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Comparative evaluation of mesophase pitches derived from coal tar and FCC-DO

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Three kinds of mesophase pitches (MPs) derived from FCC-DO (P) and hydrogenated QI free coal tar (QIF) were comparatively evaluated in terms of their spinnability and stabilization reactivity based upon their structural characterizations. MP-P, which is meso-phase pitch from FCC-DO, preserved considerable amount of aliphatic and naphthenic hydrogens to show higher solubility, fusibility and softening temperature of as low as 245° C in spite of its complete anisotropy. MP-C1 derived from catalytically hydrogenated QIF carried less hydrogen content and smaller molecular weight although its solubility and softening temperature were almost the same to those of MP-P. MP-C2 which was prepared from QIF treated with tetrahydroquinoline (THQ) showed the least hydrogen content, the lowest solubility and the highest softening temperature of 290° C. MP-P allowed smooth spinning for much longer time at the temperature from 320 to 350° C. MP-C1 could be spun at the temperature from 340 to 370° C, which was much higher than that of MP-P in spite of their similar softening temperatures. MP-C2 showed spinnability at the temperature from 340 to 390° C, although evolved gases disturbed its smooth spinning at the higher temperature.

MP-P showed the highest stabilization reactivity to require the shortest time (120 min) for the sufficient stabilization at 250° C. Although much longer time of 180 min was necessary for the MP-C1 at 250° C, a higher temperature of 270° C accelerated the stabilization reactions to shorten the time to 60 min. MP-C2 showed the least reactivity, requiring 120 min at 270° C. More aliphatic and naphthenic structure of FCC-DO derived mesophase pitch is related to its superiority as the pitch fibre precursor. The catalytic hydrogenation which can produce naphthenic or aliphatic structure is a better pre-treatment to modify the coal tar as the mesophase pitch precursor.

1. Introduction

Preparation of mesophase pitch based carbon fibres (PBCFs] has been extensively investigated as the strategic material in the near future [1, 2]. Although their preparative process was established [3-6], there still remain several problems to be solved to balance the cost/performance of the carbon fibre [7, 8]. Since mesophase pitches are at present prepared from either FCC-DO or QI free coal tar pitch (QIF) [9-15], it is of value to evaluate them comparatively as the precursor pitch for the fibre. Structural analyses in relation to their properties may suggest better pre-treatment procedure before the mesophase preparation.

In the present study, spinnability in terms of stability and molecular orientation in the filament and stabilization of the mesophase pitches derived from FCC-DO and QIF were comparatively evaluated. Such properties of the mesophase pitches are the most critical factors for the production cost and quality of pitch based carbon fibre.

2. Experimental details

2.1. Mesophase pitches

Three kinds of mesophase pitches derived from FCC-DO and QI free coal tar pitch (QIF) used in the present study were provided from a petroleum and a fibre companies in their courtesy. MP-P was prepared from FCC-DO. MP-C1 and MP-C2 were obtained by the heat-treatment of QIFs which were hydrogenated with catalyst [9] and tetrahydroquinoline (THQ) [10], respectively. The precursor pitches were believed to be converted into respective mesophase pitches by the heat-treatment under vacuum.

2.2. Characterization of mesophase pitches

Solubilities of the whole mesophase pitches in benzene and pyridine were measured using a Sohxlet apparatus. Solubility in quinoline was examined at room temperature by the filtration with Fluoropore filter (Sumitomo electric IND., Ltd, FP-045) by applying a nitrogen pressure of 2 kg cm^{-2}.

Softening temperatures of the pitches were observed

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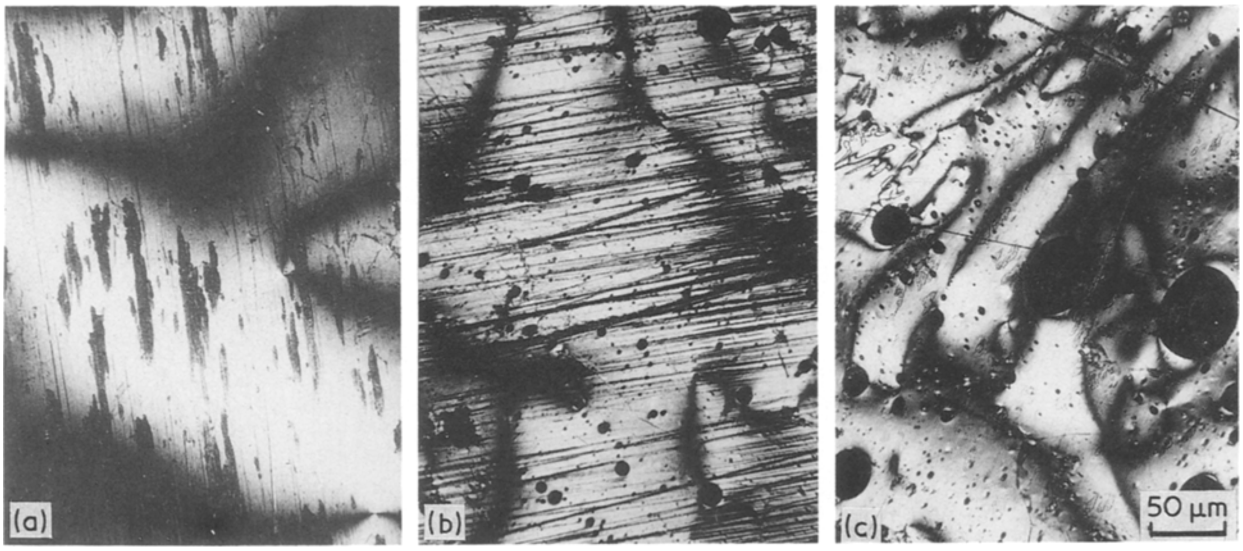

Figure 1 Optical microphotographs of the mesophase pitches. (a) MP-P, (b) MP-C1, (c) ,P-C2.

in the Hot Stage (Leitz, 1350) of the polarized-light microscope (Leitz, Orthoplam pol).

FT-IR (JEOL, JIR-03F) spectra of the pitches were observed, applying the KBr disc procedure to clarify the functional groups of the pitches.

Benzene soluble (BS) and benzene insoluble-pyridine soluble (BI-PS) fractions of the pitches were characterized by using the ^{1}H-NMR (JEOL, FT-100) and their structural parameters were calculated according to the Brown-Ladner analysis [16].

GPC profiles of the fractions were obtained using their 5% quinoline solution.

2.3. Spinning of mesophase pitches

Three kinds of mesophase pitches were spun into fibres of ca. 10 μm in diameter under nitrogen pressure of 1.1 ~ 1.2 kg cm^{-2} from a steel spinneret of which the diameter and the length of the nozzle were both 0.4 mm.

Amounts of extruded pitches at their spinning were measured at the temperature from 320 to 380° C, applying the constant nitrogen pressure of 1.2 kg cm^{-2} to estimate the viscosity of the pitches at each temperature.

2.4. Stabilization of mesophase pitches

Mesophase pitch fibres were oxidatively stabilized at 250, 270 and 280° C for different periods of time. The heating rate up to the stabilization temperature was 5° C min^{-1}. The stabilized fibres were characterized by elemental analyses and FT-IR to clarify the oxygen uptake and change of the functional groups during the stabilization, respectively.

2.5. Carbonization of stabilized fibres

The stabilized fibres were further carbonized at 600° C for 1 h in a Pyrex glass tube (30 mm diameter, 600 mm Long) heated by a vertical electric furnace. The heating rate was 10° C min^{-1}. After mounting in the resin and conventional polishing, the carbonized fibres were observed under a polarized-light microscope to define the adhesion extent of filaments and optical textures in the transverse section of the carbonized fibres.

The fibres carbonized at 1300° C were further observed under a scanning electron microscope (JEOL, JSM-25S) to define the morphology of the filaments.

3. Results

3.1. Characterization of mesophase pitches

Fig. 1 shows the optical microphotographs of the mesophase pitches. As shown in Fig. 1a, MP-P which was derived from FCC-DO exhibited anisotropic large-domain texture, its anisotropic content being 100%. MP-C1 which was prepared from QIF hydrogenated with the catalyst exhibited also flow domain texture, although some isotropic droplets around ca. 10 μm in diameter were observable as shown in Fig. 1b. Some isotropic droplets (diameters 10 to 60 μm) were distinctly observable in the anisotropic texture of MP-C2 and its anisotropic content was 95% [17].

Table I summarizes microanalyses of the mesophase pitches. MP-P carried the most hydrogens as indicated by its highest atomic H/C ratio of 0.54 to show the lowest softening temperature of 245° C and the highest solubilities in the solvents in spite of the complete anisotropy. MP-C1 exhibited slightly

TABLE I Some properties of mesophase pitches

Sample	(wt %)				H/C	S.T.* (°C)	A.P.† (%)	Solubility (wt %)			
	H	C	N	diff. (O)				BS	BI-PS	PI-QS	QI
MP-P	4.3	95.2	0.1	0.4	0.54	245	100	30	25	25	20
MP-C1	3.9	94.6	0.8	0.7	0.50	250	100	26	31	11	32
MP-C2	3.9	94.1	1.0	1.0	0.50	290	95	6	41	11	42

*softening temperature by Hot Stage.
†anisotropic percentage.

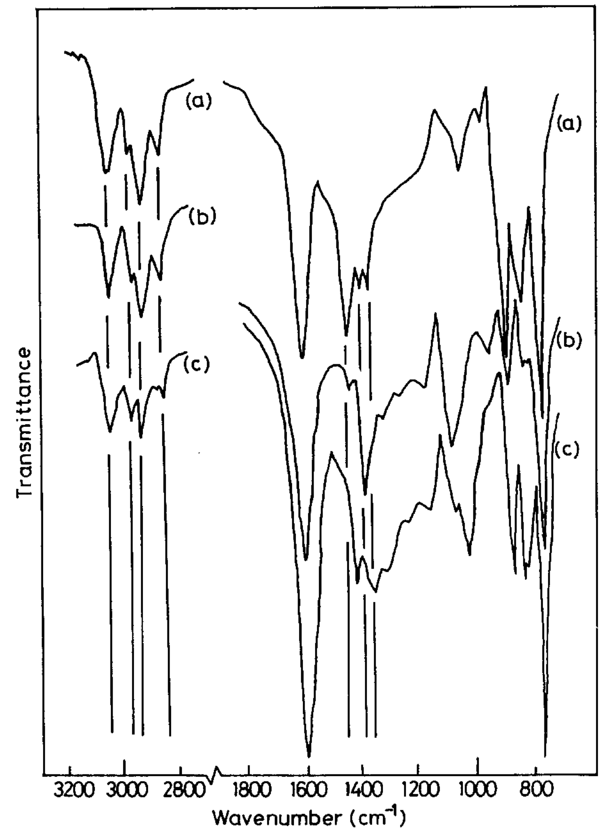

Figure 2 FT-IR spectra of the mesophase pitches. (a) MP-P, (b) MP-C1, (c) MP-C2.

lower hydrogen content (atomic H/C ratio, 0.50) and solubilities than MP-P although their softening temperatures were much the same. MP-C2, which showed a much higher softening temperature of 290° C and lower solubilities, carried the least amount of hydrogens although its anisotropic content was definitely inferior to those of the other two pitches. Its very low solubilities in benzene (BS = 6%) and quinoline (QS = 58%) were marked.

Fig. 2 illustrates the FT-IR spectra of the mesophase pitches. The adsorption bands from 2960 to 2850 cm^{-1} which are ascribed to the aliphatic and naphthenic C-H were most intense with the MP-P among the pitches. The bands of 1440 cm^{-1} (most probably methylene or naphthenic C-H) was also most distinguished with MP-P, suggesting its highest extent of alkyl substitution. The intense bands of MP-P from 1400 to 1375 cm^{-1} which are ascribed to the methyl and/or methylene C-H are also marked.

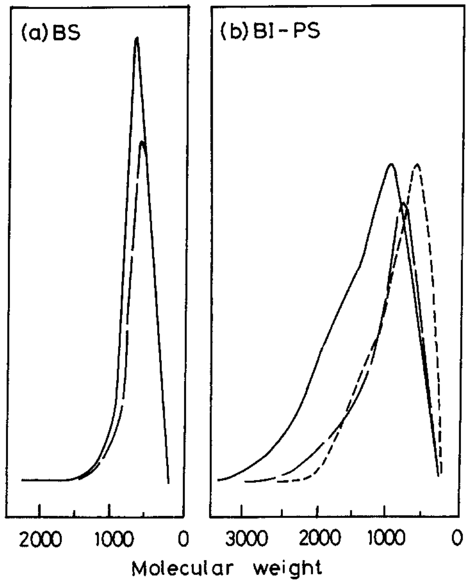

Figure 3 GPC profiles of the soluble fractions of mesophase pitches. (a) BS fraction: (——) MP-P, (— —) MP-C1; (b) BI-PS fraction: (——) MP-P, (— —) MP-C1, (----) MP-C2.

The bands from 2960 to 2850 cm^{-1} of MP-C1 were more intense than those of the MP-C2, suggesting aliphatic-rich structure of the former pitch. The band of 1400 cm^{-1} of the former pitch was also much more distinct and intense, indicating its further substitutions.

Table II summarizes the microanalyses and hydrogen distribution of the soluble fractions in the mesophase pitches. Both BS and BI-PS fractions of the MP-P showed the highest atomic H/C ratios (0.64 and 0.57, respectively), H_α (α position hydrogen content), and lowest $H_{ar.}$ (aromatic hydrogen content), respectively. The largest number of the aliphatic and naphthenic groups of its fractions was suggested by the structural parameters calculated according to the Brown-Ladner analyses. Such aliphatic and naphthenic natures were more emphasized with BS than BI-PS fraction. The BS fraction of MP-C1 exhibited more aliphatic and naphthenic ratios than those of MP-C2 although both BI-PS fractions were much the same in their parameters.

Fig. 3 shows the GPC profiles of BS and BI-PS fractions of the pitches. Although both BS fractions distributed from 200 to 1600, the BS fraction of MP-P

TABLE II Microanalyses of mesophase pitches by ^{1}H-NMR

Sample	H/C	(%)				fa*	$\sigma_{al.}$†	C_{alus}‡
		$H_{ar.}$	H_α	H_β	H_r			
MP-P								
BS	0.64	67.9	22.6	8.3	1.2	0.90	0.14	4.28
BI-PS	0.57	82.7	13.3	3.3	0.7	0.95	0.07	2.60
MP-C1								
BS	0.58	76.1	13.0	8.7	2.2	0.93	0.08	5.74
BI-PS	0.52	90.5	6.3	3.2	0	0.98	0.03	1.73
MP-C2								
BS	0.56	82.3	10.2	6.1	1.4	0.95	0.06	3.30
BI-PS	0.52	88.1	8.8	2.5	0.6	0.97	0.04	2.48

*carbon aromaticity.
†degree of aliphatic substitution for aromatic nucleus.
‡number of aliphatic and naphthenic carbon atoms per structural unit.

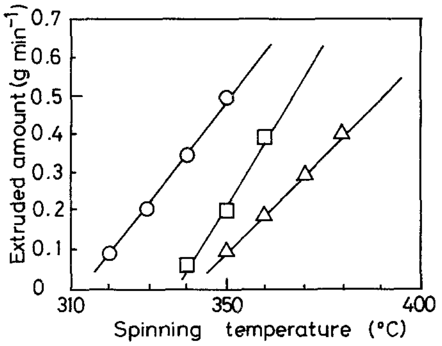

Figure 4 Extruded pitch amount of the mesophase pitches at variable temperatures. Applied pressure: $1.2\,\mathrm{kg\,cm^{-2}}$; Spinning time: 1 min; (○) MP-P, (□) MP-C1, (△) MP-C2.

showed its peak of molecular weight around 700, while that of MP-C1 was located around 500. More distinct differences of the molecular weight distributions were observable with the BI-PS fractions. The fraction of the MP-P distributed between 200 and 3500 with the peak at 1000, while those of MP-C1 and C2 did between 200 to 2500 with the peak at 700.

3.2. Spinning of mesophase pitches

MP-P showed the excellent spinnability at a temperature from 320 to 350° C to give the thin pitch fibres of ca. 10 μm in diameter for longer than 15 min. On the other hand, MP-C1 could not allow the smooth spinning below 330° C because of its high viscosity although the softening temperature of MP-C1 was almost the same as that of MP-P. Its smooth spinning was allowed at the temperature from 340 to 360° C although it was spinnable from 340 to 370° C. The sweet temperature range for the excellent spinning was only 20° C around 370° C for the MP-C2 which was a half of that of the MP-P. Fig. 4 illustrates the amounts of extruded pitch for 1 min at some spinning temperatures by applying the constant nitrogen pressure of $1.2\,\mathrm{kg\,cm^{-2}}$. Extruded amounts of all pitches increased proportionally to the spinning temperature. The extruded amount of MP-P was much larger than those of MP-C1 and MP-C2, suggesting its much lower viscosity at the same temperature of 350° C. It is noted that the increase of extruded amount of MP-C1 with the increasing temperature was clearly steeper than those of the other two pitches, suggesting its larger temperature dependence of the viscosity.

Fig. 5 shows the optical microphotographs of the pitch fibres spun at 350° C. The thin fibres of ca. 10 to 20 μm in diameter could be smoothly spun with all pitches. Fine mosaic textures were observable in the transverse sections of all pitch fibres.

3.3. Stabilization and carbonization of mesophase pitches

Fig. 6 shows the optical microphotographs of the carbonized fibres which were stabilized at 250° C for different periods of time. Considerable adhesion of some filaments of MP-P was observable when the stabilization time was 60 min although shapes of some other filaments were maintained. No adhesion of the carbonized MP-P fibres was observed after the stabilization for 120 min. Bulk cokes of mosaic and flow textures were produced from the carbonized MP-C1 fibres when the fibre was stabilized at 250° C for 60 min. The stabilization for 120 min still allowed severe adhesion of the filaments although their fibrous shapes were maintained, suggesting lower reactivity of MP-C1. Stabilization for 180 min was necessary for the MP-C1 to provide complete filaments as shown in Fig. 6.

Fig. 7 shows the optical microphotographs of the carbonized fibres stabilized at 270° C for different periods of time. When the stabilization time was 30 min, the least adhesion of the MP-P filaments was observable, suggesting that the stabilization had been almost completed. However, MP-C1 and -C2 showed still significant fusion and adhesion of the filaments under the same stabilization conditions. The stabilization time for 60 min removed adhesion completely from the filaments of both MP-P and -C1, whereas those of MP-C2 showed still significant fusion and adhesion. It took 120 min to stabilize the MP-C2 filaments [18, 19] as shown in Fig. 7.

MP-P and -C1 took 20 and 30 min, respectively, for the complete stabilization at 280° C as shown in Fig. 8.

Fig. 9 illustrates the oxygen uptake of the pitch fibres during the stabilization at 270 and 280° C. Oxygen

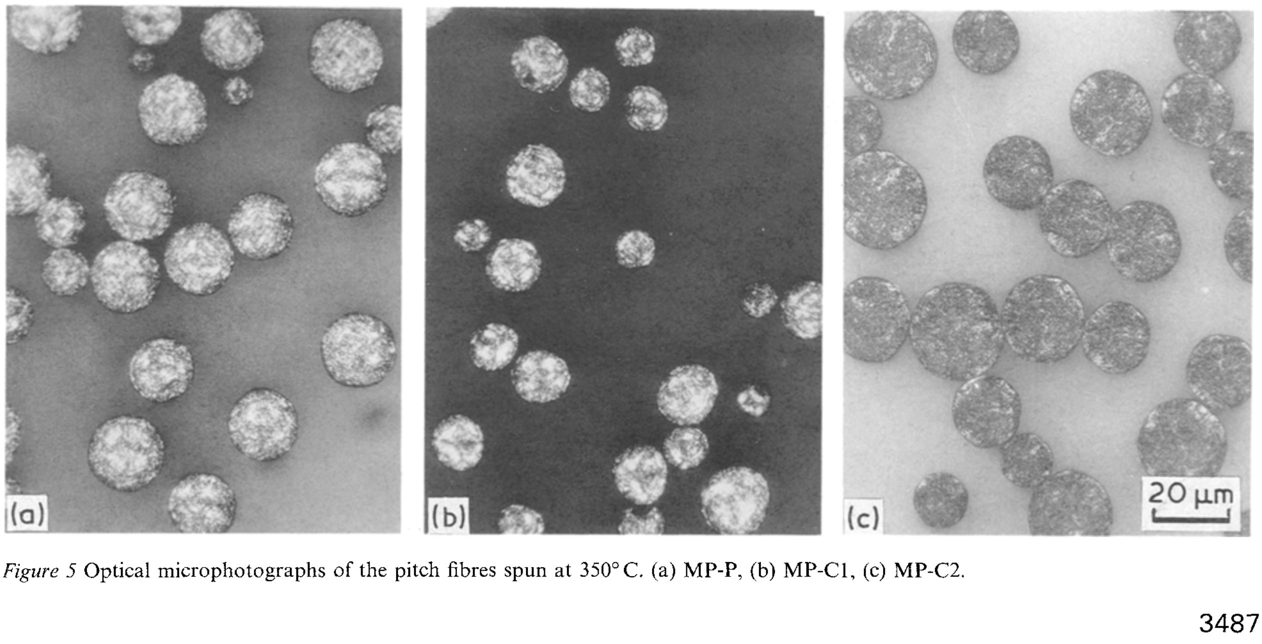

Figure 5 Optical microphotographs of the pitch fibres spun at 350° C. (a) MP-P, (b) MP-C1, (c) MP-C2.

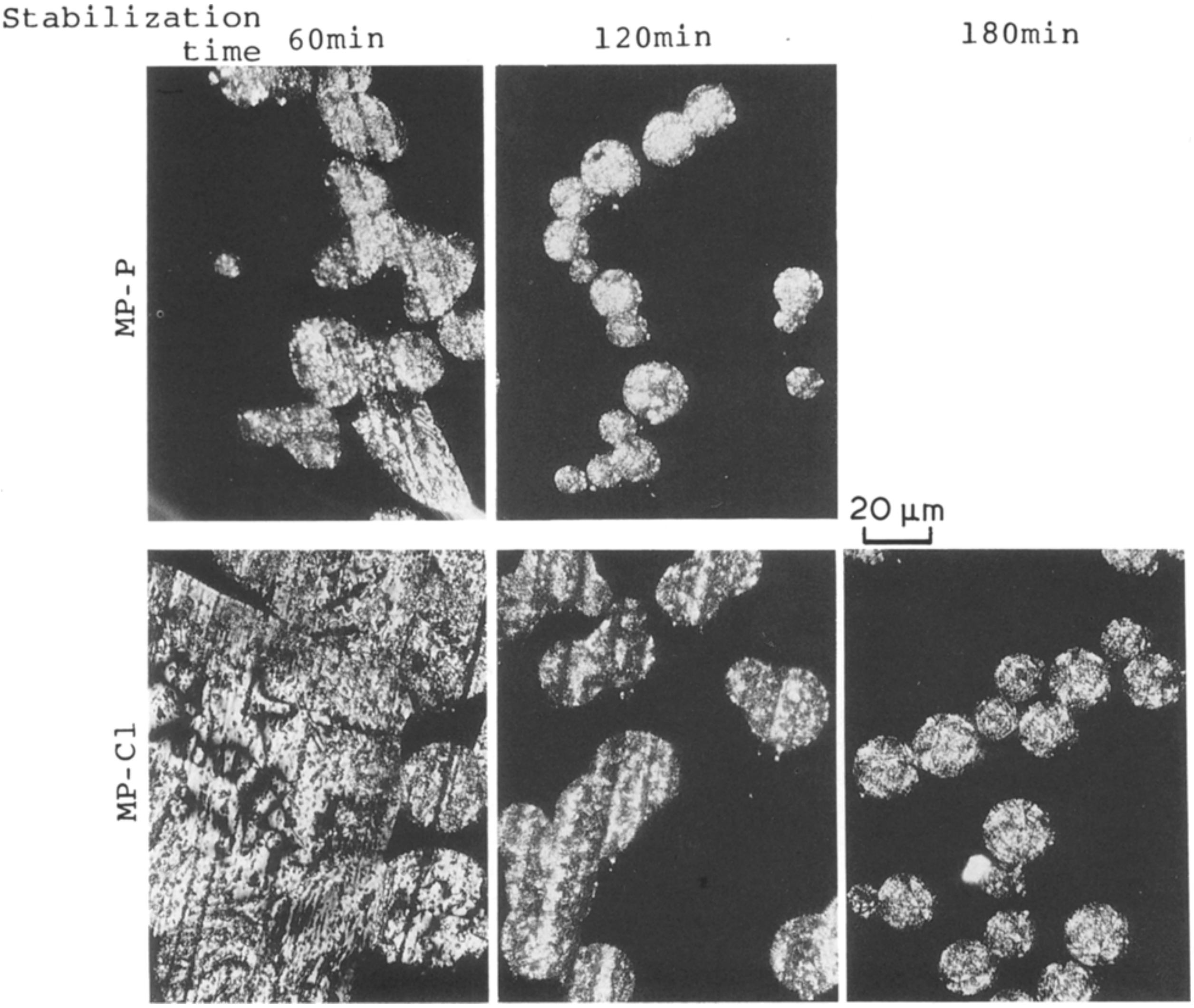

Figure 6 Optical microphotographs of the carbonized fibres. Stabilization conditions: 5° C min^{-1}, 250° C; carbonization conditions: 10° C min^{-1}, 600° C, 1 h.

uptake of the MP-P was always much faster at 270° C, where ca. 5.3 wt % of oxygen was captured until its sufficient stabilization. Similar oxygen uptakes of 5.4 and 5.6 wt % were necessary for the MP-C1 and -C2, respectively. The oxygen uptake of the MP-P was also faster than that of MP-C1 at 280° C although the oxygen content at the stabilization time of 0 min was smaller with the former fibre. The amount of oxygen necessary for sufficient stabilization was 5.3 wt % for both fibres.

Fig. 10 illustrates the FT-IR spectra of the pitch fibres during the stabilization at 270° C for 30 and 60 min. Remarkable changes in the ranges from 2800 to 3100 cm^{-1} and 1100 to 1700 cm^{-1} were observable during the stabilization. The intensities of the bands at 2920 and 1440 cm^{-1} which are both attributed to the aliphatic C–H decreased with all fibres, decrease at the latter band being more marked with the stabilized MP-P fibres. In contrast aromatic C–H appeared to be slightly changed.

The bands at 1700 cm^{-1} (carbonyl C=O vibration) and around 1260 cm^{-1} (phenoxyl group) appeared by the stabilization at 270° C for 30 min.

A weak and broad but distinct band was observed at 1180 cm^{-1} (ascribed to very probably aryl–aryl ether) after the stabilization for 60 min.

Such changes of IR-bands of MP-C1 and specially MP-C2 were much smaller and slower, suggesting their low reactivity for the oxygenative stabilization.

3.4. Morphology in the transverse section of carbonized fibres

Fig. 11 shows a series of scanning electron micrographs of the transverse section of carbonized fibres.

TABLE III Molecular orientations in the transverse section of carbon fibres

Sample / S.T.*	340° C	350° C	360° C	370° C	380° C	390° C
MP-P	Radial	Radial	Radial–Random	Random		
MP-C1	Radial	Radial	Radial	Random		
MP-C2	Radial	Radial	Radial	Radial	Radial	Radial–Random

*Spinning Temperature.

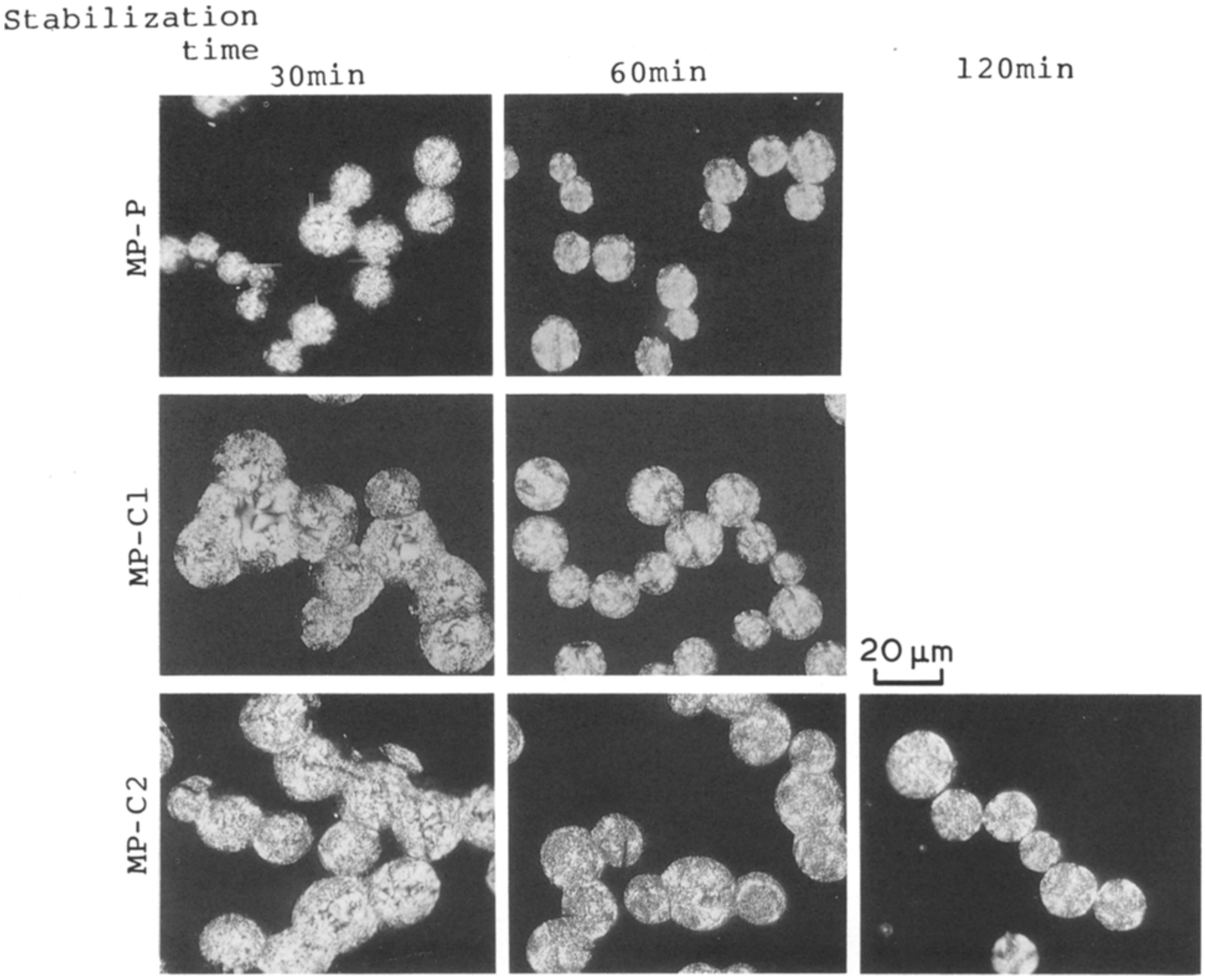

Figure 7 Optical microphotographs of the carbonized fibres. Stabilization conditions: 5° C min^{-1}, 270° C; carbonization conditions: 10° C min^{-1}, 600° C, 1 h.

The observed texture was summarized in Table III. Radial orientation was clearly observable in the transverse section of the MP-P fibre when the spinning temperature was 350° C although no radial crack along with the fibre axis was observable. When the spinning was performed at 360° C, some fibres showed the random texture as shown in Fig. 11, while the other still showed radial texture. Random orientation became dominant when the spinning temperature was 370° C.

Definite radial orientation was observable in the MP-C1 fibres when the spinning temperature was below 360° C. Random morphology started to appear when the spinning temperature was 370° C. Radial texture with radial crack was dominant in the MP-C2 fibre when the spinning temperature was 350° C. Spinning even at 360 and 370° C still provided radial texture in the MP-C2 fibres, although no radial crack was found. The random texture required a spinning at 390° C as shown in Table III. Spinning was very unstable at this temperature because some decomposition started to take place.

4. Discussion

It is very reasonable to assume that the properties, especially spinnability and stabilization reactivity, both of which should be most relevant to the carbon fibre precursor of the mesophase pitch, are strongly dependent upon its chemical structure [20–22]. Such structure is, in turn, subjective to that of the precursor pitch and its structural modification as well as the preparation conditions of the mesophase pitch [9, 10, 20, 21]. Thus, the study of the present approach is of value to design a better fibre precursor.

The three mesophase pitches examined in the present study were derived from the different precursor pitches or pre-treatment, which strongly influence the structure and hence the properties of the respective mesophase pitches. The starting materials of FCC-DO and coal tar possess rather contrast structures, although both are fairly aromatics [23–32]. The former precursor carried a significant amount of alkyl and naphthenic hydrogens and higher molecular weight. The amount of naphthenic hydrogens of coal tar derived pitch depends very much upon the hydrogenative pre-treatment because the hydrogenation of aromatic rings usually requires the catalytic one, although deoxygenation and depolymerization may be possible without the catalyst.

Compared to the mesophase pitches derived from coal tar, FCC-DO derived pitch (MP-P) carried more aliphatic and naphthenic hydrogens in the larger molecules, inheriting the characteristic of its parent precursor. Such structural characteristics provide

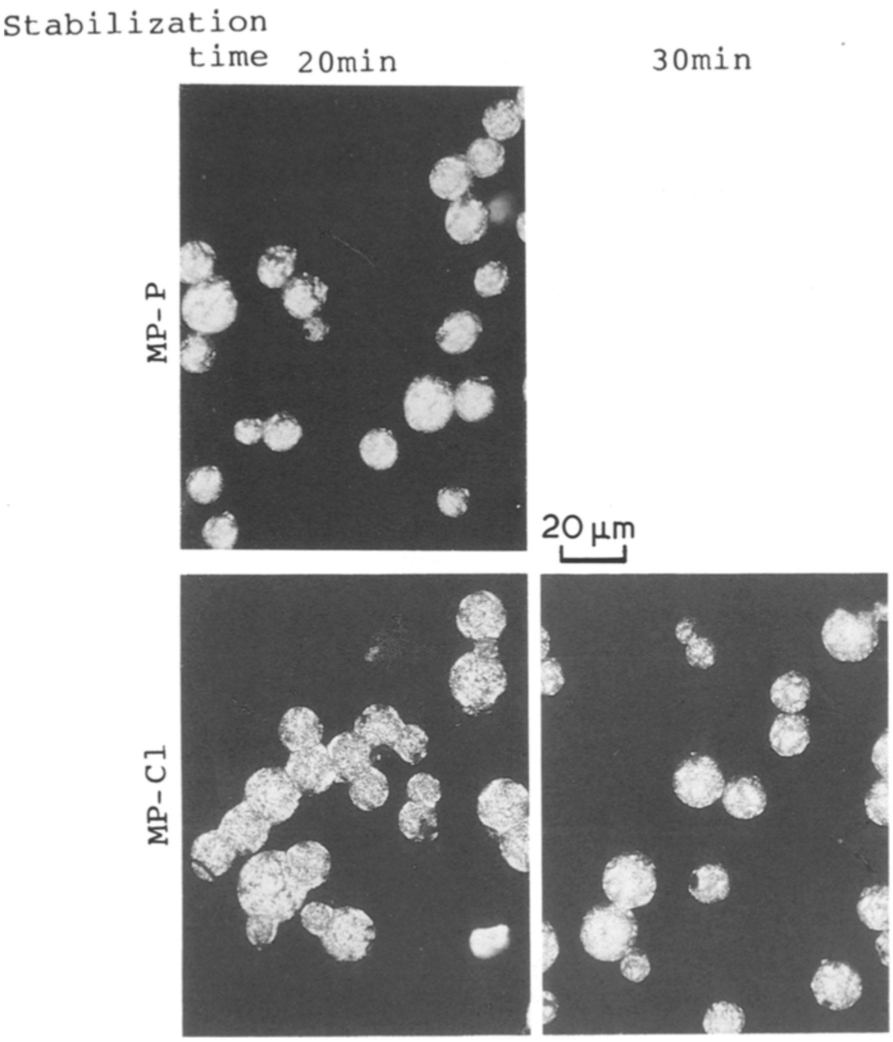

Figure 8 Optical microphotographs of the carbonized fibres. Stabilization conditions: 5° C min^{-1}, 280° C; carbonization conditions: 10° C min^{-1}, 600° C, 1 h.

higher solubility, fusibility, lower softening temperature and smaller dependence of viscosity on temperature in spite of its complete anisotropy. Such properties allow the excellent spinnability of high stability at a lower spinning temperature, where the pitch was very stable. Its low viscosity allows random molecular orientation in the transverse section of the spun fibre by the spinning at the moderate temperatures [33, 34]. Such orientations believed one of the important structural factors for high performance of the pitch based carbon fibre [PBCF].

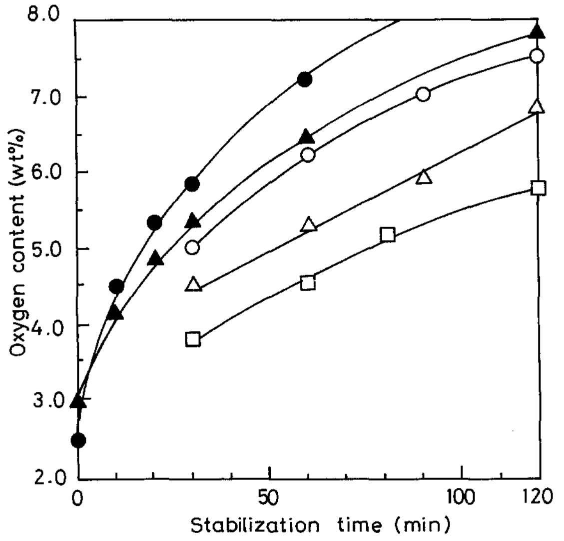

Figure 9 Oxygen uptake of the stabilized fibres. Stabilization conditions – 5° C min^{-1}, 270° C; (○) MP-P, (△) MP-C1, (□) MP-C2; 5° C min^{-1}, 280° C: (●) MP-P, (▲) MP-C1.

The two mesophase pitches both derived from coal tar pitch may earn different evaluation as the precursor for the carbon fibre. MP-C1 from catalytically hydrogenated coal tar [9], is definitely superior to MP-C2 from THQ-treated one [10]. The former pitch carries certainly more aliphatic and naphthenic hydrogens, exhibiting better spinnability and easier control of molecular orientation although their spinnable temperature was almost the same.

The stabilization reactivity is one of the most critical properties of the mesophase pitch as the precursor for carbon fibre, since the stabilization step is slowest and expensive one for its production [18, 19, 22, 23]. The reaction may be achieved by the removal of fusibility, and/or dissolving and solubility between the mesophase pitch components. The stabilization reaction may include the dehydrogenation, oxygenation, oxidative condensation and thermal polymerization through the formation of C–O–C or C–C bonds [23, 35, 36]. Such reactions are deduced definitely from the IR analyses of the stabilized mesophase pitches in the present as well as previous studies [35–38]. Such reactions may start at the naphthenic structure.

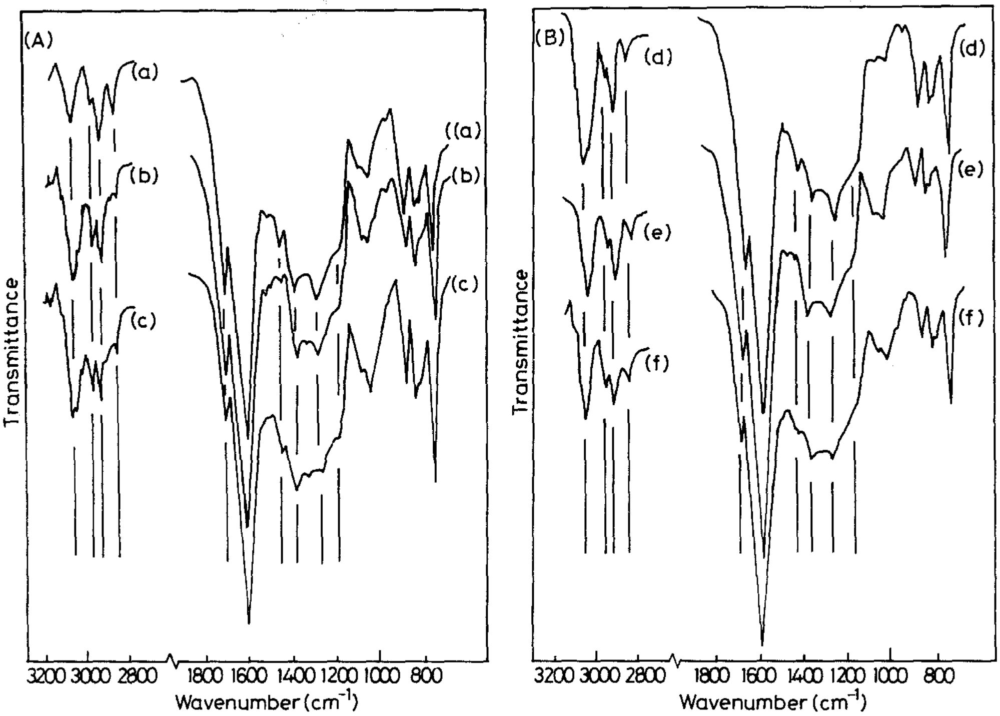

Figure 10 FT-IR spectra of the stabilized fibres. Stabilization conditions (A) 5° C min^{-1}, 270° C, 30 min – (a) MP-P, (b) MP-C1, (c) MP-C2. (B) 5° C min^{-1}, 270° C, 60 min – (d) MP-P, (e) MP-C1, (f) MP-C2.

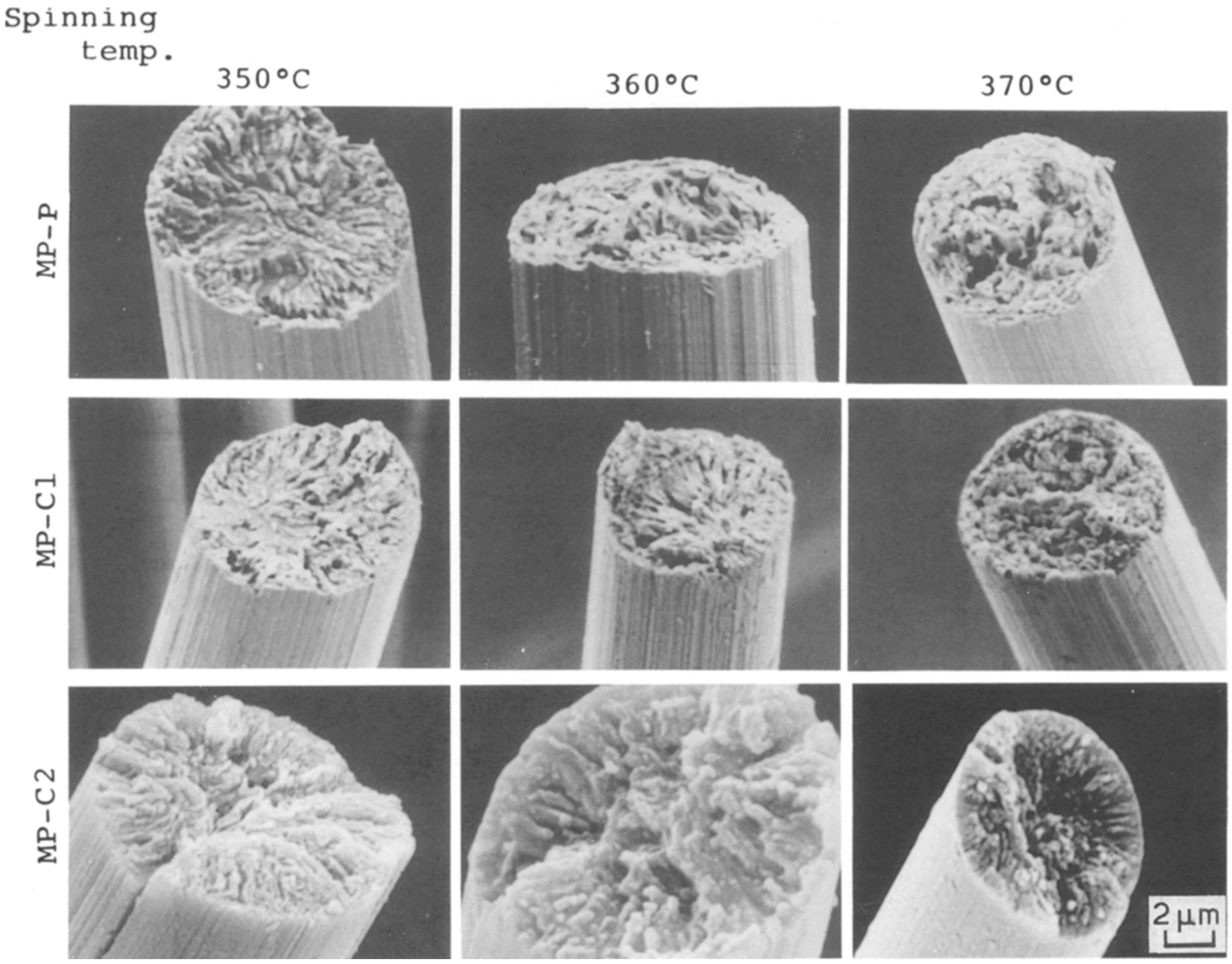

Figure 11 Scanning electron micrographs of the carbonized fibres. Stabilization conditions: 5° C min^{-1}, 270° C, 120 min; carbonization conditions: 10° C min^{-1}, 1300° C, 1 h.

Hence, more sites accelerate the reactions. The sufficient stabilization can be achieved with less extent of reaction when the concerned molecules are larger. MP-P satisfies these requirements to exhibit the highest reactivity. PC-C1 can follow, since it possesses more naphthenic hydrogens than MP-C2.

The least naphthenic hydrogen of the latter pitch certainly inherits the structure of its present pitch treated with THQ. The more extensive hydrogenation and polymerization of coal tar precursor are suggested very favourable to produce the mesophase pitch from coal tar. Blending of larger molecules may be helpful for such a mesophase pitch [17–19, 35].

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