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Control of transversal texture in circular mesophase pitch-based carbon fibre using non-circular spinning nozzles

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The transversal texture of circular-shaped carbon fibre was controlled by spinning the mesophase pitch through Y- or slit-shaped spinning nozzles. The flow direction of planar molecules along the non-circular nozzles was relaxed at their outlet into the circular shape, where the deformed texture was expected. Circular transversal shaped fibres with a random or a random–onion texture were successfully prepared by spinning the methylnaphthalene-based mesophase pitch through non-circular spinning nozzles. The spinning temperature which defines principally the viscosity of the molten pitch was the major factor to be controlled. Such carbon fibres exhibited greater strain to break and tensile strength than a fibre with a radial texture from the same pitch.

1. Introduction

Mesophase pitch-based carbon fibres have been recognized as a strategic material for the near future because of their high performance per unit weight [1, 2]. Although the principle of their preparation has been established [3–6], some critical problems still remain to be solved for broad application [7–9]. Since the physical properties of carbon fibres depend strongly on their structure and texture, it is believed that the control of the textures in their transversal sections during the spinning is one of the most relevant problems [10].

Carbon fibres have been recognized to exhibit textures of variable scales, which reflect different manners of arrangement in the basic hexagonal carbon layers in the fibre cross-sections. Transversal textures of the fibre are typically classified into three categories: radial, random and onion [11]. These arrangements are reported to be determined by the spinning conditions. Yamada controlled the transversal texture of carbon fibre by the temperature of spinning [12]. The viscosity of mesophase pitch can be controlled through the pitch blending and structural modification [8, 10]. Recently Hamada *et al.* [13] succeeded in introducing a fine mosaic texture into the pitch fibre by spinning with stirring of the mesophase pitch through the capillary, which diminishes the domain size to approximately 0.1 μm in the spun fibre [13]. Matsumoto [11] controlled the transversal texture of carbon fibre by the dimension of the spinneret where shear conditions are defined. The transversal texture of the resultant fibre was varied from onion to radial, radial-crack through random, depending on the length/diameter (L/D) ratio of the spinneret. Teijin [14] and Edie *et al.* [15] spun the pitch through the non-circular spinning nozzles into non-circular fibre, which exhibited excellent mechanical properties after stabilization and carbonization. In spite of extensive studies, the complete control of transversal texture and the mechanical properties of the resultant circular carbon fibre is far from being established in industrial manufacturing.

In this study control of the transversal texture of carbon fibre was attempted to control the flow direction of planar mesogen molecular in the molten mesophase pitch along Y- or slit-shaped spinning nozzles [15], relaxing the spun shape of the pitch fibre into a circular shape while the molecular planes are expected to be reoriented into the designed texture. A mesophase pitch prepared from methylnaphthalene with the aid of HF/BF_3 was used in the present study because of the wide range of its spinning temperatures. The physical and mechanical properties of circular carbon fibre spun through Y- or slit-shaped nozzles were investigated in comparison with fibre prepared using a circular spinning nozzle.

2. Experimental procedure

2.1. Material

Some properties of the mesophase pitch used in this study are summarized in Table I. It was prepared by Mitsubishi Gas Chemical using HF/BF_3 as the catalyst from methynaphthalene [16]. The mesophase pitch had 100 vol% anisotropic content at room temperature. Its melt viscosities calculated according to Andrade's equation were described in [17]. The reflection point of its melt viscosity with respect to temperature was near 285 °C.

TABLE I Some analytical properties of mesophase pitches prepared using HF/BF_3

Code	Raw material	Softening point (°C)	Anisotropic content (vol %)	Solubility (wt %)			H/C ratio	Carbon aromaticity
				BS	BI-PS	PI(QI)		
mNA mesophase	methylnaphthalene	205	100	52	19	33(29)	0.69	0.86

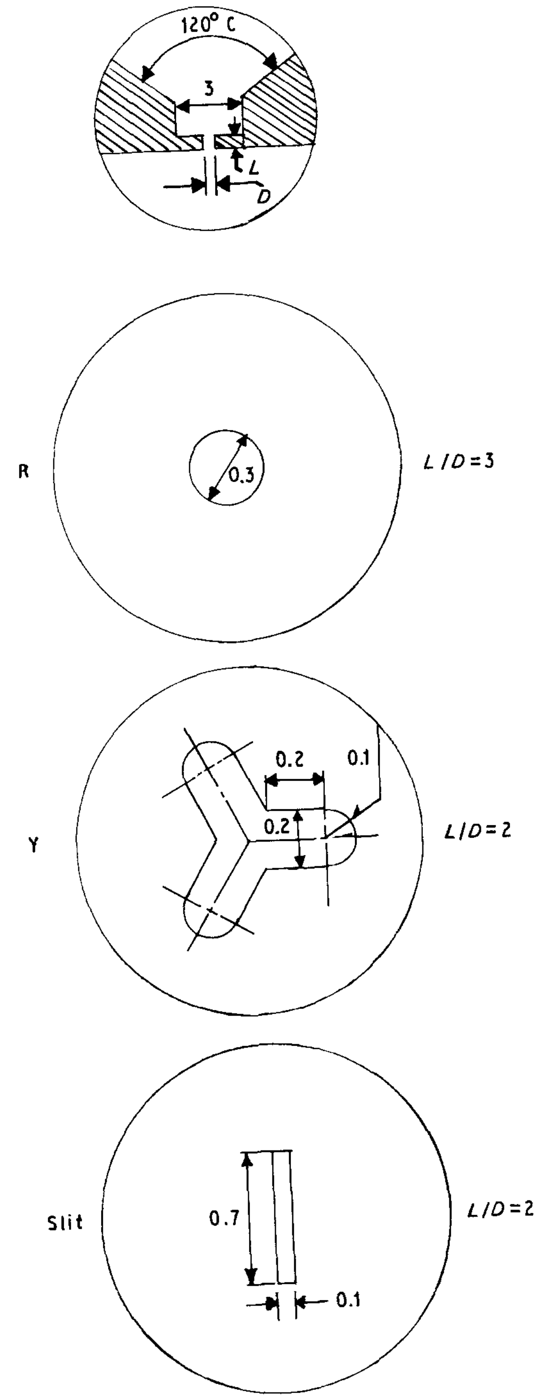

Figure 1 Spinneret capillaries used in this study.

2.2. Spinning of mesophase pitch

Three kinds of spinnerets with either circular or non-circular die hole were used for the spinning of the mesophase pitch. The shapes and dimensions of these spinnerets are illustrated in Fig. 1. Mesophase pitch was spun into circular or non-circular fibres under nitrogen pressure. The detailed spinning conditions for the study are summarized in Table II.

2.3. Stabilization of spun mesophase pitch fibres

The prepared pitch fibres were oxidatively stabilized at 270 °C for certain periods in air. The heating rate was fixed at 5 °C min^{-1}. Table II summarizes the sample codes which identified the conditions of spinning and stabilization.

2.4. Carbonization and graphitization of stabilized fibres

Stabilized fibres were carbonized in argon atmosphere at 1300 °C for 1 h at a heating rate of 10 °C min^{-1}. Carbon fibres were further graphitized at 2000 and 2500 °C respectively, for 30 min, at a heating rate of 20 °C min^{-1}.

2.5. Characterization of carbon fibres

The transversal sections of the carbon fibres produced were observed under a scanning electron microscope (SEM; Jeol JSM 25S). The degree of orientation of carbon planes along the fibre axis was calculated from the orientation angle which was determined from the intensity profile of the (0 0 2) diffraction of the fibre bundle according to Bacon using a X-ray diffractometer with an attachment for the fibre sample (Rigaku; CuK_α radiation, wavelength 0.154 06 nm, 35 kV, 30 mA) [18,19].

The crystalline size, L_c (0 0 2), and spacing of carbon planes, d (0 0 2), of the graphitized fibre were measured according to the method defined by the Japanese Society for Promotion of Science [20].

The tensile strength, Young's modulus and strain to break were measured at room temperature using monofilaments according to the procedure defined in Japanese Industrial Standard JIS R-7601, using an Instron-type tensile testing machine (Instron 4200 series) with crosshead speed of 0.5 mm min^{-1} [21].

3. Results

3.1. Shapes and transversal textures of carbon fibres produced

Methylnaphthalene mesophase pitch was smoothly spun into pitch fibres in the temperature range 265–295 °C. The shapes and transversal textures of the carbon fibres are illustrated and summarized in Fig. 2 and Table III, respectively. Fig. 2 a–d shows SEM micrographs of carbon fibres that were spun through

TABLE II Conditions of spinning and stabilization of mesophase pitch fibres

Code	Spinning conditions				Stabilization conditions
	Capillary	Spinning temperature (°C)	Amount of extrudate (mg min^{-1})	Spinning rate (m min^{-1})	HTT/ST[a] (°C min^{-1})
R-265-20	Circular	265	80	680	270/20
R-275-20	Circular	275	80	730	270/20
R-285-20	Circular	285	80	680	270/20
R-295-20	Circular	295	100	680	270/20
Y-265-20	Y-shaped	265	90	600	270/20
Y-275-20	Y-shaped	275	90	600	270/20
Y-285-20	Y-shaped	285	90	600	270/20
Y-295-20	Y-shaped	295	100	680	270/20
S-265-20	Slit-shaped	265	80	680	270/20
S-275-20	Slit-shaped	275	80	680	270/20
S-285-20	Slit-shaped	285	80	630	270/20
S-295-20	Slit-shaped	295	100	630	270/20

[a]Heat treatment temperature divided by the soaking time at a heating rate of 5°C min^{-1}.

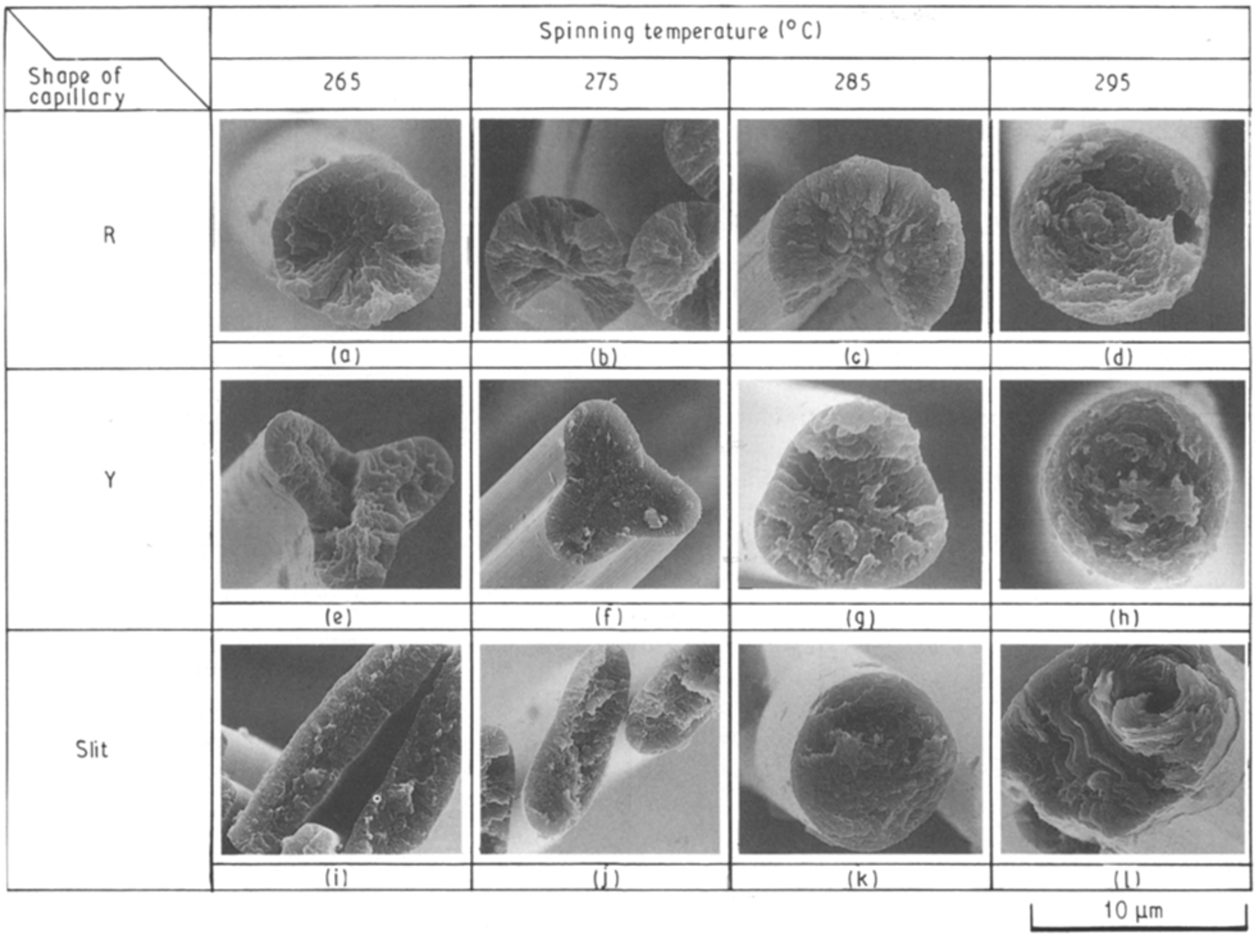

Figure 2 SEM micrographs of prepared carbon fibres: (a) R-265-20, (b) R-275-20, (c) R-285-20, (d) R-295-20, (e) Y-265-20, (f) Y-275-20, (g) Y-285-20, (h) Y-295-20, (i) S-265-20, (j) S-275-20, (k) S-285-20 and (l) S-295-20 (see Table II).

the circular spinning nozzle. A definite radial texture was observable in the transversal section of carbon fibres spun at 265 °C (Fig. 2a). Carbon fibre spun at 275 °C still exhibited a radial texture, about 50% of the fibre exhibiting cracks running along the fibre axis (Fig. 2b). All carbon fibres spun at 285 °C contained open cracks, maintaining the radial texture (Fig. 2c). The fibres spun at 295 °C showed an onion texture and contained no cracks. However, some micro-pores caused by volatilization during spinning were found in the transversal sections (Fig. 2d). The transition temperature of spinning from radial to onion texture was near 290 °C. It should be mentioned that no random texture was introduced at a temperature between 265 and 295 °C.

Fig. 2e–h shows the transversal shapes and textures of carbon fibres spun through the Y-shaped spinning nozzle. Carbon fibres spun at 265 and 275 °C exhibited trilobal transversal shapes which contained radial textures (Fig. 2e and f). The fibre spun at 285 °C exhibited

TABLE III Transversal shapes and textures of carbon fibres

Code	Shape	Texture
R-265-20	Circular	Radial
R-275-20	Circular (50%) + circular crack (50%)	Radial
R-285-20	Circular crack (100%)	Radial
R-295-20	Circular	Onion
Y-265-20	Trilobal	Radial
Y-275-20	Trilobal	Radial
Y-285-20	Trianglular	Random
Y-295-20	Circular	Random–onion
S-265-20	Slit	Radial-dominant
S-275-20	Slit	Radial-dominant
S-285-20	Circular	Random–onion
S-295-20	Irregular[a]	

[a]Cannot be spun uniformly.

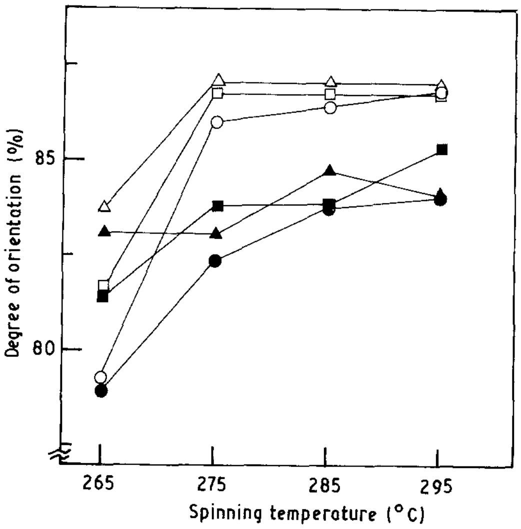

Figure 3 Degrees of orientation of the pitch and carbon fibres at various spinning temperatures: (open symbols) pitch fibre and (closed symbols) carbon fibre from (○, ●) circular (△, ▲) Y-shaped and (□, ■) slit-shaped nozzle. (Carbonization temp: 1300 °C).

a triangular shape with a random texture (Fig. 2g). This indicates that the flow pattern of molten mesophase pitch during the extrusion was changed and distorted against the fibre axis before solidification. Carbon fibre spun at 295 °C showed a completely circular shape with an onion–random texture (Fig. 2h) which exhibited an onion but a random in whole transversal texture.

Fig. 2i–l shows the transversal shapes and textures of carbon fibres spun through the slit-shaped spinning nozzle. Carbon fibres spun at 265 and 275 °C exhibited slit shapes with radial-dominant textures (Fig. 2i and j) as reported in a previous paper [17]. The ratio of the thickness to the width (T/W) of the carbon fibres spun at 265 °C was found to be definitely larger than that of fibres spun at 275 °C. An increasing spinning temperature tends to modify the transversal shape of pitch fibre towards circular. Carbon fibre spun at 285 °C exhibited a completely circular shape with an onion–random texture (Fig. 2k). The transition temperature from a non-circular to a circular form for the slit-shaped spinning nozzle was 285 °C, 10 °C lower than that for the Y-shaped spinning nozzle. It should also be noted that the onion–random texture is very different from the radial texture obtained through the circular nozzle at the same spinning temperature.

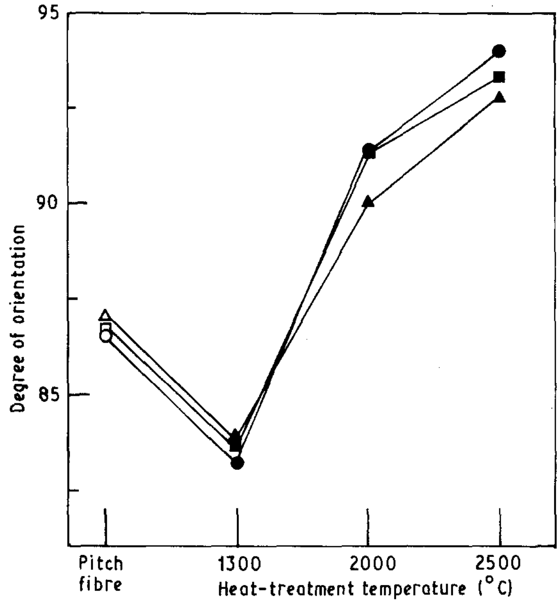

Figure 4 Change in degree of crystalline orientation of fibres with increasing of heat-treatment temperature: (●) circular nozzle (▲) Y-shaped nozzle and (■) slit-shaped nozzle. (Spinning temp: 280 °C).

3.2. Crystallographic parameters of carbonized and graphitized fibres

Fig. 3 shows the degrees of crystalline orientation in the pitch and carbon fibres spun through the three kinds of nozzles at various temperatures. Pitch fibres spun at 265 °C showed a lower degree of orientation than pitch fibres spun above 275 °C, regardless of the spinning nozzle. The circular spinning nozzle produced a higher degree of orientation at higher spinning temperature, whereas the non-circular spinning nozzles produced the same degree regardless of the spinning temperature above 275 °C. Thus, carbon fibres spun at 295 °C through the Y-shaped nozzle and at 285 °C through the slit-shaped nozzle exhibited the same degrees of orientation as fibres spun 285 and 295 °C through the circular nozzle, respectively. All pitch fibres exhibited a higher degree of orientation than the carbon fibres carbonized at 1300 °C, regardless of the nozzle. A higher spinning temperature increased the difference.

Fig. 4 shows the changes in the crystalline orientation of fibres spun through the three nozzles at 280 °C by calcination and graphitization. Fibres spun through all nozzles showed a lower degree of orientation after calcination at 1300 °C as described above. However, the graphitization at 2000 and 2500 °C increased sharply the degrees beyond those of the pitch fibres.

Table IV shows the crytallographic parameters of the graphited fibres. The crystalline thickness, L_c, and the interlayer spacing, d_{002}, exhibited similar values regardless of the spinning nozzle. The values of L_c increased in the order Y-shaped < circular < slit-shaped spinning nozzle.

TABLE IV Crystallographic parameters and mechanical properties of carbon fibres

Code	Heat-treatment temperature (°C)	Carbon fibre diameter (μm)	d_{002} (nm)	L_c (nm)	Strain at break (%)	Tensile strength (kg mm^{-2})	Young's modulus (t mm^{-2})
R-285-20	2000	7.4			0.49	254	49.2
R-285-20	2500	6.8	0.3427	21	0.38	283	74.4
Y-285-20	2000	7.2			0.62	268	43.2
Y-285-20	2500	7.2	0.3419	23	0.43	304	70.6
S-285-20	2000	7.8			0.60	268	44.6
S-285-20	2500	7.3	0.3428	19	0.47	332	70.7

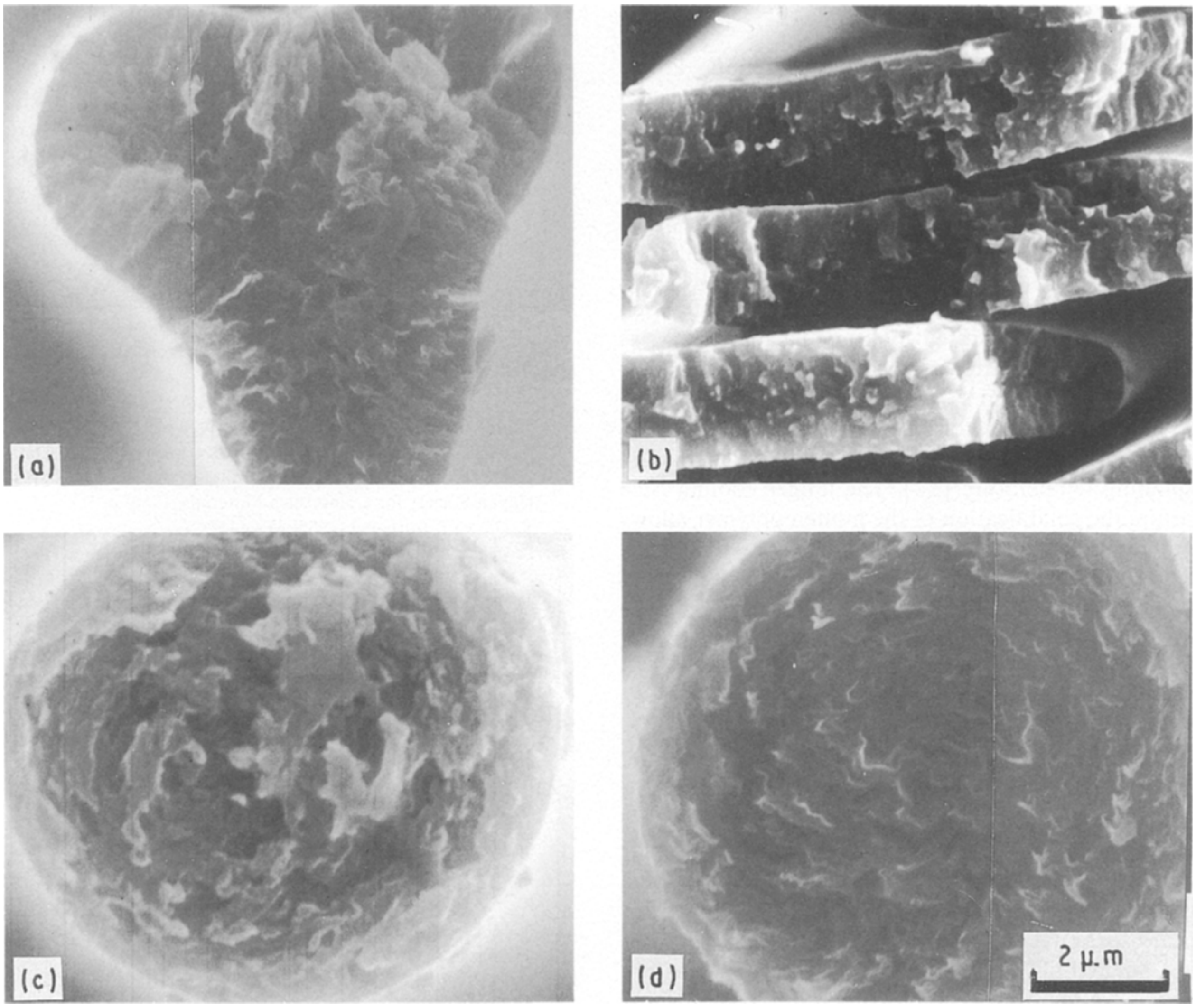

Figure 5 SEM micrographs of griphited fibres prepared with non-circular spinning nozzles: (a) Y-275-20, (b) S-265-20, (c) Y-295-20 and (d) S-285-20 (see Table II).

Fig. 5a–d illustrates the transversal shapes and textures of graphited fibres spun at 275, 265, 295 and 285 °C, respectively, with the Y- and slit-shaped spinning nozzles. Even though the transversal textures changed from a radial to a random or random–onion type with changing transversal shapes, the sizes of the domains (about 0.4 μm) in the graphitized fibres were very similar.

3.3. Mechanical properties of graphited fibres

The strengths of graphitized fibre spun at 285 °C with the circular nozzle graphitized at 2000 and 2500 °C were 254 and 283 kg mm^{-2}, respectively, as shown in Table IV. The fibres spun at the same temperature through Y- or slit-shaped spinning nozzles showed higher strengths of 304 and 332 kg mm^{-2}, respectively, after graphitization at 2500 °C. The fibres with a random or a random–onion texture appeared to be stronger than those with a radial texture.

The Young's moduli of fibres were also different for the different transversal textures. Graphitized fibres of radial–wedge spun at 285 °C through the circular nozzle and of random texture spun at 285 °C through the Y-shaped nozzle exhibited the highest and lowest Young's modulus, respectively.

The strains to break of the present graphitized fibres were around 0.4% after graphitization at 2500 °C. The fibres with the smallest L_c spun at 285 °C through the slit-shaped nozzle showed the largest value (0.47%).

4. Discussion

The stable spinning of the mesophase pitch into thin fibres of 7 μm with a series of transversal textures is one of the major tasks in carbon fibre production. This study revealed that the transversal texture of circular carbon fibres can be controlled by spinning mesophase pitch through non-circular spinning nozzles.

It has been empirically proven that spinning at low and high viscosity of the pitch tends to provide radial and random–onion orientation, respectively [12]. In this study the transversal texture of carbon fibre spun with non-circular spinning nozzles was found to change from a radial to a random or random–onion texture with increasing spinning temperature, as shown in Fig. 2. Such results indicate that the flow direction of planar mesogen molecules in the molten mesophase pitch through non-circular capillary was relaxed into the circular shape of spun pitch fibre before solidification.

The cross-section of nylon 6 fibre was found to change from a slit to a circular shape with increasing spinning temperature [22]. The longer cooling time before the solidification of the molten polymer allows more time for the cross-section of the spun fibre to be deformed into a circular shape. The shape of fibres at the outlet of the spinneret reflects shear of planar molecules on the wall of the spinneret and, in turn, defines the cooling rate according to the surface area. The lowest temperatures for forming a circular fibre are 295 and 285 °C, respectively, with Y- and slit-shaped spinning nozzles. The Y-shape may allow the rapidest cooling, requiring a higher temperature for the rearrangement than the slit shape.

The graphited fibres spun through the circular nozzle showed a slightly better modulus at the same graphitization temperature. The BAF of fibres appears to be related to the Young's modulus. Bright and Singer [23] reported that pitch-based carbon fibre with a random transversal texture is less graphitizable than that with a radial texture. In the present study, however, the L_c of fibres were very similar regardless of the transversal textures (Table IV). The domain size of the textures in the present fibres was much larger than the crystal size, no relationship between these parameters being expected. A relationship was reported by Hamada *et al.* [13], who prepared very fine mosaic texture of 0.1 μm in carbon fibre, which was the same range as its crystalline parameters.

Circular transversal-shaped fibres with a random or a random–onion texture prepared by spinning through the Y- or slit-shaped spinning nozzles exhibited a larger strain to break and tensile strength than the fibre spun through the circular nozzle. The tensile strength of the carbon fibre was recognized to be governed by the planar alignment and defects along the fibre axis as well as resistive structure for the fissure development, all of which are defined by the spinning and stabilization steps. Such an alignment of the first term may be described by BAF. However, fibres spun through the non-circular nozzles exhibited higher values of crystalline orientation after the calcination stage, but lower values after the graphitization than those spun through the circular nozzle. The BAF may not be a major determining factor for the tensile strength of the present fibres, although the complex changes in the BAF are not fully explained at present. Defects in the carbon fibres with the present level of strength are very difficult to quantify. The last term appears to be related to the transversal texture of the carbon fibre. The random or random–onion texture may be superior to the radial texture.

The flow dynamics of planar molecules in the nozzle, at the outlet of, and then into the fibre form should be established to design the texture in the resultant fibres, but its analysis is beyond the scope of the present paper. The influence of the stabilization procedure will be clarified as the next step.

References

1. S. OTANI, K. OKUDA and H.S. MATSUDA, in "Carbon Fibre" (Kindai Henshu Sha, Tokyo, 1983) p. 231 (in Japanese).
2. K. KAWATA, S. UEKAWA and K. KOBAYASHI, in "Composites '86: Recent Advances in Japan and United States" (Japan Society for Composites Materials, 1986) p. 1.
3. S. OTANI, *Carbon* **3** (1965) 31.
4. *Idem, Mol. Cryst. Liq. Cryst.* **63** (1981) 249.
5. S. CHWASTIAK, UK Patent Application GB 2 005 298 A.
6. D. RIGGS and R. J. DIFFENDORF, US Patent 4 208 267 (1980).
7. S. OTANI, K. OKUDA and S. MATSUDA, in "Carbon Fibre" (Kindai Henshu Sha, Tokyo, 1983) p. 246.
8. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. MATSUMOTO, *J. Mater. Sci.* **23** (1988) 670.
9. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. NAITO, *ibid.* **23** (1988) 678.
10. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. MATSUMOTO, *ibid.* **24** (1989) 57.
11. T. MATSUMOTO, *Pure Appl. Chem.* **57** (1985) 1553.
12. Y. YAMADA, in "New Development of Carbon Fibers" (Carbon Society of Japan, Tokyo, 1983) p. 11 (in Japanese).
13. T. HAMADA, T. NISHIDA, M. FURUYAMA and T. TOMIOKA, *Carbon* **26** (1988) 837.
14. H. SASAKI, T. SAWAKI and Y. YOSHIOKA, US Patent 4 628 001 (1988).
15. D. D. EDIE, N. K. FOX and B. C. BARNETT, *Carbon* **24** (1986) 481.
16. Y. KORAI, M. NAKAMURA, I. MOCHIDA, Y. SAKAI and S. FUJIYAMA, *ibid.* **28** (1991) 561.
17. S. H. YOON, I. MOCHIDA and Y. KORAI, *Carbon* in press.
18. G. E. BACON, *J. Appl. Chem.* **6** (1965) 477.
19. JAPAN SOCIETY OF PROMOTION OF SCIENCE (JSPS) *Tanso (Carbon)* **36** (1963) 25.
20. CARBON SOCIETY OF JAPAN, in "Tanso Zairyo Jitugen Gijyutsu" (Kagaku Gijyutsu, Tokyo, 1978) p. 46.
21. JAPANESE INDUSTRIAL STANDARD JIS R-7601 (1980).
22. A. ZIABICKI, in "Fundamentals of Fiber Formation" (Wiley, New York, 1976) p. 361.
23. A. A. BRIGHT and L. S. SINGER, *Carbon* **17** (1979) 59.

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