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Control of molecular orientations in mesophase pitch-based carbon fibre by blending PVC pitch

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Coal tar-derived mesophase pitch and its blends with PVC pitch in 5 or 10 wt% were spun at temperatures from 340 to 390° C by applying pressurized nitrogen. The parent mesophase pitch and the blended pitch showed an excellent spinnability at temperatures from 360 to 380° C and from 350 to 380° C, respectively, to give a thin pitch fibre of 10 μm diameter. The transverse texture of the fibres from the parent mesophase pitch showed the radial orientation regardless of a higher spinning temperature of 390° C. In contrast, those from the blended pitches showed random orientation even at the lower spinning temperature of 350° C. The amounts of the blend extruded by spinning at each temperature under $0.2\,\mathrm{kg\,cm^{-2}\,G^{-1}}$ were always larger than those of the mesophase pitch. It is clarified in the present study that blending PVC pitch can realize stable spinning at lower temperatures, where the molecular orientation in the transverse section of the resultant carbon fibre was controlled through decreasing the viscosity of the whole mesophase pitch.

1. Introduction

Mesophase pitch-based carbon fibres (PBCF) have been recognized as a strategic materials for the near future because of its high performance per weight [1, 2]. Although the principles of their preparation have been established [3–6], there still remain some critical problems to be solved to balance their cost/performance for wide applications [7–9]. Difficulty in controlling the texture in the transverse section of the pitch fibre during spinning is one problem to be solved, because stable spinning, high efficiency of stabilization and the texture for the best performance are all important in the spinning of the mesophase pitch, the preparation efficiency of which should also be taken into account.

Several reports have been published which establish that the texture may be controlled by the design of the spinneret [10] and by the spinning temperature [11, 12]. The latter factor may control the rheological properties of the pitch; these were studied by Nazem [13–15] and other authors [16–19] to exhibit the complexity of the Newtonian and non-Newtonian behaviours, which depend in principle upon its chemical structure and anisotropic content. Nevertheless, it is rather difficult to achieve stable spinning of the coal tar-based mesophase pitch and to control of the transverse texture in the resultant carbon fibre at the spinning temperature, because the temperature–viscosity relation of the pitch is often too steep [16–18] for stable spinning.

We have reported some merits of pitch blending to solve the problems, by enhancing the strength and reactivity of the mesophase pitch fibre to produce better handling and quicker stabilization [8, 9, 20–22].

In the present study, attempts were made to control the spinnability, spinning temperature, and molecular orientation in the transverse section of a coal tar-based mesophase pitch by blending PVC pitch at various spinning temperatures. The structure of the carbon fibre thus obtained and some rheological properties of the blended mesophase pitch were studied.

2. Experimental procedure

The mesophase pitch used in the present study was obtained from a QI (Quinoline insoluble)-free coal tar pitch (QIF) after hydrotreatment with

TABLE 1 Some properties of pitches

Sample	Element (wt %)				H/C	f_a†	R_{nus}‡	s.p.§ (°C)	Solubility (wt %)			
	H	C	N	O*					BS	BI-PS	PI-QS	QI
Meso.† pitch	3.9	94.1	1.0	1.0	0.50	0.97	0.55	290	6	41	11	42
PVC Pitch	5.9	94.0	0.1	0	0.75	0.81	0.80	200	69	13	16	2

*By difference.
†Carbon aromaticity.
‡Number of the naphthenic ring in the unit structure.
§Softening point.

BS: benzene soluble.
BI-PS: benzene insoluble but pyridine soluble.
PI-QS: pyridine insoluble but quinoline soluble.
QI: quinoline insoluble.

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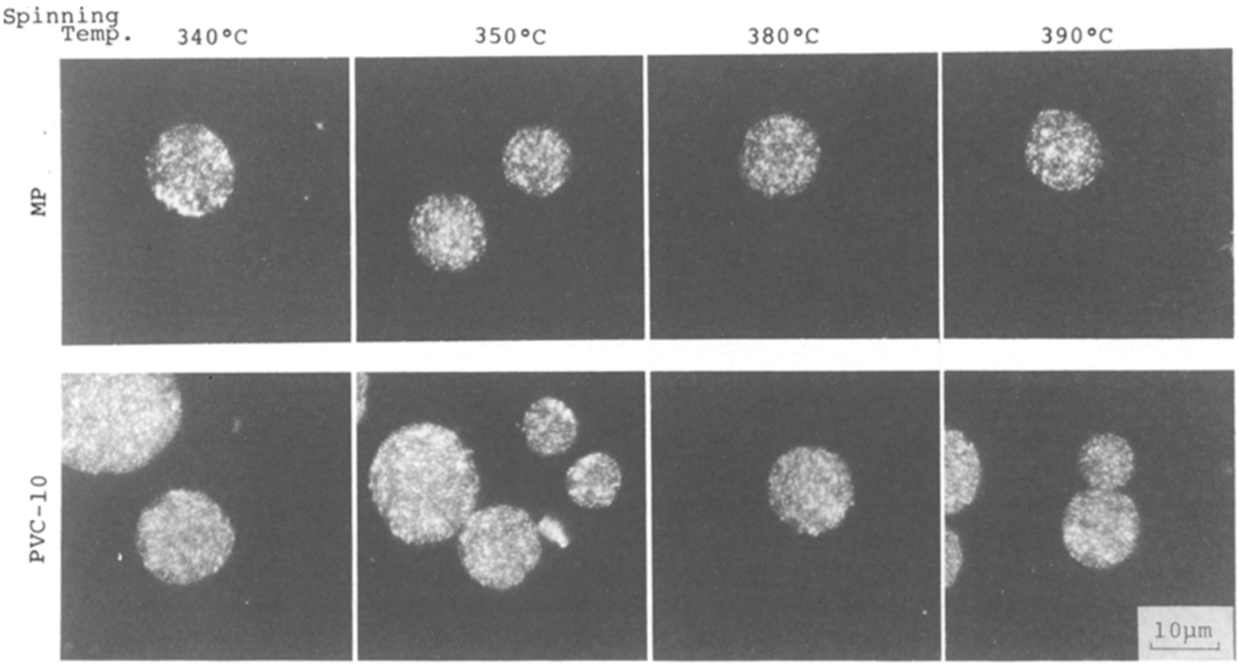

Figure 1 Optical microphotographs of carbon fibres of 10 μm diameter. Stabilization conditions: MP, 5° C min^{-1}, 270° C, 120 min; PVC-10, 5° C min^{-1}, 270° C, 80 min. Carbonization conditions: 10° C min^{-1}, 1300° C, 1 h.

tetrahydroquinoline (THQ). Polyvinyl chloride (PVC) pitch, which was used as a blending polymer, was prepared by the heat-treatment of a commercial grade PVC at 420° C for 2 h at a heating rate of 10° C min^{-1} in a pyrex tube (30 mm diameter, 600 mm long) heated by a vertical electric furnace [8, 20, 21]. Some of their properties are summarized in Table I.

The parent mesophase pitch and 5 or 10 wt % PVC pitch were blended at 360° C for 10 min under vigorous stirring in a pyrex container (30 mm diameter, 300 mm long) heated by a vertical electric furnace at a heating rate of 5° C min^{-1}.

The parent mesophase pitch (MP) and its blends with 5 or 10 wt % PVC pitch (PVC-5 and PVC-10, respectively) were spun into fibres at temperatures from 340 to 390° C from a steel spinneret (nozzle diameter $D = 0.4$ mm, ratio of the length, L, to diameter, D, of the nozzle (L/D) = 1) by applying pressurized nitrogen (0.05 to 0.2 kg cm^{-2} G^{-1}).

MP and blended pitch fibres were stabilized in the atmosphere at 270° C for 120 and 80 min, respectively [20, 21]. The heating rate to the stabilization temperature was 5° C min^{-1} in both cases.

The stabilized fibres were carbonized at 1300° C for 1 h under flowing argon in a horizontal electric furnace. The heating rate to the carbonization temperature was 10° C min^{-1}.

The carbonized fibres were observed under polarized-light (Leitz) and scanning electron (Jeol, JSM-25S) microscopes to define the orientation in the transverse section of the resultant carbon fibres. The orientation was well documented to reflect the orientation in the spun fibre.

The mesophase pitch and the blend were also spun at temperatures ranging from 350 to 380° C under a constant nitrogen pressure of 0.2 kg cm^{-2} G^{-1} to define the amount of the extruded pitch. Spinning was also performed at a constant temperature by varying the nitrogen pressure in order to clarify the rheological behaviour of the pitches. The density of the melted mesophase pitch at the spinning temperature was measured using a Flow Tester (Shimadzu), to estimate the viscosity of both pitches at the spinning temperature according to the Hagen–Poiseulle equation [10].

3. Results

3.1. Spinning of mesophase pitches

Parent mesophase pitch (MP) could be spun at temperatures from 340 to 390° C by applying different nitrogen pressures. At 340° C, MP was so viscous that spinning did not continue longer than 10 sec; thick pitch fibres of 20 to 30 μm in diameter were obtained. Its viscosity is thought to be too high for smooth spinning. At 350° C, MP showed better spinnability to allow continuous spinning for longer than 1 min and give thinner fibres, 10 to 20 μm diameter. MP showed a good spinnability to allow continuous spinning at 360 to 380° C for a much longer time to give a thin pitch fibre of 10 μm diameter. No degasification was found during spinning which may be due to partial decomposition of the mesophase pitch components. The extremely low viscosity of the pitch, and bubbles due to its partial decomposition, prevented stable spinning at 390° C, although the thin pitch fibre, 10 μm diameter, was still spinnable. Thus, the favourable (or sweet) temperature range in terms of stable spinning of MP was concluded experimentally to be from 360 to 380° C.

Blended pitches of PVC-5 and PVC-10 exhibited almost the same spinnability as MP at temperatures from 340 to 390° C except for the excellent spinnability of the blended pitches at 350° C. Thus, the sweet temperature was somewhat extended towards the lower temperature by blending PVC pitch.

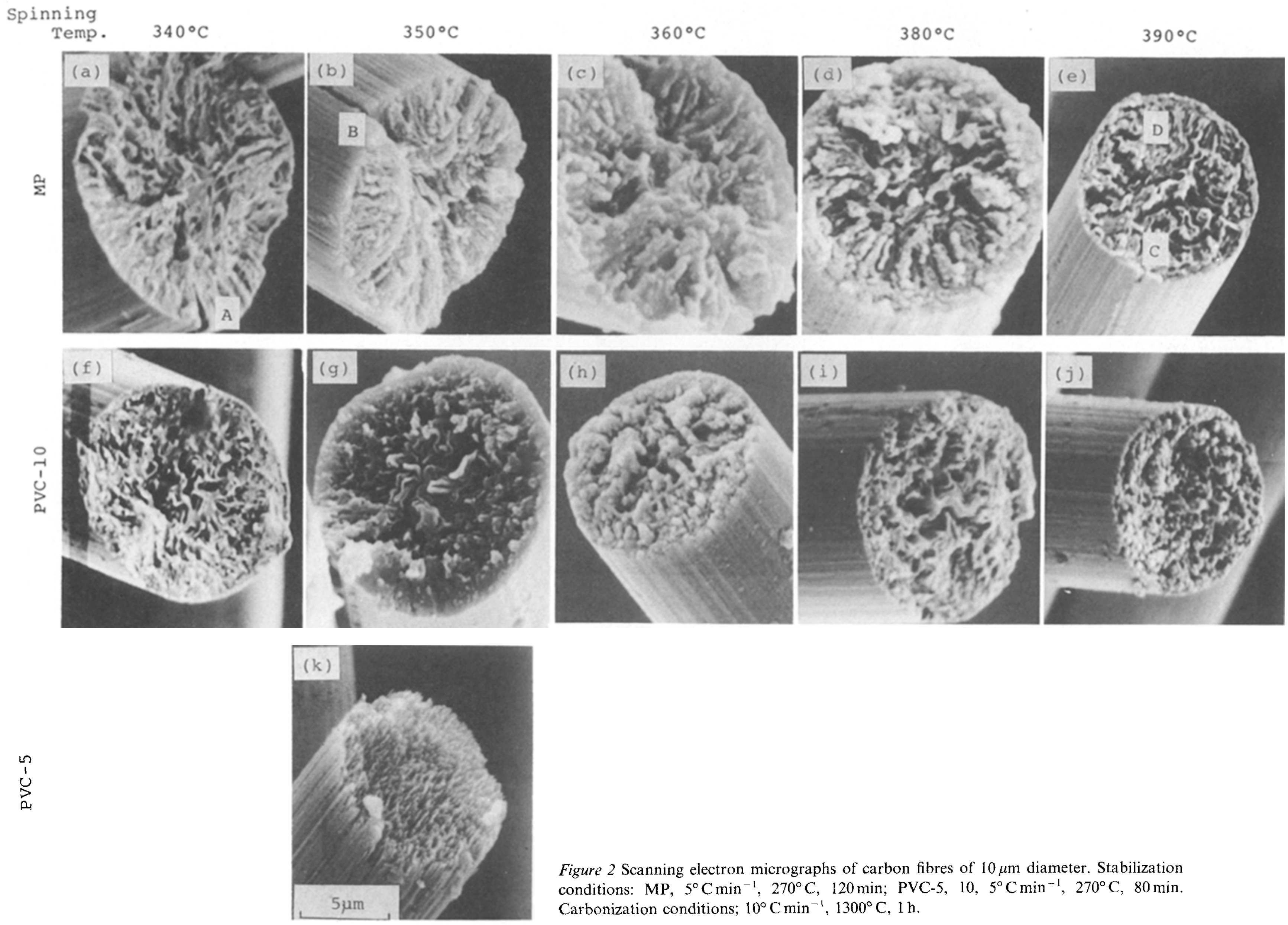

Figure 2 Scanning electron micrographs of carbon fibres of 10 μm diameter. Stabilization conditions: MP, 5° C min^{-1}, 270° C, 120 min; PVC-5, 10, 5° C min^{-1}, 270° C, 80 min. Carbonization conditions; 10° C min^{-1}, 1300° C, 1 h.

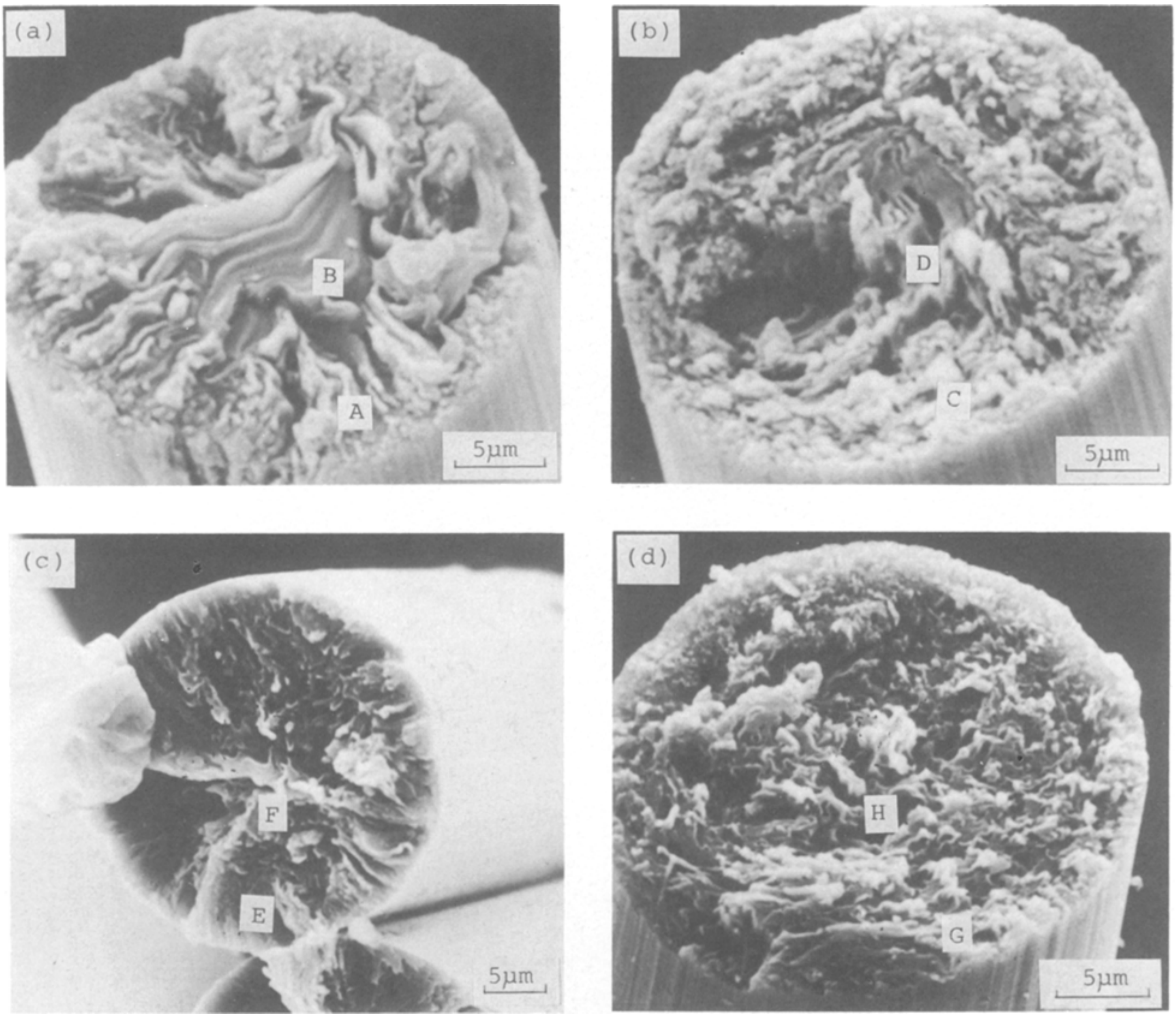

Figure 3 Scanning electron micrographs of carbon fibres of 30 μm diameter. Stabilization conditions: (a) MP, 5° C min^{-1}, 270° C, 120 min; (b) PVC-10, 5° C min^{-1}, 270° C, 80 min; (c) MP, 5° C min^{-1}, 270° C, 180 min; (d) PVC-10, 5° C min^{-1}, 270° C, 180 min. Carbonization conditions: 10° C min^{-1}, 1300° C, 1 h.

3.2. Molecular orientation in the transverse section of carbon fibre

3.2.1. *Optical microphotographs of carbon fibres*

Fig. 1 illustrates the optical microphotographs of carbonized fibres (10 μm diameter). Almost all carbon fibres from MP and PVC-10, regardless of the spinning temperatures, showed the random (fine mosaic) textures in the transverse section under the optical microscope. It is of value to note that PVC-10 carbon fibres appeared to maintain firmly the fine mosaic texture more than the MP carbon fibres during carbonization. The enhanced stabilization reactivity of PVC-10 pitch fibres is suggested as reported previously [20–22].

3.2.2. *Scanning electron micrographs of carbon fibres*

Fig. 2 shows the scanning electron micrographs of 10 μm diameter carbonized fibres. Definite radial orientation was observable in the transverse section of the MP carbon fibre spun at 340° C. Radial cracks appeared (Fig. 2a, A) running along the fibre axis. The MP carbon fibre spun at 350° C again exhibited radial orientation which also carried radial cracks (Fig. 2b, B). MP carbon fibres spun at 360 and 380° C showed radial orientation. However, no radial cracks were found to spread to the surface (Figs 2c and d), although some cracks remaining within a fibre were observable. MP carbon fibre spun at 390° C showed random orientation in some parts (Fig. 2e, C) and radial in other parts (Fig. 2e, D), suggesting a transition temperature from radial to random orientation as reported in the literature [11, 12]. In summary, MP was spinnable at temperatures from 340 to 390° C, although the radial orientation was always dominant in the transverse sections.

Radial orientation was observable in the transverse section of the PVC-10 carbon fibre spun at 340° C (Fig. 2f), although no radial cracks were observable. Spinning at temperatures ranging from 350 to 390° C produced a random structure as shown in Figs 2g to j. The transverse texture of the PVC-5 fibre spun at 350° C showed a finer random texture in the dominant area as shown in Fig. 2k; however, radial orientation, which carried a radial crack along the fibre axis, was also found in some filaments.

Fig. 3 shows the transverse textures of the thick

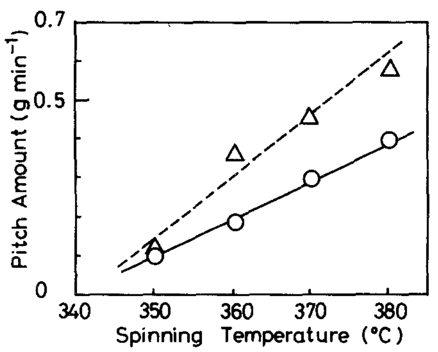

Figure 4 Amount of pitch extruded by spinning at variable temperatures. Applied pressure 0.2 kg cm^{-2} G^{-1}; (○) MP; (△) PVC-10.

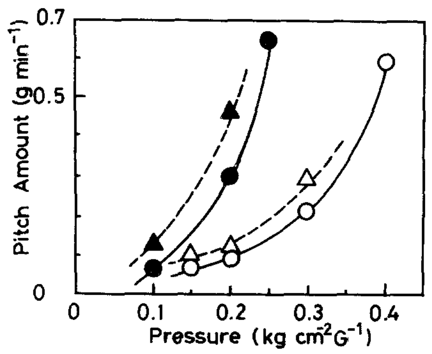

Figure 5 Amount of pitch extruded by spinning at variable nitrogen pressure. Spinning temperature: 350° C (○) MP, (△) PVC-10; 370° C (●) MP, (▲) PVC-10.

fibres (30 μm diameter) spun at 350° C. The skin–core structure was observed because of insufficient stabilization (Figs 3a and b) [21, 22]. As shown in Fig. 3a, MP fibre exhibited a radial orientation in the skin (A) where the molecular orientation was maintained during carbonization. The core (B) which fused during carbonization showed the flow domain texture. In contrast, the random orientation was observable in the skin of the PVC-10 fibre (C), although the core (D) showed the flow domain texture to fuse during carbonization. Transverse textures of the thick fibres (30 μm diameter) which were sufficiently stabilized to the core after 180 min at 270° C are also illustrated in Figs 3c and d. As shown in Fig. 3c, the radial orientation in the transverse section of the MP carbon fibre was observable in all surfaces (E, F). On the other hand, the random orientation was observable on the whole transverse section of the PVC-10 carbon fibre, suggesting that the molecular orientation was controlled not only at the skin (G) by the wall of the spinneret, but also at the core (H) by the extrusion flow.

3.3. Rheological behaviour of the mesophase pitches on spinning

3.3.1. Amount extruded

Fig. 4 shows the amounts of pitch extruded from the nozzle at different temperatures by applying a constant nitrogen pressure of 0.2 kg cm^{-2} G^{-1} for 1 min. Although the extruded amounts of both pitches increased proportionally with the spinning temperature, the amount of the blend (PVC-10) was much larger than that of the parent mesophase pitch (MP), suggesting the lower viscosity of the former pitch at the same temperature.

Fig. 5 illustrates the amounts of extruded pitches at two constant temperatures by applying different nitrogen pressures from 0.1 to 0.4 kg cm^{-2} G^{-1}. The amount of the parent mesophase pitch extruded increased sharply and non-linearly with pressure at both temperatures, indicating its non-Newtonian behaviour. Although PVC-10 pitch also showed similar non-Newtonian behaviour to the parent mesophase pitch, more pitch was extruded than for the parent mesophase pitch under the same nitrogen pressure. Figs 4 and 5 clearly indicate that blending with 10 wt % PVC pitch certainly decreased the viscosity of coal tar-derived mesophase pitch.

As shown in Fig. 6, the amounts extruded were converted into viscosity using to the Hagen–Poiseulle equation (melted density: 1.30 g cm^{-3}). The viscosity of the parent mesophase pitch (MP) and blended pitch (PVC-10) decreased sharply and non-linearly with increasing spinning temperature, ranging from 240 to 50 and from 200 to 40 P, respectively. Although a large temperature dependence of viscosity is suggested with both pitches, the values of PVC-10 were always significantly lower than those of MP at every temperature.

The viscosities of both pitches were linear and decreased steeply with pressure by similar slopes, suggesting their thixotropic features, although the values were always much smaller with PVC-10 as shown in Fig. 6b.

4. Discussion

The stable spinning of mesophase pitch into thin fibres with a desired molecular orientation in their axial direction is a major task in fibre production. Such a spinnability of mesophase pitch should be compatible with simplicity and a high yield in its preparation and high reactivity on stabilization.

Molecular orientation has been reported to be controlled by selection of the spinning temperature [11, 12], *L*/*D* ratio of the spinneret [10] or stirring of the pitch

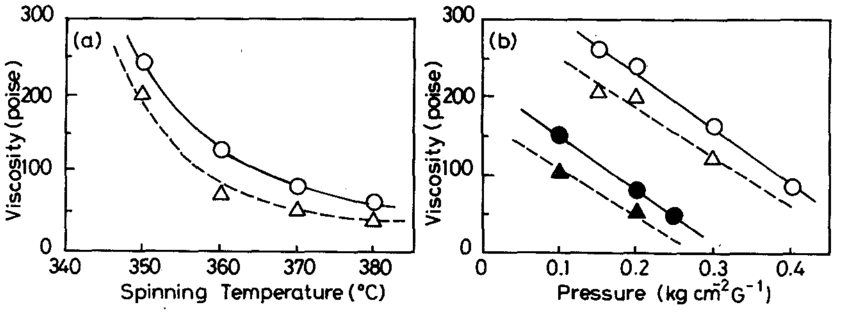

Figure 6 Change of viscosity of pitches at (a) variable temperatures and (b) variable pressures. (a) Applied pressure 0.2 kg cm^{-2} G^{-1}, (○) MP, (△) PVC-10. (b) Spinning temperature: 350° C (○) MP, (△) PVC-10; 370° C (●) MP, (▲) PVC-10.

during spinning [23]. The present study revealed that the blending of PVC-pitch into the coal tar-derived mesophase pitch can improve the spinnability and control the molecular orientation at the same time. Such blending has been reported to enhance the stabilization [20–22]. Hence, blending is a useful technique to modify simply a given mesophase pitch to render it more suitable as a carbon fibre precursor.

Mesophase pitch has been recognized to be a thermotropic liquid crystal, which consists of a number of aromatic molecules different in their molecular structures such as molecular weight, extent of condensation and polymerization, numbers of naphthenic sub-units and alkyl groups [24–36]. Such components cooperate to exist as a liquid crystal as a whole, defining its melting point, viscosity at fusion, strength in the fibre form, and reactivity for the stabilization reaction [24, 25, 34]. Such a recognition of the mesophase pitch suggests some solutions to problems in the production of mesophase pitch-based carbon fibre. In this study, blending PVC pitch solved two problems: spinning stability and control of molecular orientation.

It is understood empirically that spinning at low and high viscosity tends to provide radial and random to onion orientation, respectively [11, 12], although there will be complex interactions between the plane molecules in the mesophase pitch and the wall of the spinneret according to its viscoelastic properties. Such orientation was established in the core as well as in the skin of the thick fibre from the blend. The importance of viscoelasticity in the extensive elongation produced by spinning is suggested by the molecular orientation. A higher spinning temperature decreases the viscosity, favouring random orientation; however, gas evolution by decomposition of the components disturbs the continuous spinning concurrently.

Blending with PVC-pitch decreased the viscosity of the whole mesophase pitch, producing molecular orientation in the favourable random direction and improving the stability of the spinning, because spinning becomes impossible at lower temperatures where no decomposition of the components ever takes place. Some linear polymeric properties of the PVC-pitch may also be related to modification of the molecular orientation of the mesophase pitch [8].

Better additives may also solve other problems in the production of pitch-based carbon fibres.

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