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Some factors for the high performances of mesophase pitch based carbon fibre

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The tensile strength and Young's modulus of the carbon fibres prepared from naphthalene derived mesophase pitch were studied by varying the spinning temperature, heating rate and final temperature of the stabilization and graphitization temperatures to find the best properties obtainable from the particular pitch. The heating rate was very influential on the tensile strength of the fibre; a slow heating of 0.5 °C min^{-1}, provided the highest strength, as high as 5 GPa at the optimum final temperature of stabilization. A higher or lower final temperature reduced the strength. Insufficient oxygen uptake or decomposition of oxygen groups at the surface of the fibre could induce defects, reducing the strength. In contrast, Young's modulus of the fibres was rather insensitive to preparation conditions. The carbonization and graphitization temperature influenced the mechanical properties as follows: the strength increased stepwise with the carbonization temperature, whereas the modulus increased sharply with the graphitization temperature. The structural factors most influential differed with these properties.

1. Introduction

Mesophase pitch based carbon fibres have been recognized as strategic materials for the next century [1, 2]; excellent cost performance is expected, although neither their present cost or performances are yet satisfactory [3–6]. Since the mesophase pitches derived from aromatic hydrocarbons by the aid of HF/BF_3 are excellent candidate precursors in terms of their price and properties [7–10], factor studies which may improve the performances of the derived carbon fibre are of value.

Matsumoto and Mochida [11] studied the stabilization of coal tar derived mesophase pitch by varying the heating rate to find optimum conditions. The heating rate is reported to be influential on the tensile strength of the resultant fibres.

In this work the spinning, stabilization and carbonization of the naphthalene derived mesophase pitch fibre were studied to define their influences on the mechanical properties of the resultant carbon fibre. The highest tensile strength was primarily pursued by optimizing the spinning and stabilization conditions, since excellent performances were expected with this particular mesophase by optimum spinning properties. Based on the present study, the optimum cost performance of the mesophase pitch based carbon fibre and stabilization mechanism can be argued.

2. Experimental

2.1. Mesophase pitch

The naphthalene derived mesophase pitch was obtained from Mitsubish Gas Company; the analyses are given in Table I.

2.2. Spinning

The mesophase pitch was spun from a spinneret (diameter/length = 0.3/0.3 mm) into fibre at the temperatures of 310, 315 and 325 °C under nitrogen pressures of 0.35, 0.30 and 0.05 MPa, respectively. The spinning rate was about 500 m min^{-1}, and the spinning could be continued for longer than 30 min. The diameter of the pitch fibre was controlled to be around 10 μm.

2.3. Stabilization, carbonization and graphitization

Mesophase pitch fibre was oxidatively stabilized in air at heating rates of 0.1, 0.5 and 2.0 °C min^{-1} up to various final temperatures without any holding time. Stabilized fibres were carbonized and then graphitized to 2500 °C at the heating rate of 20 °C min^{-1}. Some stabilized fibres were carbonized at 600, 800, 1000, 1200, 1500, 2000 and 2500 °C at heating rates of 10 °C min^{-1} for the former four and 20 °C min^{-1} for the latter three. The tensile strength of the carbonized and graphitized fibres was measured according to the JIS R-7601-1986 monofilament method using a tensile

TABLE I Some properties of mesophase pitch

Elemental analyses (wt %)					Solubility (wt %)			AC	SP
C	H	N	O	H/C	BS	BI–PS	PI	(vol%)	(°C)
94.8	4.9	0.1	0.2	0.62	33.0	19.5	47.5	100	239

BS = benzene soluble; BI–PS = benzene insoluble but pyridine soluble; PI = pyridine insoluble; AC = anisotropic content; SP = softening point.

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test machine (Tensilon UTM-IV-100; Toyo Baldwin Co.). The gauge length was 25 mm, the cross-head speed was 1 mm min^{-1} and the diameter of fibres was measured with a scanning electron microscope. Strengths and moduli of 16 filaments were measured and averaged to obtain the representative value. Young's modulus was calculated based on the stress–strain curve.

2.4. Characterization of the mesophase pitch, stabilized, carbonized and graphitized fibres

The mesophase pitch and stabilized fibres were analysed by elementary analysis, FT–i.r. (JEOL, JIR-100) spectra were observed in KBr discs. Solid ^{13}C-n.m.r. were obtained using a Varian Vxr-400 under the following conditions: pulse width 10.47 μs, spectrum width 25 KHz, pulse repetition 6 s, number of transients 9000. The transversal sections of carbonized and graphitized fibres were observed under a scanning electron microscope (JEOL 25S).

3. Results

3.1. Influence of the stabilization heating rate on the tensile strength and Young's modulus of the graphitized fibres

Figs 1 and 2 show the averaged tensile strength and Young's modulus of graphitized fibres which were spun at 315 °C (solid plot). Their mechanical properties varied with both stabilization heating rate and final temperature. The tensile strength increased first by raising the final temperature to exhibit the highest values and then decreased by further temperature increase, regardless of the heating rate. The maximum averaged tensile strength of graphitized fibres which were stabilized by the heating rates of 0.1, 0.5 and 2.0 °C min^{-1} were 3.8, 4.1 and 3.5 GPa at the final temperatures of 230, 260 and 290 °C, respectively. The maximum Young's moduli were 745, 750 and 690 GPa, respectively; reflecting the heating rates of 0.1, 0.5 and 2.0 °C min^{-1}. The optimum temperatures were 220, 250 and 280 °C, respectively; which were 10 °C lower than those for the maximum tensile strengths. Again, rapid heating reduced the modulus.

3.2. Influence of the spinning temperature on the tensile strength and Young's modulus

Fig. 1 shows the tensile strength of graphitized fibres which were stabilized at a fixed heating rate of 0.5 °C min^{-1}. The maximum tensile strength of graphitized fibres which were spun at 310, 315 and 325 °C were 4.1, 4.1 and 3.6 GPa, respectively, at the respective final temperatures of 270, 260 and 250 °C. Lower spinning temperatures appeared to give higher tensile strengths. When the stabilization heating rates were the same the optimum temperatures where the highest tensile strength was obtained were different. Higher spinning temperatures allowed sufficient stabilization at a little lower temperature.

Fig. 2 shows the relationship between the Young's modulus of the graphitized fibres and spinning temperature. The maximum Young's modulus of the graphitized fibres which were spun at 310, 315 and 325 °C were 7.5, 7.5 and 7.4 GPa, by stabilization up to 270, 250 and 240 °C, respectively.

3.3. Distribution of tensile strength and Young's modulus of graphitized fibres

Distribution of tensile strength of 16 filaments prepared under the same conditions are illustrated in Fig. 3. Although the strength of the fibres distributed in a very broad range from 2.2 to 5.5 GPa with the present fibres, the majority of filaments exhibited strengths above 3 GPa, and the strongest ones exceeded 5 GPa. The strength of the fibres prepared under different conditions can be deduced from the distributions in the order of (a) > (b) > (c) > (d) >

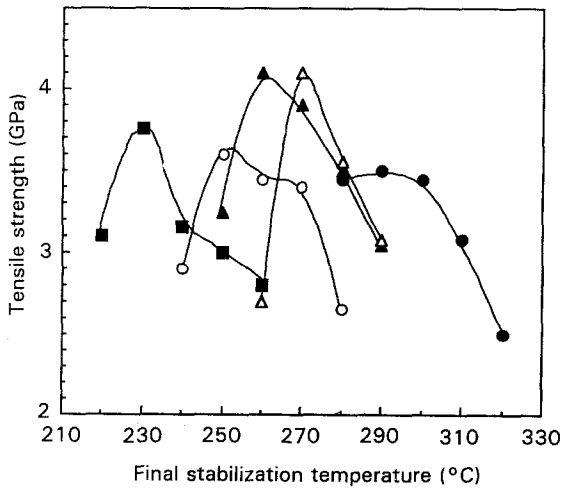

Figure 1 Relationship between the tensile strength of graphitized fibres and stabilization temperature. Spinning temperature and heating rate at stabilization: ■, 315 °C, 0.1 °C min^{-1}; ○, 325 °C, 0.5 °C min^{-1}; ▲, 315 °C, 0.5 °C min^{-1}; △, 310 °C, 0.5 °C min^{-1}; ●, 315 °C, 2.0 °C min^{-1}.

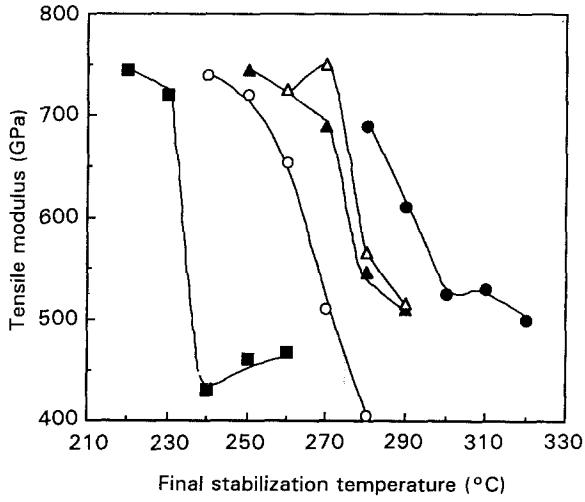

Figure 2 Relationship between the tensile modulus of graphitized fibres and stabilization temperature. Spinning temperature and heating rate at stabilization: ■, 315 °C, 0.1 °C min^{-1}; ○, 325 °C, 0.5 °C min^{-1}; ▲, 315 °C, 0.5 °C min^{-1}; △, 310 °C, 0.5 °C min^{-1}; ●, 315 °C, 2.0 °C min^{-1}.

(e), basically coinciding with their average values, which may be representative of the strengths expected when the composites are produced from bundles of fibres [12–14].

The strengths of the upper-half in their distribution may reflect those of fibres more properly spun, their averages achieving values above 5 GPa, which are very satisfactory when the rather primitive spinning and stabilization apparatus in the university laboratory are taken into account.

Young's modulus of filaments distributed in a much narrower range compared to that of tensile strength, as shown in Fig. 4. The averaged values of the graphitized fibres may be very reliable. The strong influences by the stabilization heating rate were definitely disclosed.

3.4. Oxygen uptake during stabilization

Fig. 5 illustrates the oxygen uptake of pitch fibres during the stabilization. The fibres started to uptake oxygen at lower temperatures when the heating was slower. The oxygen contents of 9.0–9.5%, when the largest strength was obtained, were achieved at 230, 270, 260, 250 and 290 °C, respectively, by the heating rates of 0.1, 0.5 and 2.0 °C min^{-1}. The slower heating led to a long residence time, allowing more oxygen to be picked up at the same temperature.

The fibres spun at higher temperatures picked up much oxygen at lower temperatures, corresponding to the completion of stabilization at a lower temperature. In a range of the present stabilization conditions, the oxygen content of the stabilized fibre increased monotonously with the higher final temperature, giving the highest mechanical properties of the resultant carbon fibre at an intermediate content. The oxidation is suggested to be necessary, but in excess it causes deterioration of the properties.

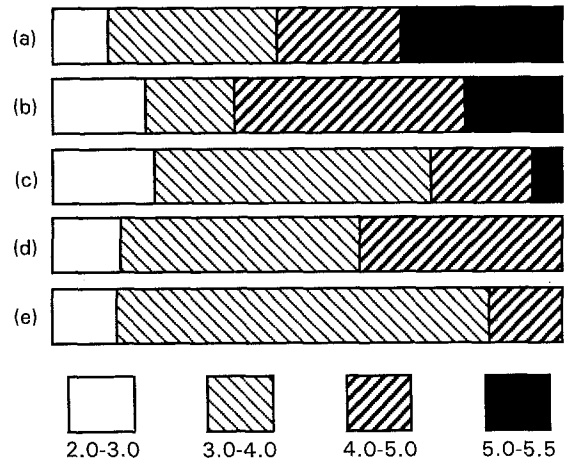

Figure 3 Tensile strength distribution of graphitized fibres. Spinning temperature, heating rate and final temperature at stabilization: (a) 310 °C, 0.5 °C min^{-1}, 270 °C; (b) 315 °C, 0.5 °C min^{-1}, 260 °C; (c) 325 °C, 0.5 °C min^{-1}, 250 °C; (d) 315 °C, 0.1 °C min^{-1}, 230 °C; (e) 315 °C, 2.0 °C min^{-1}, 290 °C.

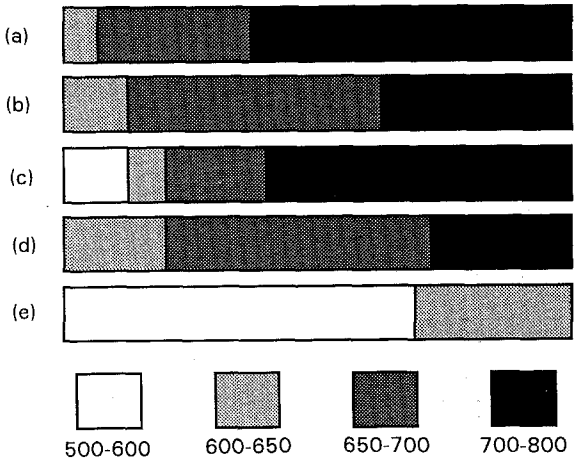

Figure 4 Tensile modulus distribution of graphitized fibres. Spinning temperature, heating rate and final temperature at stabilization: (a) 310 °C, 0.5 °C min^{-1}, 270 °C; (b) 315 °C, 0.5 °C min^{-1}, 260 °C; (c) 325 °C, 0.5 °C min^{-1}, 250 °C; (d) 315 °C, 0.1 °C min^{-1}, 230 °C; (e) 315 °C, 2.0 °C min^{-1}, 290 °C.

3.5. Influences of the carbonization temperature on the tensile strength and Young's modulus of carbon fibres

Fig. 6 shows the tensile strength and Young's modulus of fibres carbonized or graphitized at a series of

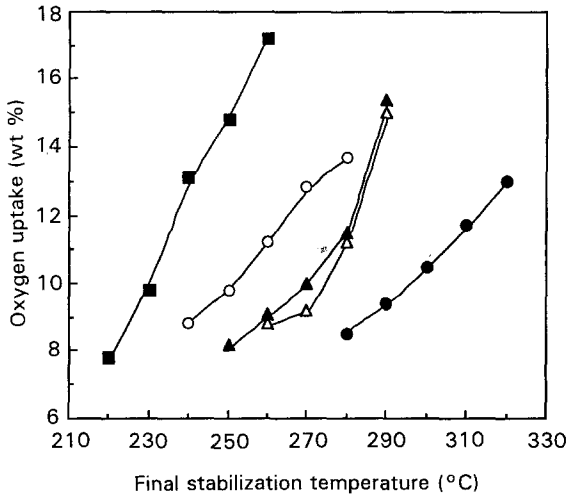

Figure 5 Relationship between oxygen uptake and final stabilization temperature of stabilized fibres. Spinning temperature and heating rate at stabilization: ■, 315 °C, 0.1 °C min^{-1}; ○, 325 °C, 0.5 °C min^{-1}; ▲, 315 °C, 0.5 °C min^{-1}; △, 310 °C, 0.5 °C min^{-1}; ●, 315 °C, 2.0 °C min^{-1}.

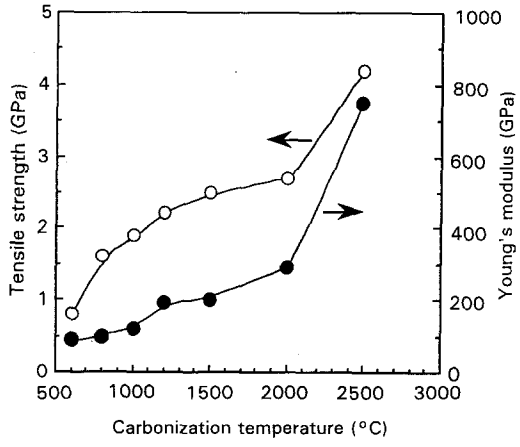

Figure 6 Relationship between the mechanical properties of fibres and carbonization temperature.

temperatures. This fibre was spun at 310 °C and then stabilized at a heating rate of 0.5 °C min^{-1} up to 270 °C. The averaged tensile strength increased very quickly from 0.8 to 2.3 GPa during the 600–1200 °C range, and stayed at ca. 2.3–2.7 GPa in the 1200–2000 °C range, and then increased sharply to 4.1 GPa at 2500 °C.

The Young's modulus increased very gradually from 100 to 300 GPa during the 600–2000 °C range, and then increased very sharply to 7.5 GPa at 2500 °C.

3.6. Scanning electron microscopic observation of pitch, carbonized and graphitized fibres

Fig. 7 shows the texture of transversal sections of graphitized fibres at 2500 °C. The fibres appear to be a

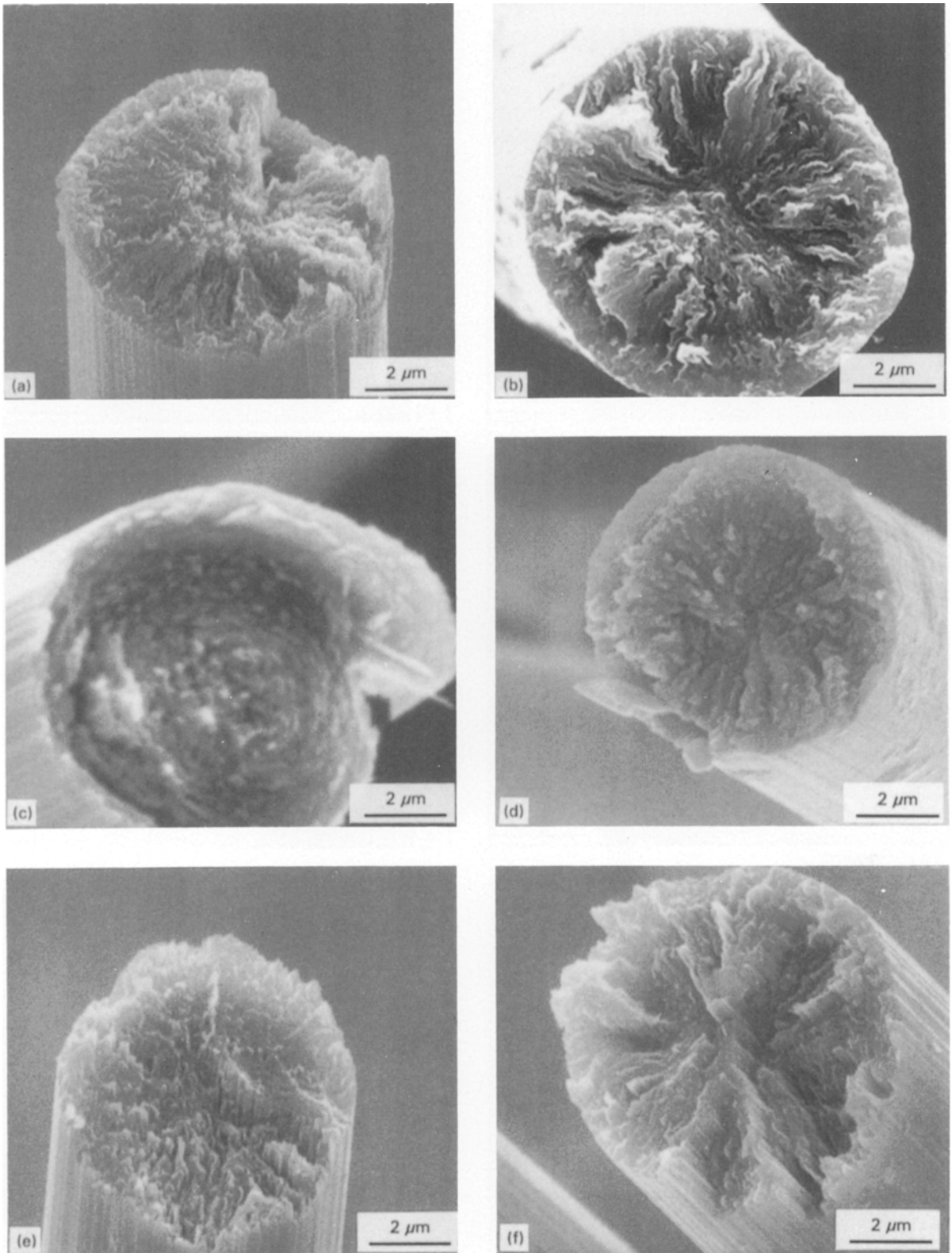

Figure 7 SEM photographs of transverse section of graphitized fibres. Spinning temperature, heating rate and final temperature of stabilization: (a) 310 °C, 0.5 °C min^{-1}, 270 °C; (b) 315 °C, 0.5 °C min^{-1}, 260 °C; (c) 325 °C, 0.5 °C min^{-1}, 250 °C; (d) 315 °C, 2.0 °C min^{-1}, 290 °C; (e) 310 °C, 0.5 °C min^{-1}, 270 °C; (f) 315 °C, 0.5°C min^{-1}, 270 °C.

collection of carbon flakes which form the texture. The spinning temperature changed the texture of the graphitized fibres from radial (310 °C) to onion (325 °C) through to deformed radial (315 °C), as reported in a previous paper [15]. The heating rate of stabilization slightly modified the texture, the faster heating of 2.0 °C min^{-1} allowed some adhesion of flakes at the core of the filament. The lower final temperature of 250 °C at the same heating rate of 0.5 °C min^{-1} provided some adhesion of the flakes (Fig. 7e and f). Such adhesion may indicate some fusion during the carbonization, probably being related to the poorer mechanical properties of the fibres [16].

Fig. 8 illustrates transversal texture of as-spun, carbonized (600–1500 °C) and graphitized fibres (2000 °C). No texture was observable in the as-spun fibre, the texture of the flake collection appeared and became gradually definite with higher temperatures of

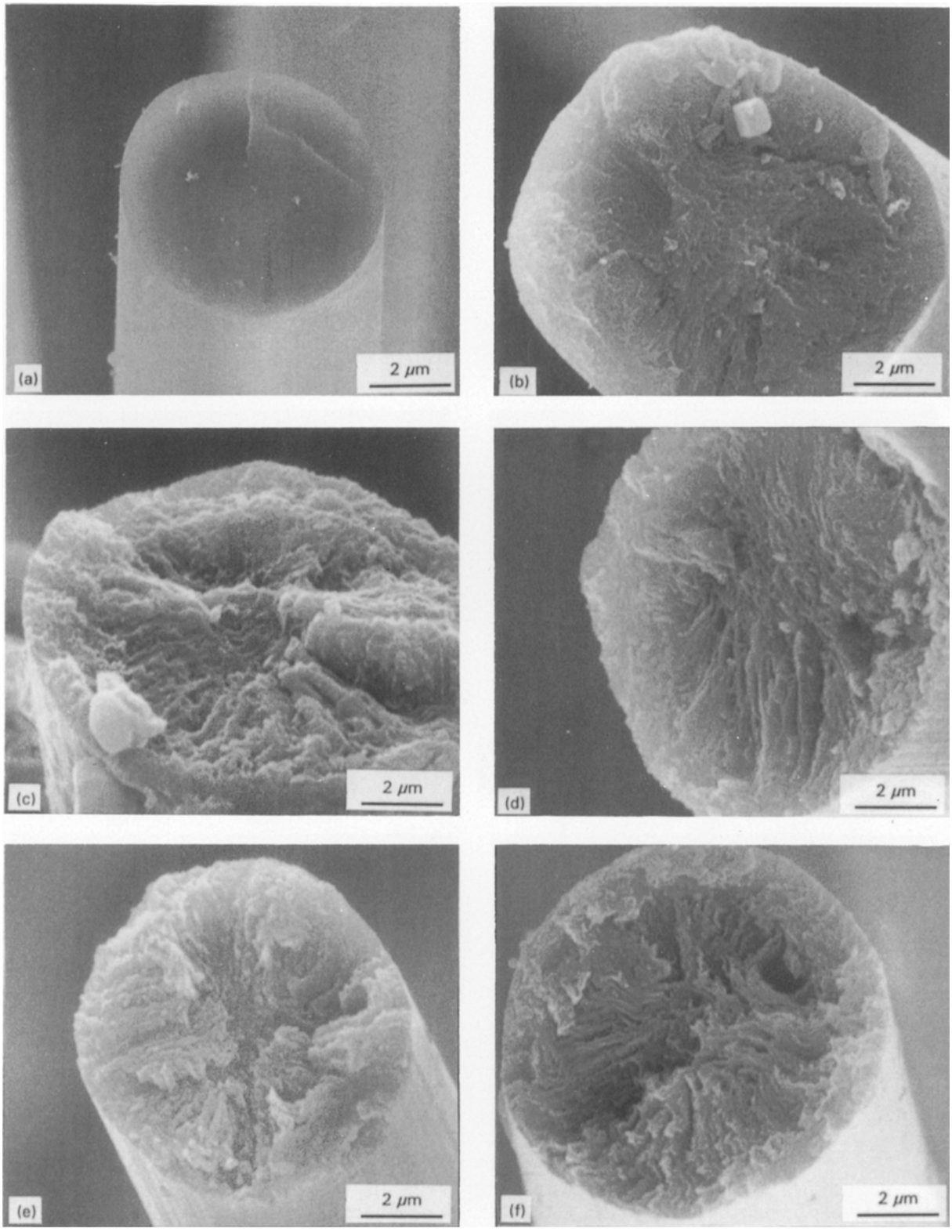

Figure 8 SEM photographs of pitch- and carbonized fibres at variable temperature. (a) Pitch fibre; (b) 600 °C; (c) 800 °C; (d) 1000 °C; (e) 1500 °C; (f) 2000 °C.

carbonization and graphitization. Shapes of the flakes appeared to be more definite with the progression of graphitization, which may allow the growth of the graphite planes. Such changes may correspond to the mechanical properties illustrated in Fig. 6.

3.7. Chemical structure characterization of mesophase pitch and stabilized fibres

Fig. 9 shows the FT-i.r. spectra of the mesophase pitch and stabilized fibres which were spun at 315 °C and stabilized by heating rates of 0.5 °C min^{-1} to 250, 260 and 270 °C and by 2.0 °C min^{-1} to 290 °C, respectively. The bands at 3050 cm^{-1} (aromatic C–H), 2720–2960 cm^{-1} (aliphatic C–H) and 870–750 cm^{-1} (aromatic C–H) decreased significantly after the oxidative stabilization, while new bands at 1650 cm^{-1}, 1750 cm^{-1} (carbonyl and aromatic ester or ether groups) and ca. 1250 cm^{-1} (ether, ester or phenolic groups) appeared after the oxidation. The intensity of the bands at 1600 cm^{-1} (aromatic C=C) increased after the oxidation. The difference among the stabilized fibres was barely observable under the present stabilization conditions.

Fig. 10 shows the solid ^{13}C-n.m.r. spectra of mesophase pitch and stabilized fibres by the heating rates of 0.5 and 2.0 °C min^{-1} up to 260 and 290 °C, respectively. The mesophase pitch exhibited carbon aromaticity of 0.7. The stabilization reduced the intensity of aliphatic carbons around 20 ppm and increased the aromaticity; the slower heating gave a slightly higher value of 0.9 than that of 0.8 obtained by more rapid heating, although the spectra were very similar. The loss of oxidized aromatic carbon was suggested under the latter condition.

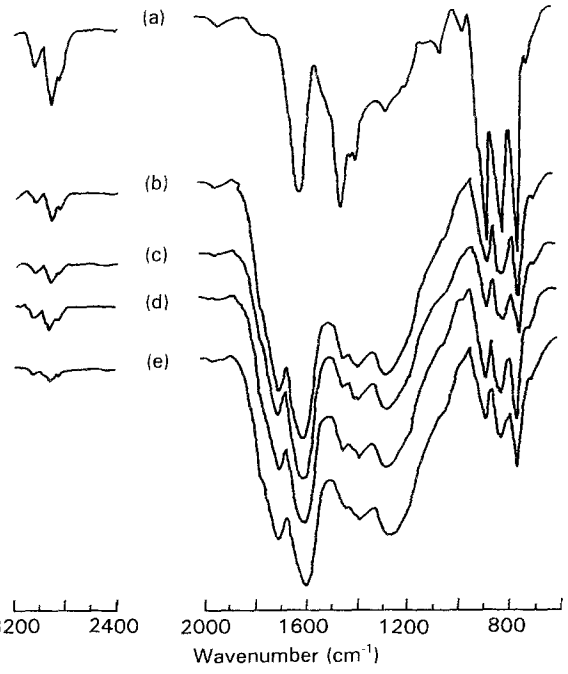

Figure 9 FT-i.r. spectra of mesophase pitch and stabilized fibres. Spinning temperature, 315 °C; heating rate and final temperature of stabilization: (a) mesophase pitch; (b) 0.5 °C min^{-1}, 260 °C; (c) 2.0 °C min^{-1}, 290 °C; (d) 0.5 °C min^{-1}, 250 °C; (e) 0.5 °C min^{-1}, 270 °C.

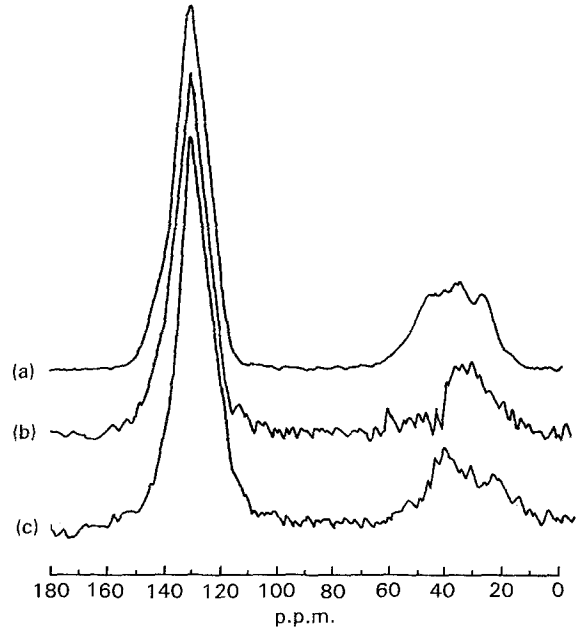

Figure 10 Solid ^{13}C-n.m.r. spectra of mesophase pitch and stabilized fibres. Spinning temperature, 315 °C; heating rate and final temperature of stabilization: (a) mesophase pitch; (b) 0.5 °C min^{-1}, 260 °C; (c) 2.0 °C min^{-1}, 290 °C.

4. Discussion

The present study revealed that very high tensile strength, as well as Young's modulus, could be obtained with the carbon fibre from the mesophase pitch derived from the naphthalene by the aid of HF/BF_3 by optimum spinning and stabilization conditions, the champion tensile strength value reaching as high as 5.5 GPa, which may be the best one among the round fibres prepared in these laboratories, using a rather primitive spinning instrument through a mono-hole spinneret. Strength ca. 2.5 GPa was obtained at the carbonization temperature of 1000–1200 °C and the modulus ca. 200 GPa was able to reduce the cost of carbon fibres in comparison with PAN based ones for broad application [17, 18]. The excellent value of Young's modulus has been recognized as another advantage of the mesophase pitch; the modulus of 750 GPa being easily obtained from the mesophase pitch by the graphitization at 2500 °C. This is another characteristic of the present mesophase pitch.

The highest tensile strength was obtained in the present study by spinning at 310–315 °C and stabilizing at 0.5 °C min^{-1} up to 260–270 °C. Rapid heating to high temperature for complete stabilization reduced the strength. The chemical structure observed by FT-i.r. and solid ^{13}C-n.m.r. were similar, although the best stabilization provided a large value of carbon aromaticity regardless of the heating rate and final stabilization temperature. The surface defects are suspected to cause the decrease of the strength and modulus by rapid heating up to a high temperature. Rapid heating may result in passing the glass transition temperature of the pitch fibre, since rapid heating might exceed the rise of the temperature. Stabilization is basically oxygenation and oxidative dehydrogenation [19]. Rapid heating up to a higher temperature may tend to decompose some of the oxygenated aro-

matic groups at the higher temperature of the stabilization, thereby introducing defects. Rapid heating may also cause decomposition, especially at the fibre surface, where oxidation progresses more quickly. A very slow heating rate (0.1 °C min^{-1}) slightly lowered the strength. Too much oxygenation may reduce the mechanical properties by decomposition at the carbonization. Hence, sufficient oxidation for the stabilization should be balanced to the least weight loss by the excess decomposition of oxygenated groups at the stabilization and carbonization, oxygen content ca. 9.5% appeared optimum with the present pitch under the present stabilization conditions.

The spinning temperatures were found to influence the rates of stabilization and oxygen uptake as well as the strength of the resultant carbon fibres. The apparent changes of the fibres were observed in the transversal sections, as reported by several researchers [20–22]. Influences of the transversal texture on the rate of stabilization and tensile strength are not straightforward. In a previous paper [11], the authors reported the influence of spinning temperature on the Young's modulus of the fibre. The slow heating of the stabilization and narrow spinning temperature range may give similar values in the present study.

At present, the remaining problem is very slow heating rate of 0.5 °C min^{-1}, which takes ca. 500 min for sufficient stabilization to obtain the highest strength, significantly increasing the cost of fibre production. It is possible to select the heating rate from the view of the cost performance balance. The stabilization time can be shortened by program heating, for example, rapid heating at 200 °C and then optimum heating rate to the final temperature or isothermal stabilization, although the oxidation chemistry involved in the temperature rising and isothermal stabilization may be different because the activation energies of the reactions involved in the stabilization influence the extent of the reaction progress. More extensive studies to accelerate the stabilization are needed. Although the thinner fibre can be one solution, higher reactivity and more rapid stabilization to assure the high strength are still major targets for the better mesophase.

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