Preferred Orientation of the Internal Structure of Carbon Layers in Carbon Fibers

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Introduction

The preferred orientation of the carbon layer planes in carbon fibers with respect to the fiber axis has been studied in detail[1], notably in connection with the relationship between structure and mechanical properties[2], in relation to the micropore orientation [3], to intercalation [4] and to fluorination [5]. In all these studies it was assumed that no preferred orientation exists for the internal structure of the carbon layers, i.e. the orientation of the two-dimensional hexagonal structure of these layers was considered random with respect to the layer normal.

Preliminary X-ray studies on carbon fibers from mesophase pitch carried out in this laboratory indicated that a preferred orientation of the internal layer structure is observable in certain cases. The aim of the work reported here was to investigate this effect in detail.

Theoretical

In the case of a random orientation of the internal structure of the carbon layers with respect to the layer normals, the orientation distribution (pole figures) of all reflections are completely defined by the orientation distribution of the layer normals (simple fiber symmetry). A detailed theoretical treatment for this case was given in an earlier paper [6]. In order to extend this treatment to include a preferred orientation of the internal structure of the carbon layers, let us assume that the orientation of the layer normals (c-axis) and of the internal layer structure (a-axis) are not correlated and that the latter is defined by the orientation distribution $g_a(\gamma)$. Figure 1 shows a schematic presentation of the geometry involved. β is the angle between the c-axis and the fiber axis, γ is the angle between the a-axis and the section of the layer plane and the plane including the fiber axis and the c-axis. If one considers only the intensity distributions on the (hk0) interference rings one obtains the relationship

$$I_{hk}(\phi) \sim \int_{\frac{\pi}{2}-\phi}^{\frac{\pi}{2}+\phi} \frac{g_a(\gamma)\, g_c(\beta)\, \sin\beta\, d\beta}{\sqrt{\sin^2\phi - \cos^2\beta}} \qquad (1)$$

where $g_c(\beta)$ is the orientation distribution of the layer normals and ϕ is the angle between the fiber axis and the direction of the intensity measurement in reciprocal space.

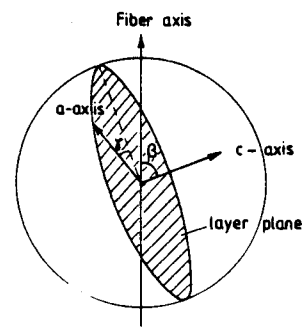

Fig.1

For carbon fibers with a high preferred orientation of the layer normals, $g_c(\beta)$ is non-zero only in a narrow range of β values in the vicinity of $\pi/2$. In that case, equation (1) can be approximated by

$$I_{hk}(\phi) \sim g_a(\phi)\, F_c(\tfrac{\pi}{2},\phi) \ ,$$

where $F_c(\frac{\pi}{2},\phi)$ is a function of $g_c(\beta)$ only [6].

A simplified determination of the a-axis orientation consists in measuring the intensity distribution $I_{10}(\phi)$ and $I_{11}(\phi)$. The ratio $J(\phi)$ of these distributions is related to $g_a(\phi)$ by

$$\frac{I_{10}(\phi)}{I_{11}(\phi)} = J(\phi) \sim \frac{g_a(\phi)}{g_a(\phi - \frac{\pi}{6})} \ , \qquad (2)$$

i.e. the maxima and minima in $g_a(\phi)$ are enhanced. Choosing a suitable mathematical expression for $g_a(\phi)$ which defines an orientation parameter q_a ranging from -1 to 1 one can show that the ratio Q of the maximum to the minimum values of $J(\phi)$ are related to q_a by

$$|q_a| = \left(\frac{Q^{1/4} - 1}{Q^{1/4} + 1}\right)^{1/3}$$

The sign of q_a is determined by the direction of the a-axis orientation. For an orientation of the carbon hexagons with the corner in the direction of the fiber axis, q_a is positive, for an orientation with the side of hexagons in this direction it is negative, $q_a = 0$ represents random orientation, $|q_a| = 1$ perfect orientation.

Experimental

Four samples of mesophase pitch carbon fibers (M), five samples of PAN-base fibers (P) and four samples of cellulose-base carbon fibers (C) were chosen for the studies. X-ray scattering intensities were obtained by photofilm and by counter techniques. CuK_α radiation was used in both cases. The diffractometer set-up for the counter measurements consists of a curved quartz crystal as focussing monochromator with the sample in symmetrical transmission.

Results and Discussion

Figure 2 shows the evaluation of $J(\phi)$ in terms of equation (2) for the sample M3 in comparison with a theoretical curve for $g_a(\phi)/g_a(\phi-\frac{\pi}{6})$. Systematic deviations from the theoretical curve occur for $\phi < 15°$ and $\phi > 75°$. The former are due to the fact that the calculation neglects the influence of the finite width of the (hk) rods on $I_{hk}(\phi)$, the latter are due to the influence of the tails of the (001) lines.

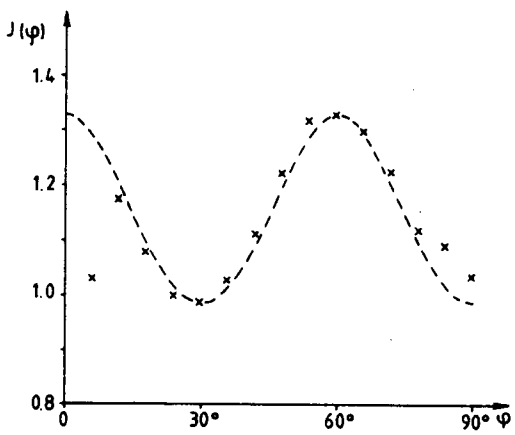

Fig.2

The q_a-values listed in table 1 indicate that mesophase pitch and cellulose-base fibers show an a-axis orientation with the corner of the hexagon in the direction of the fiber axis, whereas PAN-base fibers show a-axis orientation with the side of the hexagon in the direction of the fiber axis. In the case of mesophase pitch and cellulose-base fibers the a-axis orientation increases with increasing heat treatment temperature (HTT), no a-axis orientation is present at lower HTT. In PAN-base fibers the a-axis orientation goes apparently through a maximum with increasing HTT.

Table 1

Sample	Heat Treatment Temperature (°C)	Tensile Modulus (GPa)	q_a	$\lvert q_c \rvert$
M1	(thermoset pitch)		0	
M2	2500	607	0,30	0,90
M3	2750	586	0,33	0,92
M4	3000	634	0,41	0,93
P1	2500	400	-0,30	0,82
P2	2750	434	-0,27	0,83
P3	3000	483	-0,19	0,87
P4	1350		0	0,62
P6	2700		-0,27	0,82
C1		290	0	0,83
C2		359	0	0,85
C3		455	0,30	0,87
C4		524	0,31	0,88

The type of preferred orientation of the a-axis orientation resembles the expected orientation of the intermediate stages of pyrolysis in the case of PAN-fibers [7,8] ("black orlon") and of cellulose fibers [9] ("longitudinal polymerization"). This orientation is, however, not detectable at lower HTT. This may be due to the fact that the orientation of the carbon hexagons formed in the early stages of pyrolysis is primarily with respect to the direction of growth of the ribbon-shaped carbon layers and that the increase of the c-axis orientation is correlated with an increase of the orientation of the long axis of the ribbons in the direction of the fiber axis. This does, however, not explain the decrease of the a-axis orientation at higher HTT in the case of PAN-base fibers.

An explanation for the a-axis orientation in the case of mesophase pitch fibers would be the preponderance of aromatic molecules in the mesophase pitch with a shape in favor of a corner-on orientation of the carbon hexagons on uni-axial deformation.

References

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