for the detailed correlation between processing parameters, structural orientation and physical properties. Some preliminary results of the characterisation of preferred orientation and textures in novel tape structures compared with other carbon materials are reported here.

## 2. Experimental procedure

The as-spun mesophase pitch fibres and tapes were prepared from a naphthalene derived mesophase pitch ARA24 (100% anisotropic content, softening point: 237°C) using a bench-scale melt-spinning apparatus. The spinning precursor was formed into fibre or tape by melt-extrusion at 280–300°C. The molten mesophase pitch was extruded through a single hole spinneret (either a circular or a slot-shaped hole). With an appropriate drawdown ratio during extrusion from the spinneret, fibres or tapes were produced. A roller on a variable speed motor was used for fibres for the take-up of fibres and tapes.

The as-spun tapes were oxidatively stabilised by heating in air or oxygen at a heating rate of 5°C/min to 150°C and from 150°C to 270°C at a heating rate of 1°C/min, and finally held for 20 min at 270°C. The stabilised tapes were carbonised at a heating rate of 5°C/min to 1500°C or 2700°C respectively under an inert atmosphere, which was maintained for 2 hours.

Carbon tapes from an isotropic pitch (Aerocarb 75) were also produced in the same way and heat treated to 1500°C to compare their texture with that of the mesophase pitch-based tapes. A Highly Oriented Pyrolytic Graphite (HOPG) sample and a commercially available mesophase pitch-based carbon fibre P100 (BP-Amoco) were also used as reference materials. All samples studied by XRD texture goniometry are listed in Table I.

To examine the microstructures of the carbon or graphite tapes, they were cut into ~8–10 mm lengths and attached with double-sided carbon sticker to aluminium stubs. The samples were gold-coated and examined using a CAMSCAN Series 3 or 4 scanning electron microscope at an accelerating voltage of 20 kV.

The X-ray texture scan was conducted in a Philips texture goniometer using Cu $K_\alpha$ radiation with a Schulz reflection-specimen holder, in which the source and detector were positioned at the fixed $2\theta$ Bragg angle for reflection from the (0002) planes. The $2\theta$ values for different samples were determined in separate Bragg scans and listed in Table I. The $2\theta$ value of HOMG tape (HTT 2700°) was used for the mesophase pitch based-carbon tapes (HTT 1500°). The HOPG sample (2 cm square and thickness: 1 mm) was glued to the glass slide with its basal planes parallel to the glass slide. The fibres or tapes were aligned parallel on a glass slide, they were straightened and glued to the glass slide to cover about 2 $cm^2$. One layer of tapes was mounted on the glass slide and in the case of fibres they were spread as evenly as possible on the glass slide. The sample was then rotated around the $\Phi$ axis at a speed of 72°/min. The sample was tilted by 2.5° with respect to the $\psi$ axis for every revolution around $\Phi$. The geometry is indicated in Fig. 1. The recorded intensity arose from the 0002 graphite planes lying in a spiral of 2.5° pitch. The cycle of rotation around the $\phi$ axis was continued up to a $\psi$ value of 85° and data plotted on a stereographic projection—a pole figure—and presented in terms of contours of intensity data. The data can also be presented more quantitatively as an orientation distribution function. The preferred orientation is reported as the misorientation angle of the (0002) planes along the chosen axis, taken as full width at half maximum (FWHM) obtained from a plot of relative intensity as a function of $\psi$. The better the layer plane orientation parallel to the chosen sample axis, the lower the spread in intensity along the $\psi$ axis and the smaller the FWHM value. The orientation distribution functions were curve-fitted to a Gaussian function to obtain the FWHM values; the experimental errors of the FWHM values are within $\pm 1^\circ$.

## 3. Results and discussion

Fig. 1 is a schematic diagram showing the carbon sample arrangement in an XRD texture goniometer, together with the corresponding (0002) plane pole figures. In the case of a sample with completely

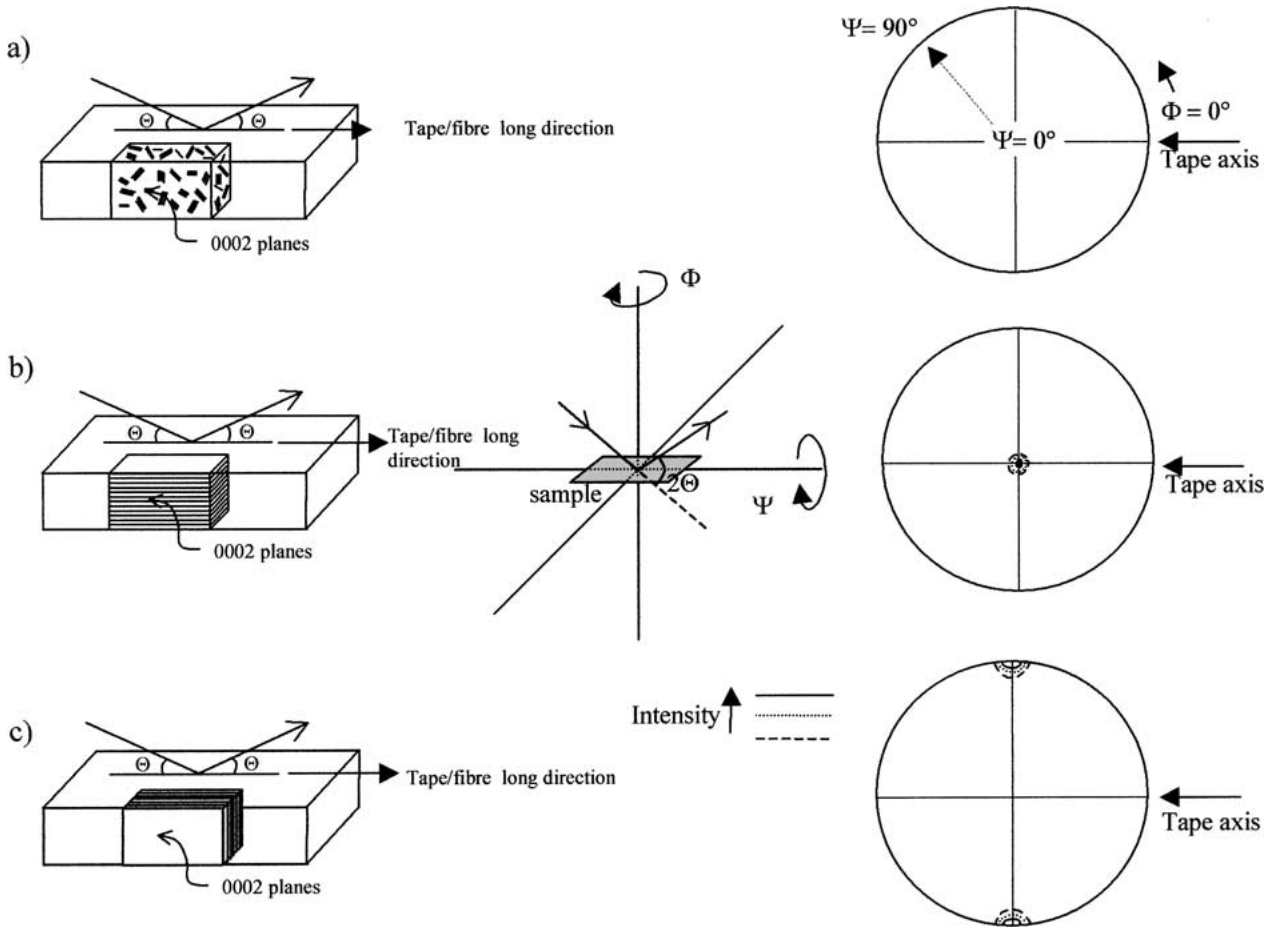


*Figure 1* Schematic diagram showing sample arrangement with respect to X-ray beam and the corresponding pole figures from materials with different ideal lateral and longitudinal arrangements of the layer planes.

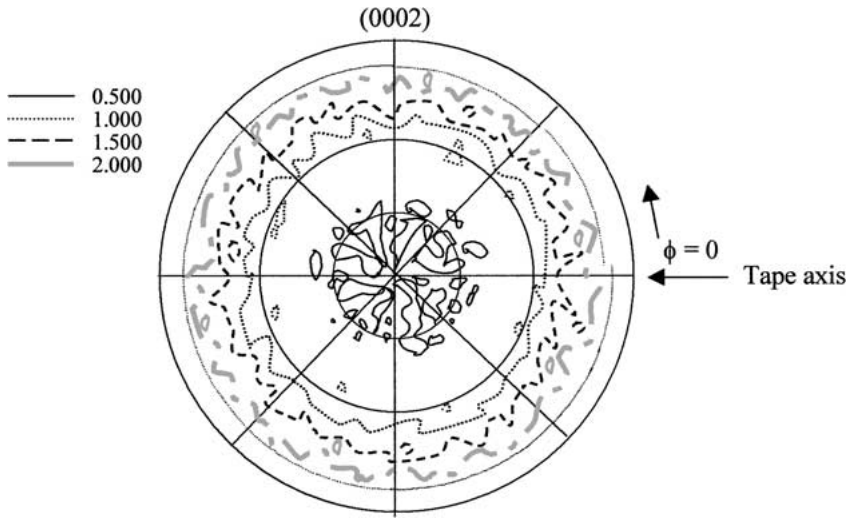


*Figure 2* Pole figure of the isotropic pitch-based carbon tape (from isotropic pitch Aerocarb 75) heat treated at 1500°C.

randomly oriented graphite crystals, the corresponding pole figure (a) shows no intensity contours–the poles are randomly distributed. When the graphite crystals are highly oriented, the pole figures can clearly show the degree of preferred orientation and the basal plane arrangement with respect to the specimen. If the basal planes are oriented parallel to the plane of the specimen, (b), the pole figure will show high intensity contours in the centre, i.e., at low $\psi$ values, whereas when the basal planes lie perpendicular to the plane of the specimen and along the tape direction, (c) high intensity contours are located at the edges, i.e., at high $\psi$ values. Of course, Fig. 1 represents a simplified model, but these pole figures will be exemplified in the following practical samples.

Fig. 2 is the pole figure of the "isotropic" carbon tape that has been heat-treated at 1500°C. It demonstrates an arrangement of 0002 planes which are oriented at high $\psi$ values (i.e., perpendicular to the plane of the tape as in Fig. 1c) but which are also randomly orientated

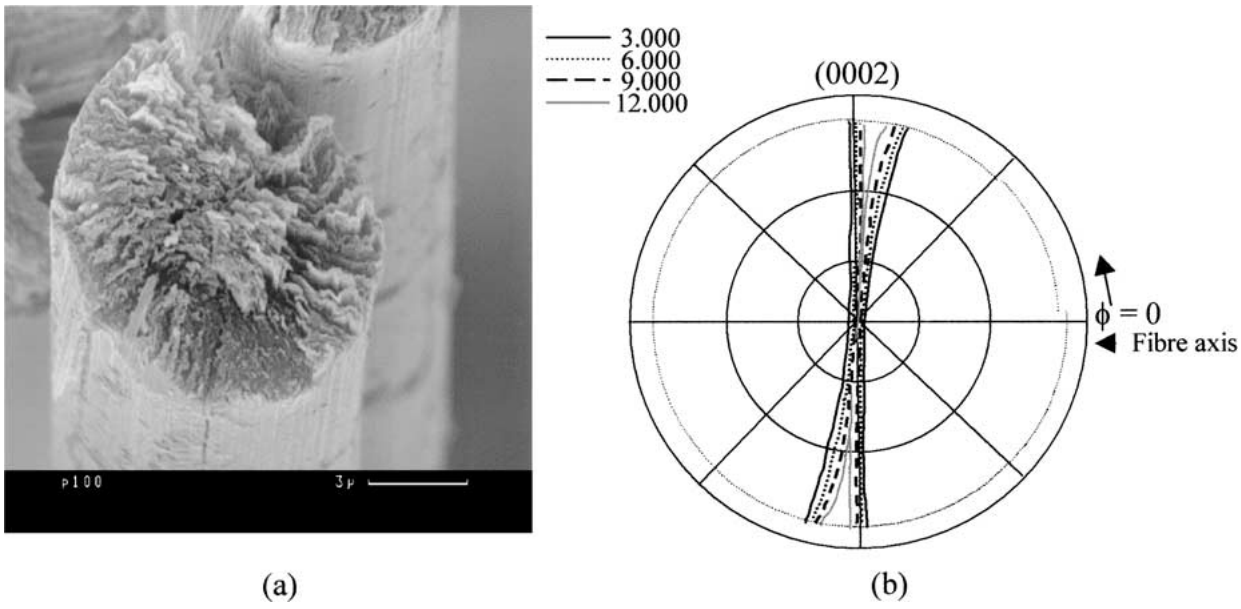


*Figure 3* SEM microphotograph of commercial carbon fibre P100 and the corresponding pole figure.

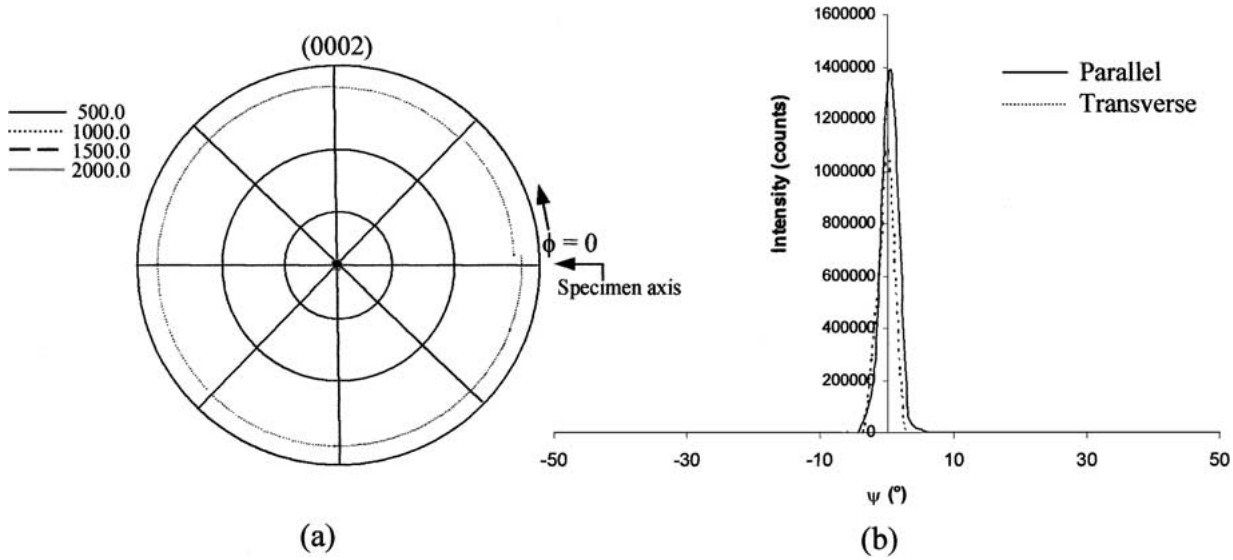


*Figure 4* Pole figure of HOPG and measured orientation distribution functions in the directions of parallel and perpendicular to the specimen axis.

with respect to the tape direction rather than along the tape direction, giving rise to a uniform distribution of intensity around the perimeter of the projector. The low values of relative intensity indicate the lower graphitic order in the sample.

Fig. 3a shows the typical microstructure for a cross-sectional P100 fibre under SEM, where roughly radial-aligned sheets can be observed, the sheets also aligned along the fibre axis. It shows no significant differences across the fibre, the graphite planes organised in a radial manner. The intensity distribution of basal planes in the pole figure of P100 (Fig. 3b) confirms that they are indeed aligned closely parallel to the fibre axis with a spread in orientation of about 5.4°. It should be noted that the intensity contours follow the arcs of small circles centred along the fibre axis and do not indicate a greater range of misorientation at high $\psi$ values.

The pole figure of HOPG (Fig. 4a) shows the highly oriented basal planes parallel to the sample plane similar to Fig. 1b with a concentric circles of relative intensity contours concentrated in the centre ($\phi = 0/180°$, $\psi = 0°$). When these intensity contours or orientation distribution functions are plotted in directions parallel and perpendicular to the axis of the specimen, the Full Width at Half Maximum (FWHM) values in both directions can be obtained (Fig. 4b). The FWHM along the sample direction is 2.1° and across sample direction 2.6°, indicating a high degree of basal plane orientation in both directions.

Fig. 5 presents a SEM image of carbon tape with graphite layers aligned mainly parallel to the tape surface and its corresponding pole figure (Fig. 5b), which shows the high intensity contours are mainly concentrated in the central region of the pole figure indicating that the basal planes lie parallel to the tape surface. Fig. 5b shows a narrower spread of intensity contour along the tape direction than transverse to the tape direction, indicating that the basal planes are more strongly oriented parallel to the tape direction than transverse to the tape direction. When the

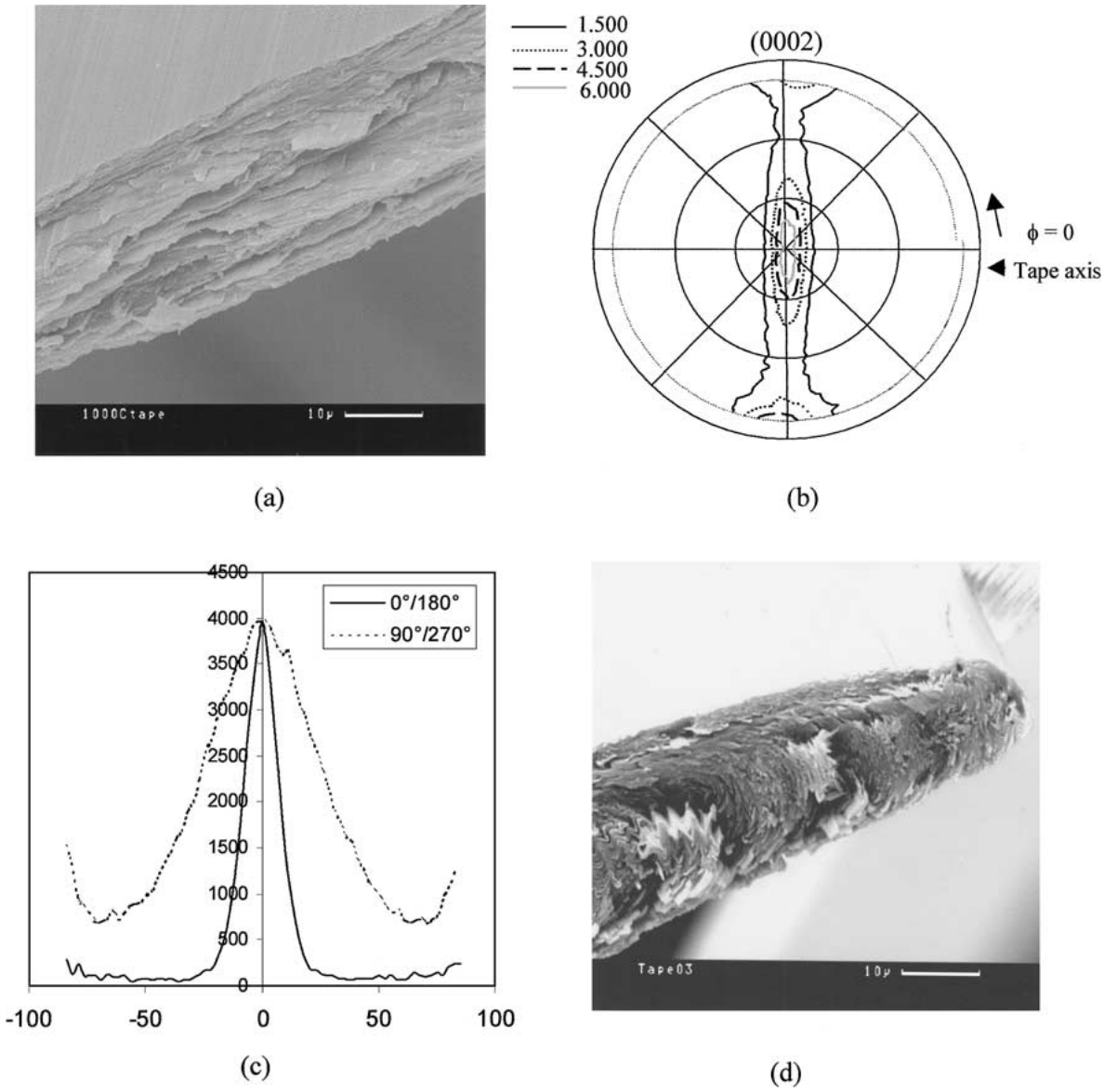


*Figure 5* Gross transverse texture of carbon tape heat treated at 1500°C (a), the corresponding pole figure (b), orientation distribution functions in the directions parallel and perpendicular to the tape (c), and transverse texture of tape edge (d).

orientation distribution functions parallel and perpendicular to the tape direction within the sample plane are plotted, the FWHM values in both directions are 17° and 54° respectively (Fig. 5c). This arises from the orientations of the basal layers close to tape edge where graphite planes align perpendicular to the main tape surface as illustrated in Fig. 5d. However, the prevailing parallel orientation is evident in the pole figures. It should be noted that the extra spreading is present at high angle of $\psi$ apart from that caused by the pole figure distortion, which is believed to be due to the edges of the tapes where the graphite layers are less oriented parallel to the direction of the tapes.

Depending on the processing conditions used during tape spinning, tapes with different transverse textures can be obtained. Fig. 6 shows a SEM image of mesophase pitch-based carbon tape heat-treated at 1500°C and its corresponding pole figure. Fig. 6a shows the graphite layers lying predominantly although curved vertical to the tape surface. The pole figure in Fig. 6b shows the high intensity contour lines concentrated near $\psi = 85°$. The extra spreading caused by the tape edges is also present at high angle of $\psi$. This transverse texture has been found in ribbon carbon fibres but has not been presented in the form of a pole figure possibly due to the fact that ribbon carbon fibres are often distorted and difficult to flatten and mount onto the glass slide. This problem also occurs with carbon tapes that have smaller transverse areas, i.e., with an aspect ratio of less than 20. This problem rarely occurs as the aspect ratio of the tape increases above this value. When the orientation distribution functions parallel and perpendicular to the tape direction within the sample plane are plotted Fig. 6c, it is obvious that the orientation distribution function perpendicular to the tape direction is strikingly different from that seen in Fig. 5c. However, the FWHM value in parallel to the tape direction is 17°, same as that of tape having parallel layer texture, indicating that the preferred orientation is not dependent on the transverse texture of the tape. It is interesting to note that the edges of carbon tapes also show different transverse textures (Fig. 6d) according to the different

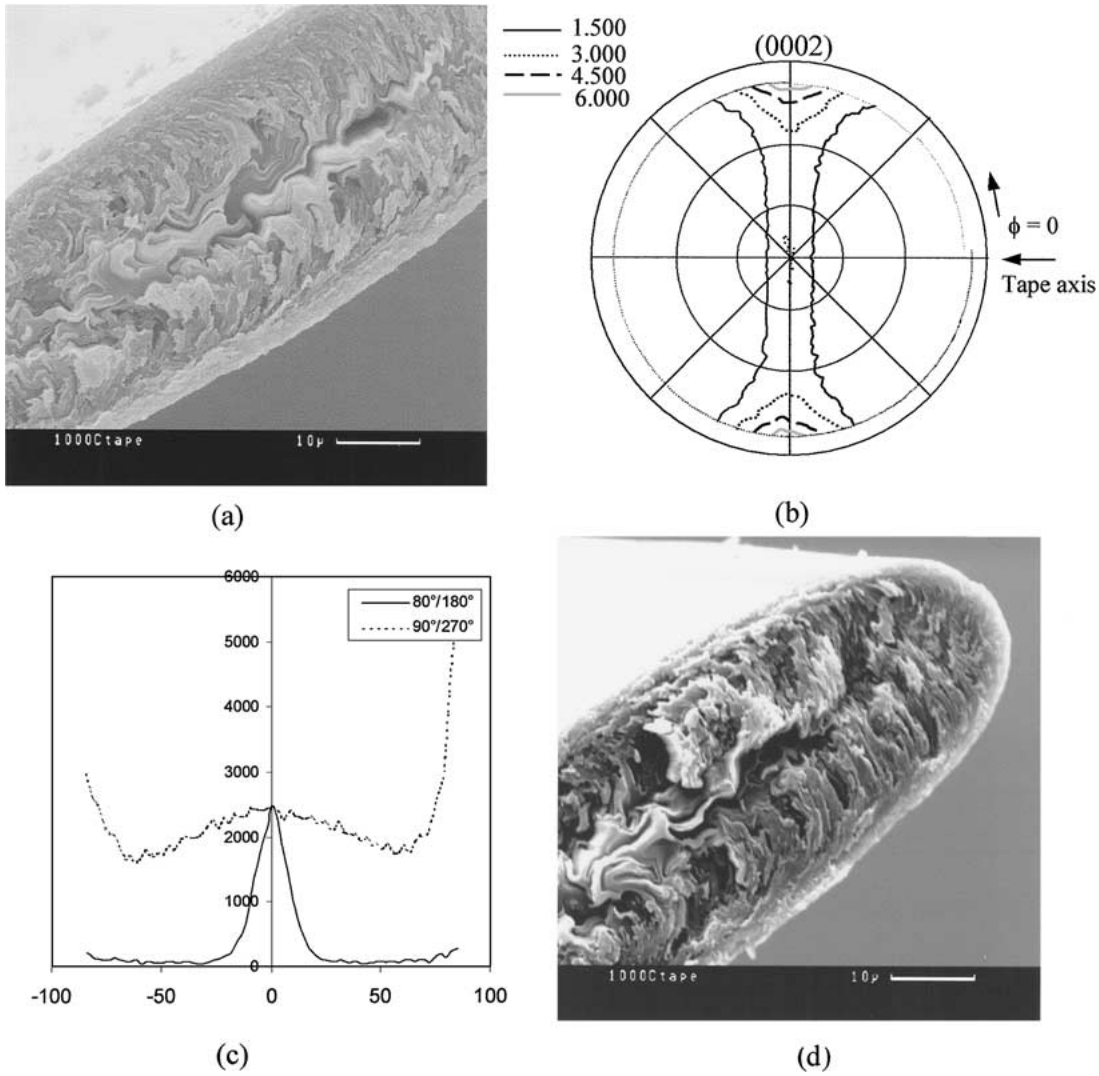


*Figure 6* Gross transverse texture of carbon tape heat treated at 1500°C (a), the corresponding pole figure (b), orientation distribution functions in the directions parallel and perpendicular to the tape (c), and the transverse texture of the tape edge (d).

transverse textures displayed in the main tape body. In Fig. 5d, graphite planes curve round the surface and some effectively lie perpendicular to the major tape surface. Fig. 6d shows the graphite planes mostly perpendicular to the surface similar to the main body of the tape.

HOMG tapes have a highly ordered microstructure with graphitic layer planes predominantly parallel to the tape surface as shown in the SEM image (Fig. 7a). The pole figure shows clearly that the basal planes are highly oriented along the tape direction like that of P100, it also shows the highest relative intensity contours located in the central area, indicative of predominant orientation of the basal layers parallel to the plane of the tape.

In the pole figures of carbon tapes heat-treated at 1500°C, the wider spreads of the intensity contour in tape direction indicate a lower degree of preferred orientation along the tapes compared to high temperature heat-treated HOMG tapes. The pole figures clearly show the difference between the carbon tapes with predominantly either parallel or perpendicular orientation with respect to the specimen surface. It is probably worth mentioning that the correlation between the pole figures and cross-sectional microstructures seen in SEM images are rarely observed for mesophase pitch-based carbon fibres except for completely symmetric structure along the axis. This is mainly due to the difficulty to arrange the fibres according to the transverse texture on the glass slide. These clear pole figures of carbon tapes are noteworthy examples because the relationship between the texture and microstructure can be very easily visualised. In most other materials the micrographs do not reveal the orientations of the reflecting planes at all and their orientations are only revealed in the pole figure [10].

It is well established that the high values of Young's modulus and thermal conductivity of mesophase pitch-based carbon fibres are directly related to the degree of preferred orientation of the graphite basal planes with respect to the fibre axis, which is inherited from the preferred mesophase molecular orientation in the precursor pitch fibres. The preferred orientation of the discotic liquid crystalline mesophase molecules parallel to the fibre axis can also be characterised by XRD texture scan. Fig. 8 shows the degree of the preferred orientation (FWHM value) of as-spun circular mesophase pitch fibres and tapes as a function of their average cross-sectional areas. It is evident that the

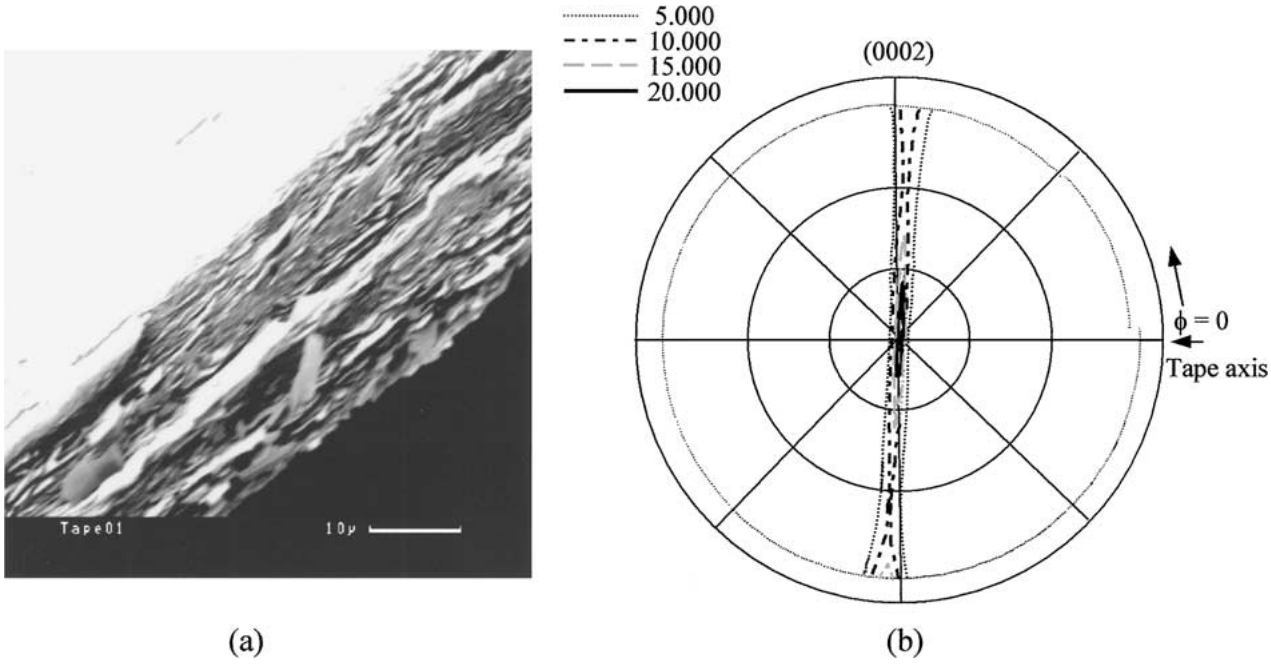


*Figure 7* SEM microphotograph of HOMG tape (2700°C) and the corresponding pole figure.

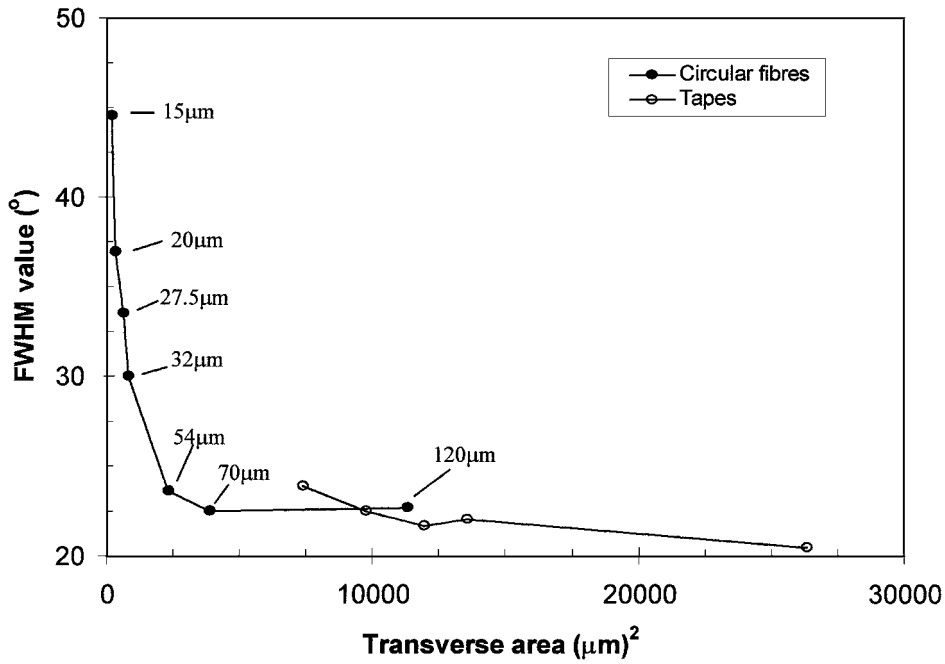


*Figure 8* Preferred orientation of the as-spun circular fibres and tapes as a function of transverse areas.

preferred orientation of as-spun mesophase pitch fibres improves significantly as the fibre cross-sectional areas increases from 100 to 2000 $(\mu m)^2$. A further increase of fibre cross-sectional area shows a lesser effect on the preferred orientation of mesophase molecules along the fibre axis. It was mentioned earlier that the increase of the cross-sectional areas of circular fibres is restricted by the diffusion-controlled stabilisation process. Stabilisation of pitch fibres of diameter larger than 30 $\mu$m takes a long time and is not economically viable. The cross-sectional areas of pitch tapes can be made significantly larger than circular fibres and the preferred orientation of mesophase pitch tapes is comparable to mesophase pitch fibres of the largest possible diameter. The advantage of the tapes is that they can readily be stabilised because their thickness is only 10–20 $\mu$m. That means that the preferred orientation induced during tape formation can be retained. This is in contrast to the large diameter circular fibres, the preferred orientation of which relaxes to a lower degree during carbonisation even after an extended period of stabilisation [7]. The effect of the cross-sectional area on preferred orientation can probably be explained in same way as Diefendorf *et al.* [11] explained the diameter effect of the circular fibres by the degree of thermodynamic disorder of mesophase pitch molecules; a pitch fibre with a smaller diameter is cooled more rapidly during spinning, retaining the disordered state prevailing at high temperature and resulting in a lower degree of preferred orientation.

In addition, the mechanical properties decrease rapidly as the cross-sectional area of circular fibres

increases [7]. The carbon tapes, on the other hand, show significantly better mechanical properties compared with the circular fibres having equivalent cross-sectional areas [8, 9].

## 4. Conclusion

XRD texture goniometry is a useful technique for the examination of preferred orientation and transverse textures of carbon materials and their precursors. It is especially important in studying the flow-induced preferred orientation and textures during fibre and tape spinning because the arrangement of discotic liquid crystalline molecules in as-spun form can not be revealed effectively by other techniques. In the case of carbonised materials, although SEM images can give a clear graphic portrait of local structure, the pole figures represent an average structure and present a more quantifiable method of describing two-directional orientation of the carbon materials. The pole figures of carbon and graphite tapes presented in this study are of particular interest since they provide a clear correlation between arrangement of (0002) graphite crystal planes shown in both the SEM images and pole figure intensity contours.

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