Carbon Fibre from a High-Modulus Polyamide Fibre (Kevlar)

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Carbon fibres were prepared with a yield of about 40% from an aromatic polyamide fibre, Kevlar, by heating it in an inert atmosphere to 550–660°C or higher temperatures. When prepared appropriately, they retained as high a strength and twice as high a modulus of rigidity as those of commercial low-modulus carbon fibres. Up to 1000°C, cross-section of the carbon fibres was always circular and isotropic over the entire area, while the shapes of the cross-section of the fibres prepared above 2000°C were mixed with isotropic circular and locally-anisotropic irregular ones. The fibres were non-graphitizable and rich in micro- and transitional voids. Electron- and optical microscopical observation suggested for the ideal Kevlar-based carbon fibre a structural model consisting of the hypothetical sinusoidal fibrillar units which extended along the fibre axis and whose crest-to-trough direction was tilted in relation to the direction of the fibre diameter in varying degrees from the core to the skin of the fibre. The graphitic layers were roughly parallel to the sinusoidal fibril axis but their c-direction had almost no particular relationship with the crest-to-trough direction. This structure was reasonably consistent with a reported Kevlar's structural model.

1. Introduction

Kevlar, an aromatic polyamide fibre developed by E. I. Du-Pont de Nemours and Co., is one of the most remarkable inventions in recent years in the fibre industry. As the fibre is new in many respects, it has attracted the attention of a number of researchers, and several papers have been published on its structure and behaviour at room and elevated temperatures^{1),2),3),4)}. Those papers are, however, concerned with the fibre in limited situations; while carbon fibres from Kevlar are of considerable interest because this fibre is composed of linear polymer of single aromatic rings, there are no reports of carbon fibre from that type of material. This paper deals with thermal degradation of the Kevlar 49 (high-modulus type of the Kevlar) and with fine structure of the carbon fibres obtained from it.

2. Experimental

2.1 Heat-treatment

About 260mg of the Kevlar fibre, 13 μ m in average diameter and about 20mm in length, was

set in a platinum crucible (9mm in depth), placed in a thermobalance and heated to various temperatures not exceeding 1000°C, at several constant heating rates in argon with a flow rate of 1000cc/min (low-temperature carbon fibre).

Bundles of the fibre having been heated to 800°C (which is to be referred to as 800°C fibre) at the heating rates of 0.5 and 20°C/min were further heated in an hour to 2000°C or to 2800°C in a graphite tube furnace in a nitrogen atmosphere. After kept at the high temperature for 30min or 10min respectively, they were left in the furnace until they were cooled to room temperature (high-temperature carbon fibre).

2.2 Procedures of observation

Strength and Young's modulus averaged over 30 monofilaments were determined by testing each filament (gauge length 9.8mm) at a strain rate of 0.4mm/min in an Instron-type tester. The cross-section was assumed to be circular. The Young's modulus was evaluated from the stress-time curve.

Azimuthal high-angle x-ray diffraction patterns to evaluate preferred orientation function of the

crystallites were recorded in a flat film camera in an ordinary way. The diffraction patterns to obtain inter-layer spacing (d_0) and crystallite size (L_c) were observed by a diffractometric method with an ordinary apparatus. Cu-K α radiation was used throughout.

Small-angle x-ray diffraction patterns were recorded in a conventional camera using Cu-K α radiation without monochromatization. Quantitative data were obtained separately with a goniometer incorporating a Kratky's U-slit using Co-K α radiation. The details were reported in a previous paper⁵⁾.

Optical microscope observation was made with an instrument fitted with a polarizer and an analyzer on a bundle of the fibres fixed with an adhesive of low viscosity (cyanoacrylate type) and then embedded in epoxy resin, followed by polishing with cloth and powder so that a flat near-meridian or radial cross-sectional face could be available.

Transmission electron microscope (TEM) observation was made on ground fibre placed on a commercial micro-mesh grid. Secondary-electron image (SEM) observation was made on the fibre coated with gold. Conventional machines were used for both observations.

3. Results and discussion

3.1 Weight change

Fig. 1 shows thermograms up to 1000°C of the fibres heated at three different heating rates. When the rate is 0.5°C/min a sudden and abrupt weight decrease, certainly due to carbonization, is seen between 450 and 550°C, particularly between 475 and 525°C. The carbon yield at 1000°C over the starting material is around 40%. The increase of

Fig. 1 Thermograms up to 1000°C.

heating rate to 55°C/min causes a shift of the carbonization temperature towards the high temperature side by about 50°C, leading also to the weight decrease in a narrower temperature range and a little more rapid weight decrease after the carbonization. Table 1 summarises the carbon yields after heat-treatment at 800, 2000 or 2800°C. This indicates that the carbon yield of the high-temperature carbon fibres is decided by the rate of heating up to 800°C rather than the final temperature of the heat-treatment.

Table 1. Carbon yields (%).

Rate of heating (°C/min)	Heat-treatment temperature (°C)		
	800	2000	2800
0.5*	47	40**	40**
20*	41	34**	34**

* Applicable only up to 800°C.

** Obtained as the yield at 800°C multiplied by the yield after another further heat-treatment.

3.2 Strength and Young's modulus

From practical point of view, carbon fibre must have reasonable strength and Young's modulus. Actually, Kevlar-based carbon fibres manufactured appropriately are considered to be applicable to some practical purposes, since the strength of the carbon fibres obtained by heat-treatment around 800°C, being 50–60kg/cm², is comparable with that of commercial carbon fibres manufactured without stretch, and since the formers retain up to twice as high a modulus of rigidity as that of the latters (Table 2).

In terms of the strength for the individual single filaments the fibre reduces its strength by a significant amount on carbonization, on further heating of the resultant carbon fibres to higher temperature, or on increase of the heating rate. When the comparison is made in terms of the values for a unit cross-sectional area, however, the reduction is less remarkable, because these processes resulting in reduction of the strength are always accompanied by reduction of the area of the cross-section.

3.3 X-ray diffraction

High-angle x-ray diffraction observation along the equator (Fig. 2) reveals that the specimens retain the principal structure of Kevlar until immediately before the carbonization, and that the

Table 2. Tensile strengths and Young's moduli.

Rate of heating ($^{\circ}\text{C}/\text{min}$)	0.5	20
Strength for single filament (g)		
Kevlar	38.4	
800 $^{\circ}\text{C}$	6.4	4.0
2000 $^{\circ}\text{C}$	4.1	3.3
2800 $^{\circ}\text{C}$	2.4	—
Strength for unit cross-sectional area (kg/mm^2)		
Kevlar	69.3	
800 $^{\circ}\text{C}$	59.8	58.3
2000 $^{\circ}\text{C}$	54.7	55.6
2800 $^{\circ}\text{C}$	34.0	—
Young's modulus (kg/mm^2)		
Kevlar	13000	
800 $^{\circ}\text{C}$	4400	3786
2000 $^{\circ}\text{C}$	5268	3786
2800 $^{\circ}\text{C}$	4811	—

Fig. 2 High-angle x-ray diffractograms for 0.5 $^{\circ}\text{C}/\text{min}$ fibres.

resultant carbon fibre is non-graphitizable. Compared with the equivalents for the pitch-based carbon fibres⁶⁾, one of the typical carbon fibres prepared without stretch, Kevlar-based carbon fibres were almost the same in d_0 , slightly larger in L_c and much higher in orientation of the crystallites along the fibre axis. The last character-

Heating rate ($^{\circ}\text{C}/\text{min}$)	HTT ($^{\circ}\text{C}$)				
	2800	2000	1000	720	600
0.5	☐	☐	☐		☐
20	☐	☐	☐	☐	
55			☐	☐	

☐ holds for 1 & // ☐ holds for 1 only ☐ holds for neither

Fig. 3 Chart depicting whether or not Porod's law holds.

istic will be the reason for the higher Young's modulus of the Kevlar-based carbon fibres.

Small-angle x-ray scattering was observable for every sort of the Kevlar-based carbon fibres. The scattering was so intense that it was certainly due to voids in the specimen⁷⁾. The azimuthal scattering pattern from the carbon fibres was a diamond shape; extending more along the equator than along the meridian. This is the pattern commonly seen for the carbon fibres with high degree of preferred orientation of crystallites, and is known to be caused by the voids a significant amount of which are oblong along the fibre axis. Depending on the specimens, and on the direction of obser-

Table 3. Inter-layer spacings (d_0) and crystallite size along the c-axis (L_c).

HTT (°C)	Rate of heating (°C/min)							
	0.5		5		20		58	
	d_0^*	L_c^{**}	d_0^*	L_c^{**}	d_0^*	L_c^{**}	d_0^*	L_c^{**}
2800	341	25	—	—	340	25	—	—
2000	344	33	—	—	346	33	—	—
1000	344	1.1	345	1.2	—	—	342	1.2
800	343	1.1	—	—	—	—	—	—
720	—	—	—	—	—	—	349	1.2
600	353	1.2	354	1.2	—	—	—	—

* in pm

** in nm.

vation, Porod's law⁷⁾ did or did not hold (Fig. 3). A summarized conclusion was that the boundary of voids along the fibre axis is not clear-cut for the low-temperature carbon fibres unless the heating rate is very low, and that the longer ends of the voids terminate in a well-defined manner only for the high-temperature carbon fibres. Non-linear Guinier plots and $I^{-1/2}$ against ϵ^2 plots (here I and ϵ are scattering intensity and scattering angle, respectively) suggested that the void size distribution would be likely to have two or more maxima. According to Porod's characteristic functions (Fig. 4)⁹⁾, which are not approximated with a single exponential function and which extend almost to 15nm, the Kevlar-based carbon fibres contain various types of voids including those in the transitional-void range and in the microvoid range. Comparison of the width of the individual peaks

seen in the characteristic functions implies that a decrease of heating rate or an increase of heating temperature makes the void size more spread around its most-frequent-value, so far as the meridian direction is concerned.

3.4 Optical microscopy

Parallel band patterns were observed on longitudinally polished diametrical and off-diametrical cross-sections of the fibres under an optical microscope fitted with a polarizer and analyzer (Fig. 5). This pattern was seen in all the specimens examined, covering from 600 to 2800°C fibres. They are considered to be, partly at least, to a particular orientation of "mini-graphitic layers" in the fibres because the contrast changed when the direction of the fibre axis was rotated around the optical axis and almost disappeared at certain angles. The periodicity of the band varied slightly from one

Fig. 4 Porod's characteristic functions for two selected carbon fibres.

Fig. 5 500nm-bands observed with an optical microscope under near-crossed nicols.
 a: bands extending across the centre axis. (1000°C–0.5°C/min fibre), scale 10 μ m.
 b: bands with alternating contrast beyond the centre axis. (2800°C–20°C/min fibre), scale 5 μ m.

specimen to another, and even along the length of an individual specimen, but it measured about 500nm in most cases. There were two types of the pattern. The first was the type shown in Fig. 5a in which the bands extend across the full width of the section, sometimes with a stronger contrast along the central area of the fibre. The second was the type shown in Fig. 5b in which the contrast reversed beyond the centre line of the fibre. The latter was observed less frequently and only for wide, presumably diametrical, cross-section.

The radial cross-section of the low-temperature carbon fibres were almost always circular and appeared isotropic. On the other hand, the equivalent cross-section of the high-temperature carbon fibres, especially of those of the 2800°C fibres, were often mixed in shape: some had a straight edge or horn-like protrusions in part of its circumference, while some were almost circular. Examination with a test plate revealed that the graphitic layers were preferentially in parallel with a straight edge or the axis of the horn, while no preferred orientation was recognized in the smoothly edged areas. This likely means that the polygonization of the cross-section is caused by a directionally unbalanced development of the graphitic layers over the cross-section.

3.5 Electron microscopy

Although the surface of the low-temperature fibres, as observed with a scanning electron micro-

scope, was too smooth to give any hint for structural investigation, their diametrical-longitudinal split plane demonstrated a wavy relief (Fig. 6), which was well comparable to the band structure shown in Fig. 5b and reminded duly the structure model suggested for Kevlar by Dobb et al⁴⁾. The surface of the high-temperature fibres was very rough; and in extreme cases it had ridges (Fig. 7) which appeared as “horn” when its radial cross-section was observed with an optical microscope. Furthermore, it demonstrated a series of relieves surrounding the surface of a periodicity of about

Fig. 6 Longitudinal fracture surface of 1000°C –0.5°C/min fibre as observed with a scanning electron microscope.
 Scale: 3 μ m

Fig. 7 An extreme example of the rough surface of $2000^{\circ}\text{C}-0.5^{\circ}\text{C}/\text{min}$ fibre as observed by a scanning electron microscope.
Scale: $3\ \mu\text{m}$

500nm, which was, unlike those in Fig. 6, hard to expect from Dobb et al's model. Observation on crushed fibres (Fig. 8), however, revealed that wavy relief existed simultaneously on two mutually perpendicular split planes. This will be a clue to obtain a structure model of the carbon fibre which can make both Fig. 6 and Fig. 7 compatible.

For the low-temperature carbon fibres TEM images were so featureless that the only structural information available from them was the electron diffraction pattern which illustrated a certain preferred orientation of the crystallites in the fibre.

TEM images from the high-temperature carbon fibres revealed several clues which were helpful for structural investigation. At low magnifications oblong fragments were observed very frequently whose longer edge was sinusoidal and whose axis was, as confirmed from the electron and x-ray diffraction patterns, in parallel with the fibre axis (Fig. 9a). The periodicity of the wave was approximately 500nm, which agrees with the periodicity of the band in Fig. 5 as well as with that of the "pleat" reported in Kevlar⁴). The crest-to-trough distance varied from one place to another but lay between 25–100nm. Normally, many parallel lines were observable along the wave-shaped edges (Fig. 9b), and the dark field images (Fig. 9c) re-

Fig. 8 Two mutually perpendicular wavy fracture surfaces seen among a split $2800^{\circ}\text{C}-0.5^{\circ}\text{C}/\text{min}$ fibre.
Scale: $3\ \mu\text{m}$

The inset depicts the whole view of the split fibre, at the arrowed part of which the main picture is located. (The inset is viewed from a slightly different direction than the main picture; scale in the inset: $10\ \mu\text{m}$).

Fig. 9 Wavy edge of a fragment seen by a transmission electron microscope in the $2800^{\circ}\text{C}-0.5^{\circ}\text{C}/\text{min}$ fibre.

a: at low magnification, scale: $1\ \mu\text{m}$

b: at high magnification, scale: $0.1\ \mu\text{m}$

c: (002)-dark field image of b, scale: $0.1\ \mu\text{m}$

vealed graphitic layers which were discontinuous and extended along the parallel lines. The situation was qualitatively identical even after the fragment was rotated about 90° around its longer axis in the electron microscope. This means that preferred

orientation of graphitic layers is low around the fragment axis, while that is high along it. At high magnification, lattice images of the graphitic layers continuing over a considerable distance were well discerned for the high-temperature fibres (Fig. 10). The lattices were well oriented for a carbon fibre prepared without stretch; the images of the 2800°C fibre were, on the whole, very similar to those seen in the pitch-based carbon fibre prepared

under stretch⁶⁾. The Kevlar-based carbon fibres were rich in fringe-less area (arrowed in Figs. 10b and 10c), which was likely due to the voids in the specimen.

3.6 Structural model of the carbon fibre and its relationship to Kevlar's structure

Now we will illustrate a model of the ideal Kevlar-based carbon fibres, i.e. a model for the carbon fibres with isotropic cross-section. For its easy understanding, it is useful to assume a fibrillar unit, which may or may not exist actually. This fibrillar unit is sinusoidal in a plane, which we will refer to as plane of fibril (Fig. 11), and the centre line of the sinusoidal fibril extends along the fibre axis. An important feature of the model is that the plane of fibril is tilted by a certain angle to the diametrical-longitudinal plane (angle α in Fig. 11). The angle of the tilt varies gradually from the core to the skin of the fibre: near the skin, the plane is more parallel to the diametrical-longitudinal plane than in the inner part of the fibre, although at the very core area the structure can be different (presumably less organized). With this tilt and its variation along the radius, gradual disappearance

Fig. 10 High-resolution electron micrographs.
a: 1000°C–0.5°C/min fibre, scale 5nm.
b: 2000°C–0.5°C/min fibre, scale 5nm.
c: 2800°C–0.5°C/min fibre, scale 5nm.

Fig. 11 Hypothetical sinusoidal fibril and its position on the "plane of fibril" in the carbon fibres.
For details, see text.

of wavy relief towards the skin seen in Fig. 6 and the clear relieves on two mutually normal split-face seen in Fig. 8 are understood in a reasonable way. The graphitic layers are roughly parallel to, but considerably twisted around the sinusoidal fibril axis; as a result the c-axis is sometimes in parallel, but sometimes normal to the plane of fibril. With this twisted graphitic layers, the discontinuous (002) bright bands in the dark field image (Fig. 9c) and the low preferred orientation of the graphitic layers around the fragment axis are well explained.

Our observation has provided little information on the structural organization of the low-temperature fibres. Judging from the optical micrograph (Fig. 5a) and the SEM image (Fig. 6), however, it is likely that the arrangement of graphitic layers is essentially very similar to the high-temperature fibre, but that the number of graphitic sheets in each stack and the number of aromatic rings in each graphitic sheet are far smaller.

Dobb et al reported a structural model of Kevlar which consisted of a system of sheets regularly pleated along the axis of the fibre and arranged radially⁴⁾. Our model is reasonably consistent with that model; it is easy to believe that the pleated sheets in Kevlar were transformed during the carbonization to wavy graphitic sheets in the carbon fibre. However, there are several points to be noted.

1. Each component plane of the pleated sheets in Kevlar is comparatively flat and is joined through a narrow transition region. On the other hand, in the carbon fibre, direction change of graphitic layers along the fibril is smooth and continuous, and the transition region is not well defined. This is presumably because stress release in the transition region can be spread over wider range in the carbon fibre due to weaker bonding between graphitic layers than the force of the hydrogen bonding in Kevlar.

2. The possible reason of graphitic layers in the carbon fibre being twisted around the fibril axis will be either because Kevlar's a-axis (or b-axis) is poorly aligned, or because Kevlar's a-axis direction is nothing to do with the direction of the graphitic layers in the carbon fibre. Up to now, no conclusive evidence has been obtained, but the latter reason is slightly more possible because two consecutive benzene rings along the c-direction in

Fig. 12 Suggested sinusoidal structural unit in Kevlar superimposed on Kevlar's structural model reported by Dobb et al.

"c" in the picture stands for the c-direction of Kevlar's unit cell; the directions of a- and b-axes are uncertain.

Kevlar's unit cell are approximately 80° twisted with each other²⁾. This angle will be too large to arrange the graphitic layers to one particular direction in relation to the crystal axis of Kevlar.

3. In the carbon fibres, the plane of fibril is tilted by a certain angle in relation to the diametrical-longitudinal plane of the fibre. Although Dobb et al's model mentioned almost nothing in this respect, our view is that a similar structure (Fig. 12) would exist in Kevlar as well, rather than that the corresponding "plane of pleat" for the Kevlar would always be normal to the diametrical-longitudinal plane and it would rotate during the course of the carbonization.

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学振第117委員会第164回会議

学振第117委員会第164回会議が、昭和56年5月8、9日の両日、東京市ケ谷の私学会館において開催された。A, B, Cの各分科会に下記の資料が提出され、活発な討論が交わされた。

- 117-164-A-1 石炭液化触媒の評価に関する研究(I)
(北大工) 横野哲朗ほか
- 117-164-A-2 ハイドロピレンの炭化収率に影響を及ぼす諸因子について
(九大生研) 持田 勲ほか
- 117-164-A-3 炭素繊維の気相成長におよぼすイオウ、ハロゲンの効果
(長崎大工) 江頭 誠ほか
- 117-164-A-4 フェノール樹脂を結合剤とする成形炭素材の製造
(群馬大工) 大谷杉郎ほか
- 117-164-A-5 黒鉛化処理した炭素繊維を用いたCF-RCの特性
(群馬大工) 大谷杉郎ほか

- 117-164-A-6 黒鉛-臭素残存化合物の電極挙動
(東京高専) 小島啓太郎ほか
- 117-164-A-7 爆発法で得られたカーボンブラックの特徴
(東工大) 川村和郎ほか
- 117-164-B-1 炭素繊維/炭素複合材料の熱伝導
(東工大) 木村脩七ほか
- 117-164-C-1 気相成長炭素繊維のひずみ抵抗効果
(信大工) 遠藤守信ほか
- 117-164-C-2 炭素繊維強化プラスチック(CFRP)のひずみ抵抗効果
(信大工) 遠藤守信ほか

5月9日午後2時より、大谷杉郎主査の“カーボンファイバー電池”と題する講演があり、活発な質疑応答がなされた。