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Structure and properties of mesophase pitch carbon fibre with a skin–core structure carbonized under strain

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Coal tar mesophase pitch fibres stabilized at 270° C to different extents were carbonized under strain by the constant load or constant length, using different heating rates, and further graphitized at 2500° C. Shallow and moderate stabilization provided a skin–core structure in the resultant fibres which exhibited higher orientation, tensile modulus, and better graphitizability after calcination at 1300° C and graphitization at 2500° C than deep stabilization. The tensile strength and modulus of the graphitized fibre was significantly improved through the strained carbonization when the stabilization was performed to a moderate extent. The strain tended to give an onion-like alignment in the fibre to improve the preferred orientation of carbon planes. Larger load and more rapid heating during carbonization modified the structure and properties of resultant fibres through a significant longitudinal elongation. The stabilization extent of pitch fibres governs the mobility or fusibility of mesogen molecules at the carbonization which allows their better alignment by the strain.

1. Introduction

High tensile and compressive strengths as well as tensile modulus are required in mesophase pitch-based carbon fibre (MPCF) for its broad application [1–3], because such mechanical properties are governed by microscopic alignment of carbon planes, which inherits basically the arrangement or orientation of aromatic planes of mesogen molecules. The orientation is determined by the molecular structure of the mesogen molecules and their stacking during the manufacturing steps of spinning, stabilization, carbonization, and graphitization.

It has been described [4–10] how a skin–core structure could be introduced in the resultant carbon fibre by controlling the stabilization and carbonization conditions. The skin–core structure exhibits some fusion during carbonization in the core where the mesogen molecules are stabilized insufficiently. Such a controlled fusion may allow improvement in the orientation of carbon planes and densification of their stacking during carbonization when a proper strain is applied in the direction of fibre axis. It has been established that the strain at stabilization, carbonization, and graphitization is very essential to give high strength and modulus of polyacrylonitrile (PAN)-based carbon fibre [1, 11]. The folded fibril structure of stabilized PAN, which inherits that of starting the PAN, allows a large extension along the fibre axis under strain.

Full stabilization of pitch fibre, which has been performed by the usual procedures, may not exclude carbonization under strain; however, fully stabilized fibre is too brittle for sufficient extension. Hence the skin–core structure appears to be very essential for extension.

In previous papers, the influences of strain on the fibre stabilized at 350° C to introduce the skin–core structure, was reported [6, 7]. Favourable influences were certainly observed. However, the stabilization at this temperature appeared to bring about some adhesion among the filaments, deteriorating the mechanical properties.

Mesophase pitch fibres stabilized at lower temperature of 270° C to different extents were carbonized under strain, to reveal how the stabilization extent and carbonization under strain cooperatively modify the orientation of carbon planes and mechanical properties of the MPCF.

2. Experimental procedure

2.1. Material, spinning and stabilization

A coal tar mesophase pitch was spun into pitch fibres from a stainless steel spinneret ($L/D = 1$, $D = 0.4$ mm)

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at 356°C [8]. The fibre drawn from the die was continuously wound for 80 s at a speed of 560 m min^{-1} (1755 r.p.m), so that a bundle of approximately 2300 filaments was obtained.

The fibre bundles thus obtained were divided into several groups for stabilization under different conditions. The denier of the pitch fibre was calculated from the weight, length and number of filaments in the bundle.

The stabilization conditions are summarized in Table I.

2.2. Carbonization and graphitization

Pitch fibre bundles stabilized to different extents were carbonized freely or under strain in an inert gas flow. During the carbonization, the strain was applied to the fibre bundles in two ways.

1. The fibre bundles were constrained with a constant load during heat treatment to 600°C, and further calcined freely to 1300°C.

2. Both sides of the fibre bundles were fixed with two graphite spacers in a graphite boat during carbonization up to 1300°C so that the fibres were always fixed at a constant length. The heating rates were selected according to the extents of stabilization for no adhesion of filaments after carbonization.

The carbonized fibre bundles were further graphitized at 2500°C in an argon flow.

TABLE I Stabilization conditions of pitch fibres

Run	Stab. temp. (°C)	Heating rate[a] (°C min^{-1})	Holding time[b] (min)	Oxygen conc. (vol %)
1	270	15	90	10
2	270	5	90	21
3	270	5	150	21

[a]To stabilization temperature.
[b]At stabilization temperature.

2.3. Evaluation of the properties and structure of carbonized and graphitized fibres

2.3.1. Mechanical properties

The tensile strength of carbonized and graphitized fibres was determined by single filament testing of 20 individual filaments (mono-filament method). The gauge length was 25 mm. The tensile modulus was calculated based on the slope of the stress–strain curve obtained from the tensile strength measurement.

2.3.2. Structural analyses

Cross-sectional morphologies of the carbonized and graphitized fibres were observed by SEM (Jeol-25S). The preferred orientation degree of the carbon planes in the fibres was described by the orientation angle (OA) which usually could be characterized by the (0 0 2) diffraction of carbonaceous material [12]. The (0 0 2) diffraction intensity of the graphitized fibre bundle was measured against its rotation using an X-ray diffractometer with an attachment for fibre samples (Rigaku, CuK_α, 0.15406 nm, 35 kV, 30 mA) [13, 14].

The crystalline size, $L_{c(0\,0\,2)}$ and spacing of carbon planes, $d_{0\,0\,2}$, of the graphitized fibres were measured by means of the method prescribed by the Japan Society for Promotion of Science [13, 14].

3. Results

3.1. Fibres with a skin–core structure carbonized under different loads and heating rates

The stabilization at 270°C in 10 vol % O_2 (see Run 1 of Table I) introduced a skin–core structure into the resultant carbon fibres as reported previously [8]. The influences of strain and heating rates during carbonization on the structure and mechanical properties of carbonized and graphitized fibres were investigated (see Table II).

TABLE II The influences of load and heating rate on the mechanical properties and structural parameters of the cabonized and graphitized fibres

Carbonization conditions			Carbonized fibre				Graphitized fibre			
No.[a]	Load[b] (g/denier)	Heating rate (°Cmin^{-1})	d[c] (μm)	Tensile strength (GPa)	Tensile modulus GPa	Morphology	OA (deg)	L_c (nm)	d_{002} (nm)	Morphology
1	0	5	11.4	1.7	181	Fig. 1a	92	23	0.3397	Fig. 3a
2	4.4	5	11.0	2.1	175	Fig. 1b	94	24	0.3393	Fig. 3b
3	8.6	5	10.9	2.4	166	Fig. 1c	96	27	0.3389	Fig. 3c
4	0	10	10.8	2.2	168	Fig. 1d	91	23	0.3397	Fig. 3d
5	4.4	10	11.0	1.9	163	Fig. 1e	94	23	0.3393	Fig. 3e
6	9.4	10	13.8	1.8	175	Fig. 1f	96	25	0.3385	Fig. 3f
7	4.4	30	13.0	1.7	168	Fig. 1h	96	28.5	0.3385	Fig. 3h
8	9.0	30	14.2	1.5	152	Fig. 1i	96	28	0.3383	Fig. 3i

[a]Stabilization: see Run 1, Table I, with a skin–core structure.
[b]Load during carbonization to 600°C.
[c]Average diameter.

3.1.1. Effects of strain on the morphologies and mechanical properties of the carbonized fibres

Fig. 1 a–c show the cross-sectional morphologies of carbonized fibres obtained through the carbonization without or under strain at a heating rate of $5°C\,min^{-1}$. The strain modified the texture significantly, densifying the stacking of carbon planar sheets in the core, although its influence was smaller than that observed in previous papers [6, 7]. With a load of 4.4 g/denier, the thin skin exhibited random or loose onion-like arrangement of carbon planes, while the core showed the texture of bent radial or small onions with many centres. Larger strain made the skin thinner and decreased the number of onions at the core, the uniformity of the onion-like alignment being emphasized.

Fig. 2 shows the longitudinal elongation of the fibre bundles under different loads and heating rates during the carbonization. The fibres longitudinally shrank around 6%–7% when they were carbonized freely, regardless of the heating rates. The strain elongated the fibre according to the applied load, 5% elongation being observed with 8.6 g/denier at a heating rate of $5°C\,min^{-1}$. Such elongation may be responsible for the changes in morphologies described above and the properties described later. Table II summarizes the tensile strength and modulus of the carbonized fibres with the skin–core structure. The strain increased the tensile strength (from 1.7 GPa to 2.4 GPa) and decreased slightly the modulus of the fibres (from 181 GPa to 166 GPa) (nos 1–3) according to the size of the load.

3.1.2. Effects of heating rate

Fig. 1d–f, and g–i illustrate the cross-sectional morphologies of the fibres carbonized without or under strain at heating rates of 10 and $30°1C\,min^{-1}$, respectively. The morphologies were modified by the levels of load and heating rates during carbonization. Rapid heating at $10°C\,min^{-1}$ increased markedly the width of the carbon planes at the core. Onion-like texture in the skin and loose onion of broad planes with some winding in the core were distinguished. The strain aligned the carbon planes in a more onion-like arrangement at the core and made the skin of the almost perfect onion thinner. The complete stabilization of the outermost skin was not distinguishable under the SEM. A larger load emphasized the onion-like alignment, removing the voids at the core to densify the fibres.

The influences of heating rate on fibre morphologies and arrangement of carbon planes at the core were more marked when the carbonization was performed at a more rapid heating rate $30°C\,min^{-1}$. Rapid heating to carbonization without strain enhanced the growth of mesogen molecules at the core, giving a

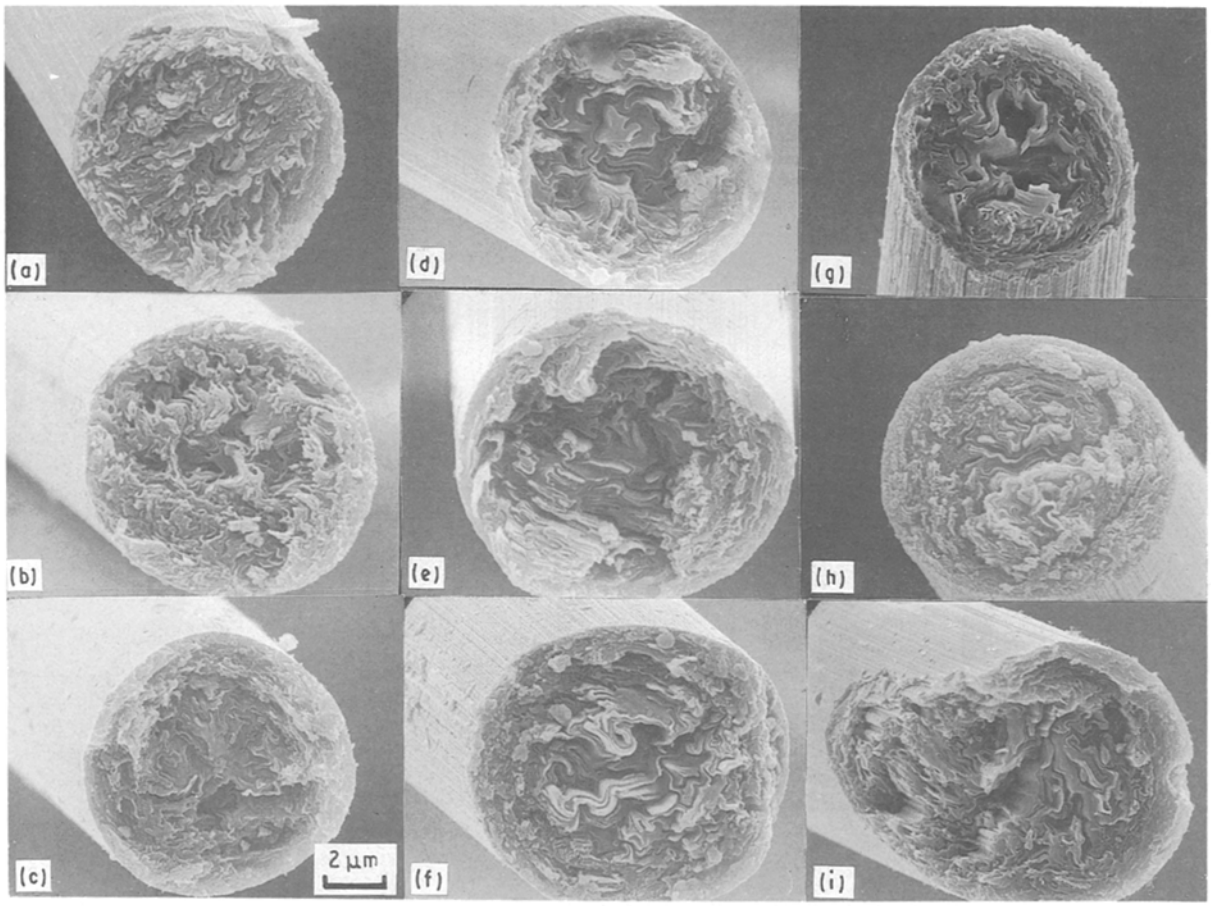

Figure 1 Scanning electron micrographs of the carbonized fibres with skin–core structure after stabilization at 270°C for 90 min in 10 vol % O_2. Carbonization 600°C, 1 h. Load: (a, d, g) without strain (b, e, h) around 4.5 g/denier, (c, f, i) around 9.0 g/denier. Heating rate ($°C\,min^{-1}$): 5, (d–f) 10, (g–i) 30. Calcination: $10°C\,min^{-1}$, 1300°C, 1 h.

large domain texture as shown in Fig. 1g. Some voids were also observed between the carbon planes. In contrast, the strain densified the stacking of carbon planes, allowing very broad cores where the carbon planes were aligned in onion-like texture as shown in Figs. 1h and i. More rapid heating and larger loads elongated the fibres more, as shown in Fig. 2. Approximately 13% elongation was obtained when a rapid heating of $30°C\,min^{-1}$ and a large load of 9.0 g/denier were used. However, heating rates faster than $5°C\,min^{-1}$ caused some adhesion between the filaments.

Table II summarizes the influences of rapid heating during carbonization under strain. Unexpectedly, a larger strain decreased the strength by more rapid heating to carbonization. Rapid heating and large load in the present stabilization and carbonization may increase the adhesion of filaments, introducing more defects on the fibre surface because of fusibility which is enhanced at the thinner skin by rapid heating.

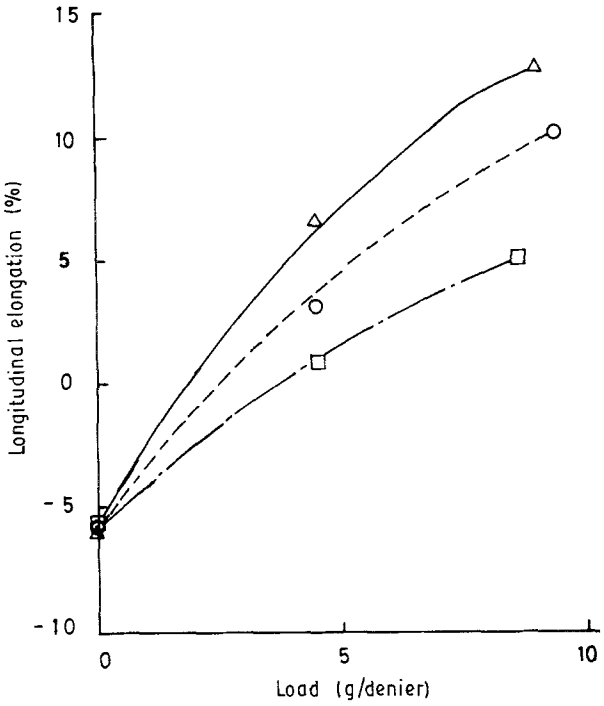

Figure 2 Longitudinal elongation of fibre bundles during carbonization to 600°C under different loads and heating rates. (△) 30°C min^{-1}, (○) 10°C min^{-1}, (□) 5°C min^{-1}.

3.1.3. Influences on the graphitized fibres

Fig. 3a–i show several representative cross-sectional morphologies of the graphitized fibres after cabonization under the conditions described above. In major cases, the fibres exhibited oriented and densely stacked texture. The morphological characteristics appeared essentially unchanged by the graphitization, although the carbon planar sheets in the core became markedly thinner because of macroscopic shrinkage.

Fig 4 shows the X-ray diffraction profiles of the graphitized fibres. All of them exhibited diffraction

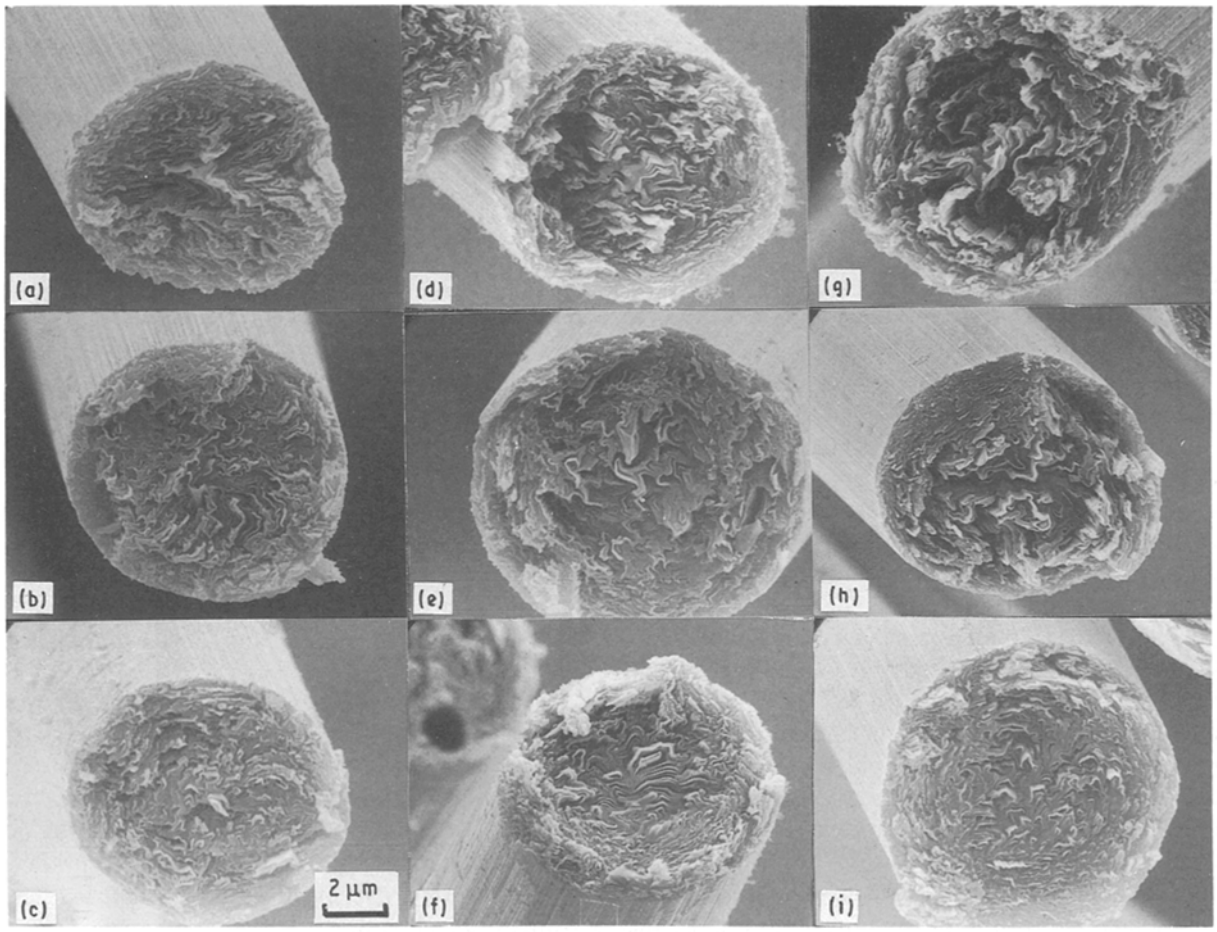

Figure 3 Scanning electron micrograph of the graphitized fibres with skin–core structure after stabilization at 270°C, 90 min in 10 vol% O_2. Carbonization: see Figure 1. Calcination: $10°C\,min^{-1}$, 1300°C, 1 h. Graphitization: 2500°C.

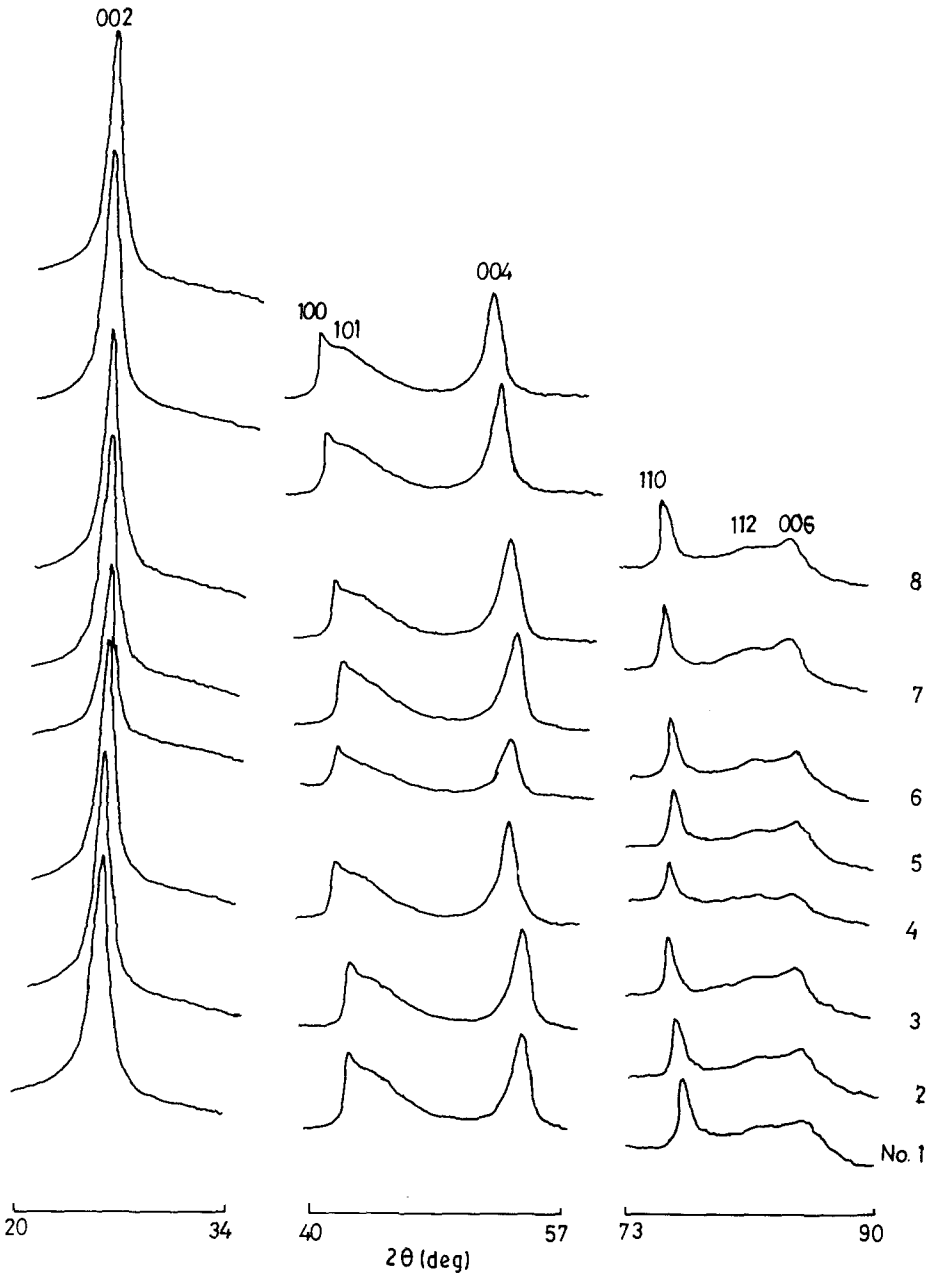

Figure 4 X-ray diffraction profiles of the graphite fibres with skin–core structure carbonized under different loads and heating rates. Carbonization: see Figure 1. Calcination: 10° C min^{-1}, 1300° C 1 h. Graphitization: 2500° C.

peaks at $2\theta = 25.9°$–$26.6°$ (0 0 2), 42.4°–44.6° (1 0 0, 1 0 1), 53.2°–54.7° (0 0 4), 77.6° (1 1 0), 83.6° (1 1 2) and 87.2° (0 0 6). The profiles were very similar regardless of the heating rates and loads, except for the peaks of (1 1 2) and (0 0 6). The peaks became more definite and sharp with more rapid heating and larger loads, suggesting better alignment or stacking of carbon planes.

Table II also summarizes X-ray crystallographic parameters of the graphitized fibres. Initially the strain increased the orientation angle by 4–6%, according to the heating rate and loads applied during carbonization. Secondly, more rapid heating and larger load increased the crystalline size L_c, and decreased the interlayer spacing, d_{002}, improving the crystallinity of graphitized fibres. Because larger loads and more rapid heating during carbonization led to larger longitudinal elongation of the fibres (see Fig. 2), the stacking, alignment, and orientation of carbon planes may be improved along the fibre axis.

3.2. Fibres stabilized at 270°C for different extents and carbonized under a constant strain

The fibre bundles were stabilized at 270° C for different periods (see Runs 1–3, Table I), carbonized under a constant load to 600°C or by fixing the two sides of bundle at a constant length up to 1300° C, using a heating rate of 5° C min^{-1}, and further graphitized at 2500° C.

3.2.1. Carbonization by fixing the fibre at a constant length

Table III summarizes the properties and X-ray crystallographic parameters of the graphitized fibres stabilized to different extents and carbonized under strain. Crystalline size, L_c, orientation angle (OA), and interlayer spacing, d_{002}, of the fibres increased and decreased, respectively, with the stabilization. The

TABLE III Mechanical properties and structural parameters of the graphitized fibres stabilized to different extents and carbonized by fixing at a constant length

No.	Stabilization extent	Carbonization[a]	d[b] (μm)	Tensile strength (GPa)	Tensile modulus (GPa)	OA (deg)	L_c (nm)	D_{002} (nm)
1	Shallow	F	10.4	2.1	703	92	23	0.3397
2	Shallow	S	10.2	2.2	706	93	23.5	0.3395
3	Moderate	F	9.9	2.2	677	91	23	0.3394
4	Moderate	S	10.2	2.1	752	95	23	0.3391
5	Deep	F	9.7	2.3	597	90	20	0.3406
6	Deep	S	9.0	2.7	661	91	21	0.3402

[a]Carbonization by fixing at a constant length up to 1300°C; F, free length; S, strain.
[b]Average diameter of the fibres.

influences of the strain were dependent on the stabilization extent. Unfortunately, the levels of tensile strength were lower regardless of the strain. The fibres stabilized shallowly to allow a skin–core structure and carbonized without (1) or under strain (2) exhibited better OA, L_c, d_{002}, and tensile modulus than those of the fibres stabilized deeply (5, 6), although the effects of strain were unexpectedly slight. This may be attributed to the adhesion of filaments due to insufficient stabilization of the skin as described above. On the other hand, OA and d_{002} of the fibre (4) were significantly improved by the strain when the stabilization was moderate, resulting in the highest tensile modulus. The deepest stabilization provided the largest tensile strength regardless of the strain. However, OA, modulus and L_c were smaller, although such reduction was very slight.

Fig. 5 shows the X-ray diffraction profiles of the graphitized fibres. The profiles were much the same regardless of the stabilization extents, except for that at 87.2° (0 0 6) which was more definite and sharp by the modest stabilization, as described above. The strain also sharpened the diffraction of (0 0 6) according to the stabilization extents.

3.2.2. Carbonization under a constant load

Table IV summarizes the mechanical properties of graphitized fibres. The changes in tensile strength due to the strain were more significant than that of the previous section and also strongly dependent on the stabilization extent. The strain markedly improved the strengths of fibres stabilized shallowly and moderately (1 and 2, 3 and 4), but only slightly improved that of the deeply stabilized fibres (5 and 6). The lower strength of the fibre stabilized shallowly (1) may be attributed to the surface adhesion of filaments, although it was certainly improved by the strain (2). The highest strength of 3.4 GPa achieved by the moderate stabilization (4) should be noted, the sufficient stabilization at the skin, and the extending core moderately stabilized, allowing no adhesion of filaments and better alignment of carbon planes, respectively.

The lower tensile modulus of the fibres in this way may be attributed to their smaller diameter (average diameter 7 μm). The preferred orientation of carbon planes and crystalline size of the fibre, in this case, may be restricted. No effective improvement could be obtained regardless of the strain. A load of 3.5 g/denier was too small to obtain a marked elongation of the fibre, especially when the heating rate was slow, as illustrated in Fig. 2.

Fig. 6a–f show the cross-sectional morphologies of the graphitized fibres thus stabilized and carbonized. Shallow and moderate stabilization allowed a skin–core structure in the fibres where the sizes and orientation of carbon planes at the core were certainly different from those at the skin, as shown in Fig. 6a and c, while deep stabilization reduced such a difference, giving a homogeneous cross-section as shown in Fig. 6e. On the other hand, the stacking of carbon planes at the core was significantly modified by the strain, when the fibres were stabilized shallowly and moderately as shown in Fig. 6b and d. Such morphological modification may be responsible for the improvement of the tensile strength described above. Some adhesion of the filaments was also observed when the stabilization was shallow (Fig. 6b). The strain, however, little changed the morphology of the fibre which was stabilized deeply, as shown in Fig. 6f.

4. Discussion

The strain during carbonization certainly influenced the structure and properties of carbonized and graphitized fibres which were stabilized to exhibit a skin–core structure. At the fused core of the pitch fibre surrounded by the sufficiently stabilized thin skin, voids were often produced during the carbonization without strain, to reduce the mechanical properties of the resultant carbon fibre. However, the strain aligned the carbon planes into an onion-like texture with one or more centres at the core of the fibre moderately stabilized, elongated and densified the fibres especially the core area, forming more ordered stacking of carbon planes and resulting in a significant increase of the tensile strength. Such morphological modification of carbon planes by the strain also tends to improve the crystallinity of the graphitized fibres.

Incomplete stabilization of the skin tended to allow some adhesion of the filaments, bringing about defects on the fibre surface to deteriorate the mechanical properties, although better alignment of carbon planes may be obtained at the core. Moderate stabilization

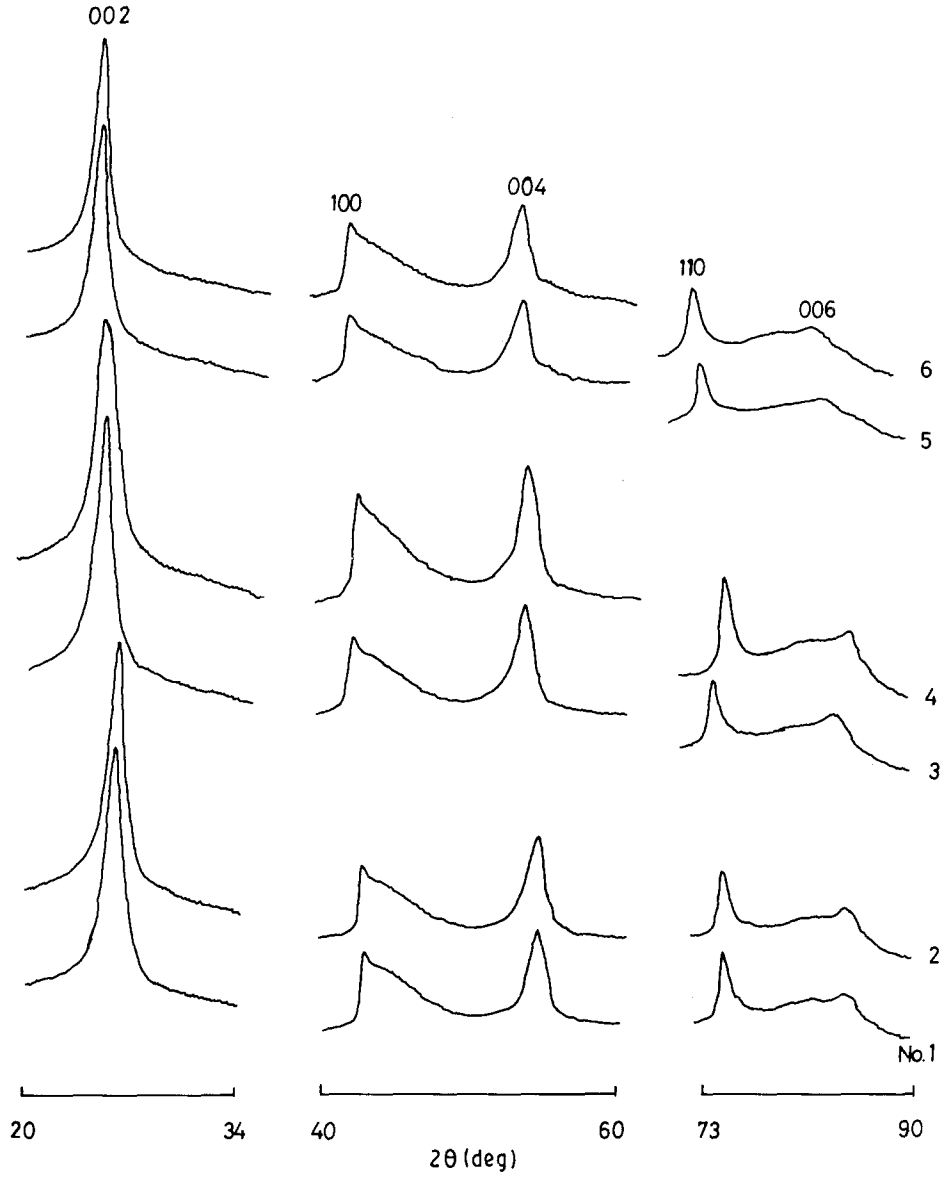

Figure 5 X-ray diffraction profiles of the graphite fibres stabilized with different extents and carbonized freely or by fixing at a constant length. Stabilization and carbonization: refer Table 3.

TABLE IV Mechanical properties of graphitized fibres stabilized to different extents and carbonized under a constant load

No.	Stabilization extent	Load[a] (g/denier)	Heating rate(°C min^{-1})	d[b] (μm)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Cross-sectional morphology
1	Shallow	0	5	6.8	2.2	433	Fig. 6a
2	Shallow	3.3	5	6.9	2.7	485	Fig. 6b
3	Moderate	0	5	6.7	2.8	2.8	Fig. 6c
4	Moderate	3.5	5	7.0	3.4	531	Fig. 6d
5	Deep	0	5	7.0	2.9	548	Fig. 6e
6	Deep	3.5	5	6.8	2.9	501	Fig. 6f

[a]Load during carbonization to 600°C
[b]Average diameter of the fibres.

prohibited the adhesion and allowed the elongation of the core through the proper skin–core structure, giving the best tensile strength and modulus. Sufficient stabilization at the core prohibits the role of strain because of the least elongation during carbonization.

A better alignment of carbon planes in the cross-section may also allow their growth or development along the fibre axis, giving better graphitizability. Thus, high modulus, which is a characteristic of the mesophase pitch-based carbon fibre, is also expected to be emphasized by such a skin–core structure. A marked improvement of tensile modulus was observed by the shallow stabilization, appearing incompatible with that of tensile strength at present, suggesting the delicate balance in the structural control of the carbon fibre.

The structural parameters such as L_c and d_{002} of the resultant graphitized fibres are strongly influenced

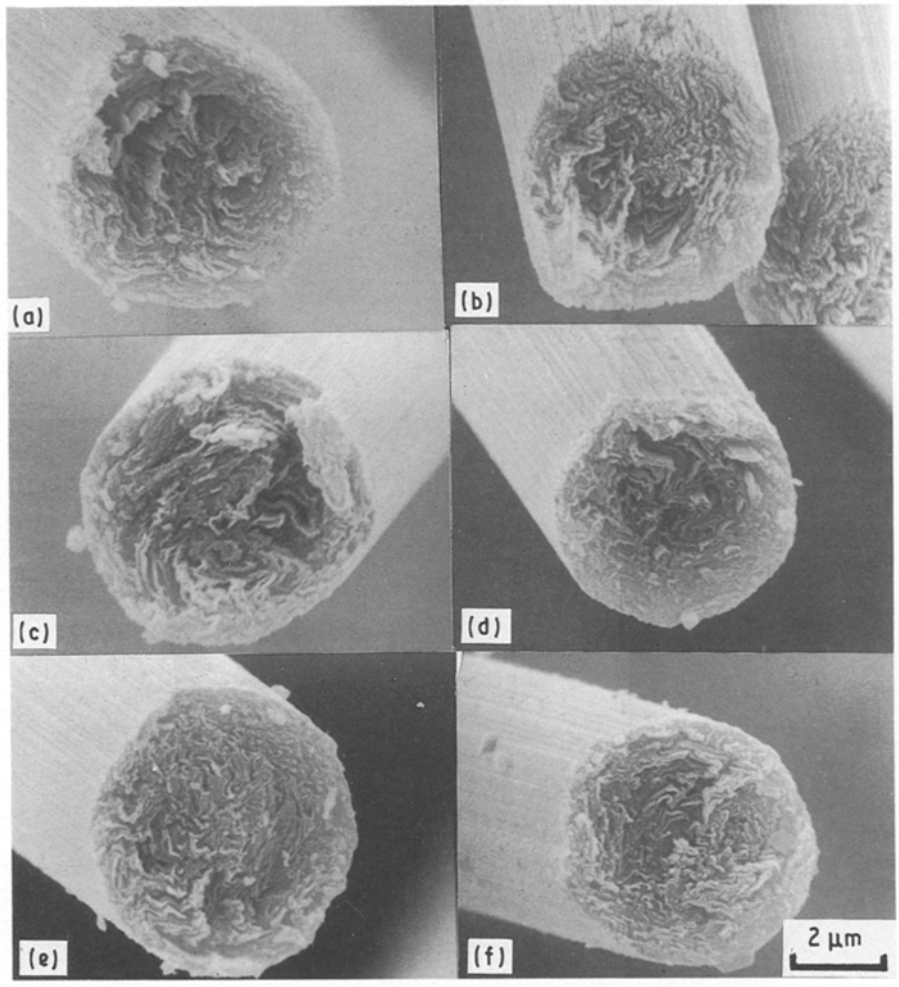

Figure 6 SEM of the graphitized fibres after stabilization to different extents. Stabilization and carbonization: refer Table 4; Calcination: 10°C/min, 1300°C, 1 h; Graphitization; 2500°C.

by the heating rates and loads applied during carbonization. Rapid heating during carbonization certainly enhances the growth or development of mesogen molecules [15–18] at the fusible core. Hence, more mesogen molecules in the core, on the average, could be oriented, aligned or stacked by the strain, introducing excellent graphitizability in the resultant fibres. Larger load enhanced the orientation and alignment of carbon planes by the significant longitudinal elongation.

Strain could be applied during the carbonization by elongating the fibre according to the load or by maintaining its length against the shrinkage. The present study strongly revealed that the former procedure is more effective because of the larger elongation by the tension.

Composite layers of the carbon fibre with a mosaic skin and an onion-like core may have high compressive or bending strength because the mosaic skin may withstand larger elongation than the core, although such a better performance was not obtained in the present study.

So far, tensile strength and modulus are not always improved by the strained carbonization of pitch fibre with a skin–core structure. More extensive and careful study on the spinning, stabilization, and carbonization under strain, appears to promise a procedure for the preparation of carbon fibres with better performances from the same mesophase pitch.

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