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Blending mesophase pitch to improve its properties as a precursor for carbon fibre

Part 1 *Blending of PVC pitch into coal tar and petroleum-derived mesophase pitches*

ISAO MOCHIDA, HIROSHI TOSHIMA, YOZO KORAI
Research Institute of Industrial Science, Kyushu University 86, Kasuga, Fukuoka 816, Japan
TADAYUKI MATSUMOTO
Toray Glasal Co., Sonoyama, Otsu, Shiga 520, Japan

The blending of mesophase pitch with isotropic PVC pitch was studied to improve their properties as a precursor for carbon fibre. PVC pitch prepared at 420° C which remained almost isotropic was found to be miscible with coal tar-derived mesophase pitch without reducing the anisotropic content and spinnability. The tensile strength of pitch fibres remained unchanged by the blending; however, the reactivity for stabilization was enhanced. The resultant carbon fibres from the blend exhibited slightly higher tensile strength. In contrast, petroleum-derived mesophase pitch failed to dissolve the PVC pitch, leaving a number of isotropic droplets. The structural factors of mesophase pitches with regard to their compatibility with PVC pitches are briefly discussed.

1. Introduction

Pitch-based carbon fibres (PBCFs) have been recognized as a strategic material because of that high strength per weight [1]. The principle of their preparation has been established [2–5] and commercial production of PBCFs has begun [6]. However, industrial production of PBCFs of high quality at a reasonable cost suffers from several serious problems yet to be solved [7, 8]. Among these, the extraordinarily low strength of the pitch fibres before stabilization, and their low reactivity for stabilization are the most critical in increasing the cost of fibre production [8]. Both problems originate essentially from the chemical structure of the components in the pitch–fibre precursors. The major constituents of the mesophase pitch to be spun and stabilized are diskotic planar aromatic hydrocarbons of limited molecular size (their average molecular weight is around 1500), being far away from linear polymers [9]. Such structures are very stable at the temperature used for the stabilization reaction, which is limited by their softening point, and fail to provide polymer effects of associative molecular interactions along the fibre axis, which are the origin of the tensile strength of the pitch fibre.

In the present study, we try to solve the problems by blending mesophase pitches (coal tar and petroleum-derived) with the PVC-derived pitches, which is expected to maintain some polymeric properties, less aromaticity and high spinnability [2]. It has been reported that mesophase pitch can be blended with some isotropic pitches within a certain mixing region without degrading its liquid crystal nature, when both pitches are compatible [9, 10]. Optical anisotropy, spinnability, tensile strength and stabilization reactivity of blended pitch fibres, as well as some properties of resultant carbon fibre, are studied in the present study.

2. Experimental details

The two kinds of mesophase pitches used in the present study were coal tar-derived mesophase pitch (MP–A) and petroleum-derived (MP–B) ones. Their analyses and some properties are summarized in Table I. PVC pitches were used as blending polymers in the present study. Their preparative conditions and some properties are summarized in Tables I and II.

The mesophase pitches and PVC pitches were blended in a glass container (30 mm diameter, 200 mm long) at 360° C for 10 min at a heating rate of 5° C min^{-1} in a vertical electric furnace before spinning them at the same temperature. The blended pitches were examined under an optical microscope after mounting it in the resin and conventional polishing to measure their mutual solubility from the optical texture.

The blended pitches were spun into fibres using a spinneret (0.4 mm diameter) with a steel container (amount of pitch $\sim$ 10 g) by applying a nitrogen pressure (0.5 kg cm^{-2}). The spinning speed was 400 m min^{-1}.

The spun fibres were stabilized by oxidation at 250° C for 2 to 3 h in the atmosphere. The heating rate was 5° C min^{-1}.

The oxidized pitch fibres were further carbonized into the corresponding carbon fibres at 1300° C for 1 h. The heating rate was 10° C min^{-1}.

The tensile strengths of pitch fibres and carbon fibres were measured according to JIS R-7601-1986,

TABLE I Elemental analyses and softening points of used pitches

Sample	Pitch* yield (%)	Element (wt %)				f_a†	THFS‡ (wt %)	QI§	S.P.¶ (°C)
		H	C	N	H/C				
PVCP-1	24	6.9	92.8	0	0.90	0.72	100	–	170
PVCP-2	19	5.9	93.8	0	0.76	0.75	95	–	200
PVCP-6	12	5.1	94.7	0	0.66	0.80	76	2	205
PVCP-7	11	5.5	94.2	0	0.71	0.77	53	–	205
MP-A	–	3.9	94.1	1.0	0.50	0.97	34	42	290
MP-B	–	4.6	93.8	0.1	0.59	0.87	45	35	290

*Based on PVC.
†Carbon aromaticity.
‡THF soluble.
§Quinoline insoluble.
¶Softening point.

using the single fibre method, with a tensile 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 micrograph.

3. Results

3.1. Characterization of pitches

Fig. 1 shows micrographs of mesophase and PVC pitches. The MP-A and MP-B exhibited anisotropy in their major areas, although the former contained some isotropic droplets while the latter was completely anisotropic. Although both mesophase pitches exhibited the same softening temperature of 290° C, MP-A certainly showed a larger carbon aromaticity (f_a), more quinoline-insoluble (QI) and lower atomic H/C ratio than MP-B, as shown in Table I, suggesting it has a more condensed aromatic structure.

The properties of PVC pitches depended very much on the preparation conditions. As shown in Fig. 1, PVCP-1 and 2 prepared at 360° C were completely isotropic, while PVCP-6 and 7 prepared at 420 and 450° C, respectively, contained a number of large and small anisotropic spheres although their QI contents were very low, as summarized in Table I. The severity of the preparation conditions increased their softening temperature from 170 to 205° C and aromaticity from 0.72 to 0.80. The atomic H/C ratios showed a reverse trend.

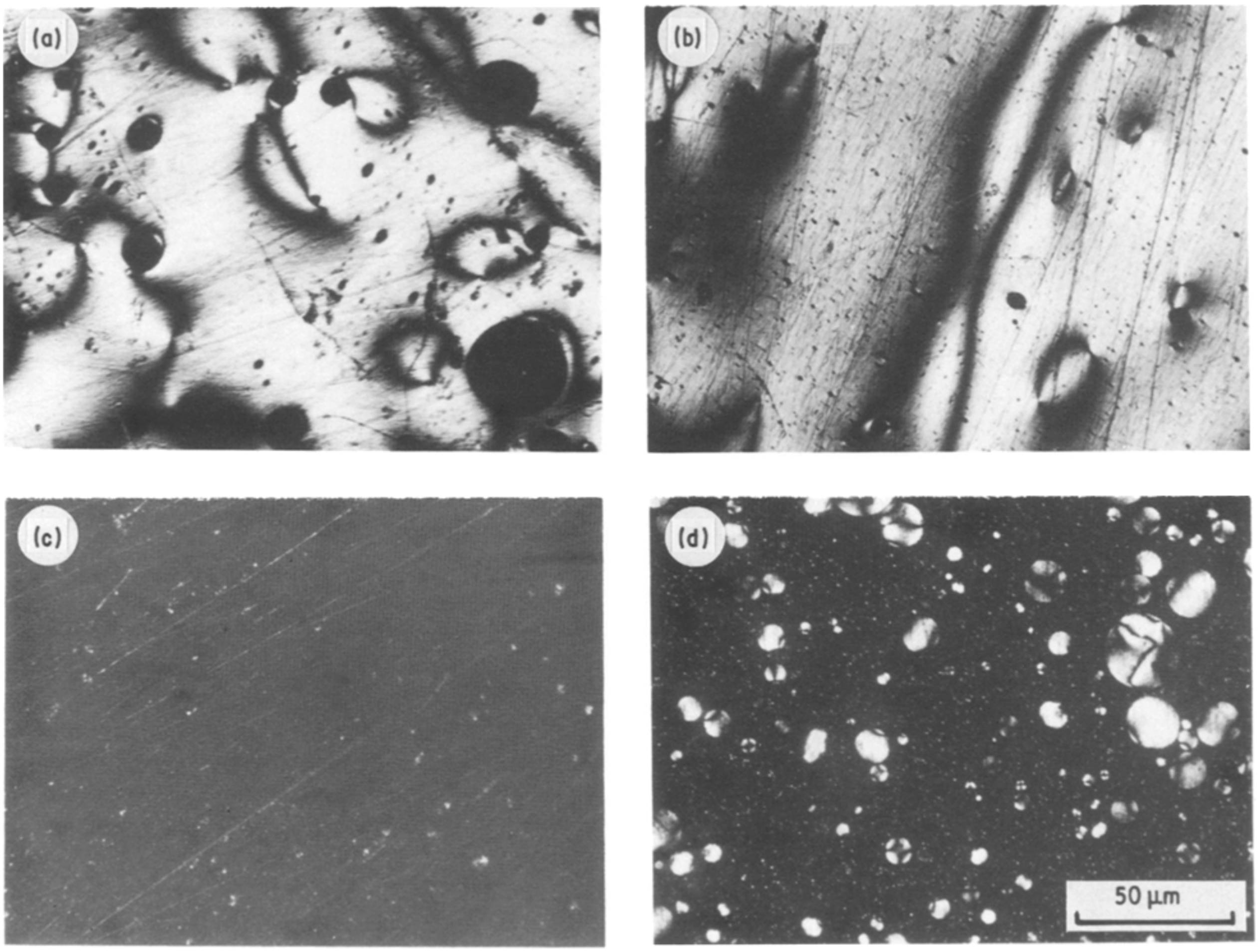


Figure 1 Optical photomicrographs of mesophase and PVC pitches. (a) MP-A, (b) MP-B, (c) PVCP-1, (d) PVCP-6.

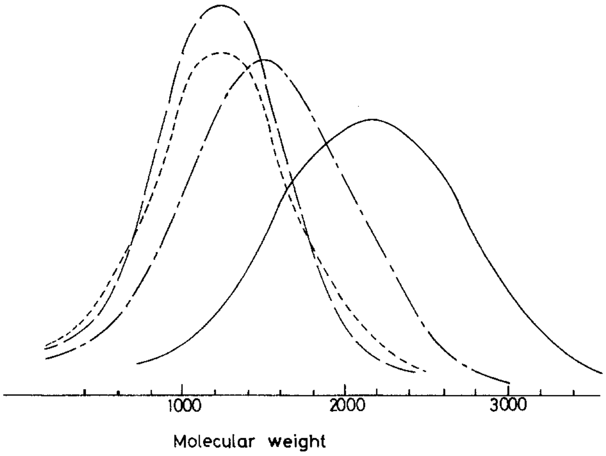


Figure 2 Gel permeation chromatograms of THF solubles of PVC pitches (molecular weight was corrected to standard polystyrene). (——) PVCP-1, (— —) PVCP-6, (- - -) PVCP-2, (– – –) PVCP-7.

Fig. 2 shows the GPC profiles of THF soluble fractions in PVC pitches, all of which consisted principally of the fractions. The peak of molecular weight distribution of the fraction shifted from 2300 to 1200 according to the severity of the preparation conditions, suggesting cleavage of the PVC polymeric chains accompanied by aromatization, although the molecular weight of the THF insoluble fraction should be larger when the preparative conditions were severer.

3.2. Blending of PVC pitches to MP-A

TABLE II Heat-treatment conditions of PVC

PVC pitch	Heating rate (°C min^{-1})	HTT (°C)	Hold time (h)
1	10	360	0.5
2	10	360	24
6	10	420	2
7	15	450	0.25

Figs 3 and 4 show photomicrographs of blends of MP-A with PVCP-1 and 6, respectively. Blending of PVCP-1 gave regions of isotropic matrix, which contained a large number of spheres, leaving the bulk mesophase area of MP-A almost unmodified, as shown in Fig. 3. The addition of more PVCP-1 increased the area of isotropic matrix, their poor mutual solubility being suggested. PVCP-2 behaved very similarly to PVCP-1.

In contrast, PVCP-6 did not change the feature of MP-A as shown in Fig. 4 even when 30% was blended. The size and number of isotropic droplets which were observed in MP-A remained essentially unchanged. The molecules in the isotropic PVCP-6 should be accommodated among the layers of mesophase-constituent molecules of MP-A.

Fig. 5 summarizes the change of anisotropic content of MP-A by blending the PVC pitches. As mentioned above, the anisotropic content of 95% found in the starting MP-A was maintained regardless of the amount of blended PVCP-6 when the amount of blended PVCP-6 was below 30% addition. The addition of PVCP-7 decreased the anisotropic content proportionally to its blended content, although addition of 30% provided 15% isotropic content, i.e. a half of PVCP-7 being assumed to be accommodated in the mesophase. The blending of PVCP-1 and 2 decreased the anisotropic content more sharply. The addition of 30% provided 55 and 45% of isotropic contents, respectively, suggesting that these pitches should dissolve anisotropic mesophase components to show isotropy when the pitch was blended.

Fig. 6 shows the softening temperature of blended pitches. The temperature decreased markedly from 290° C of MP-A on blending. The PVC pitch produced

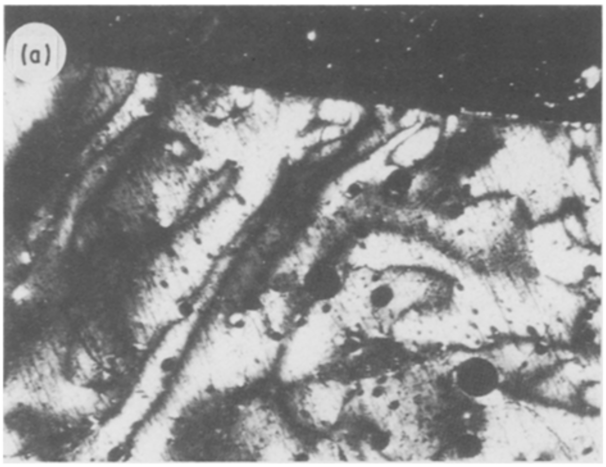
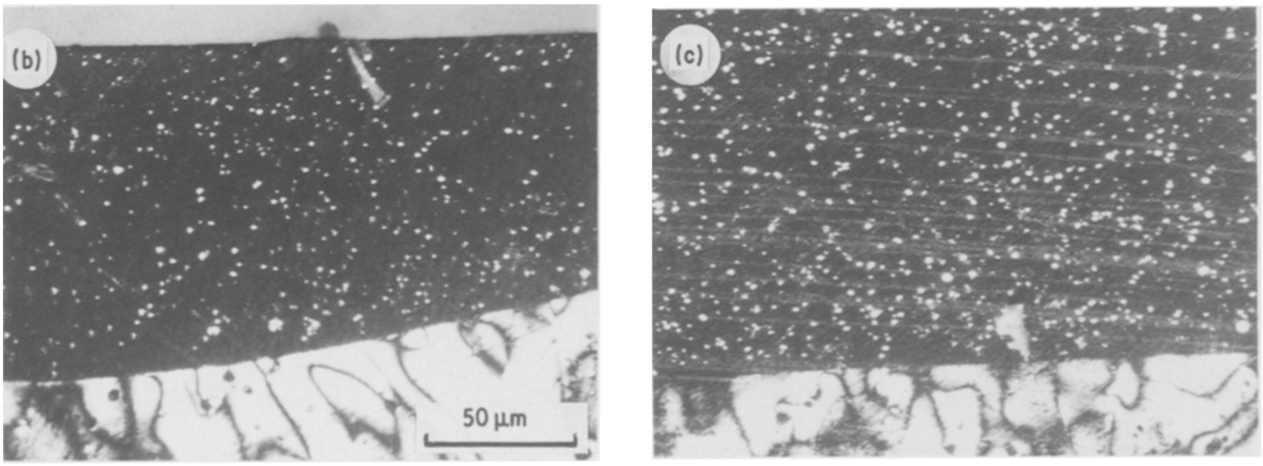
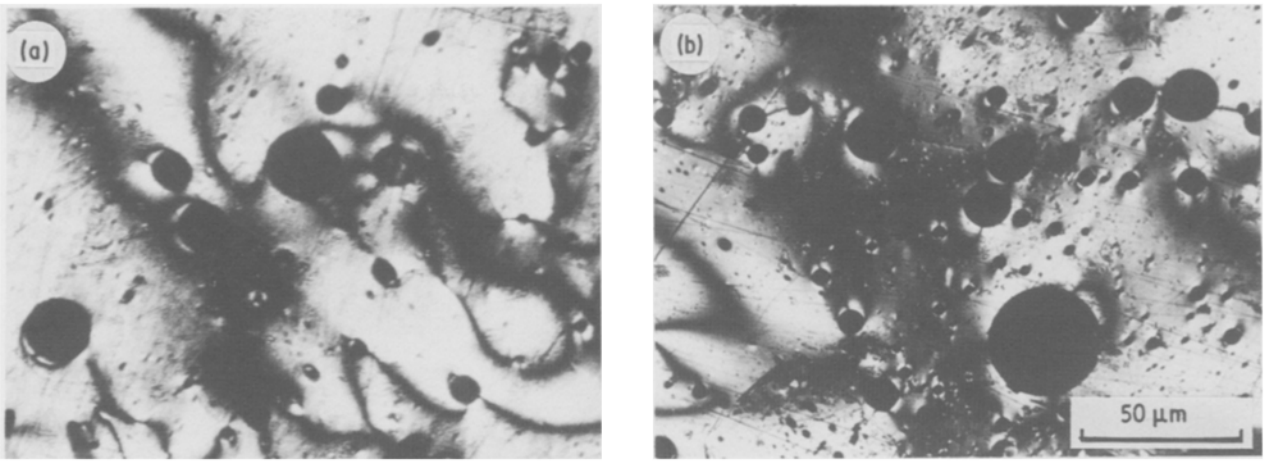


Figure 3 Optical photomicrographs of blends of MP-A with PVCP-1. Amount of blended PVCP-1: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %.





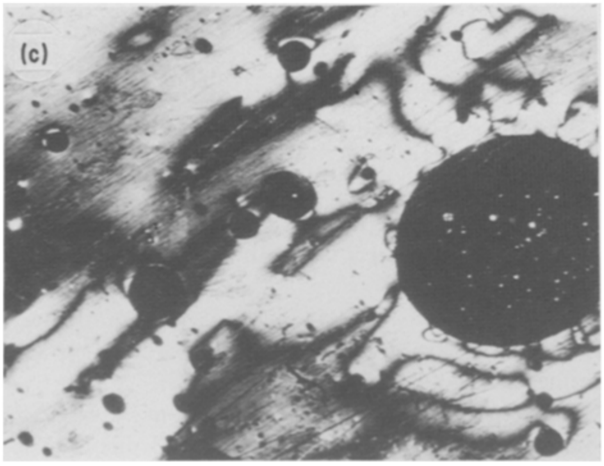


Figure 4 Optical photomicrographs of blends of MP-A with PVCP-6. Amount of blended PVCP-6: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %.

under severe conditions was more effective in decreasing the softening temperature. Addition of 10% PVCP-6 decreased the temperature to 273° C, no decrease being achieved by blending further pitch. The best solubility of the pitch and the lowest molecular weight of its THFS fraction may reduce the softening temperature of the blend.

3.3. Blending of PVC pitches to MP-B

Fig. 7 shows the photomicrographs of MP-B blended with the PVCP-6. In contrast to MP-A, blending with PVCP-6 increased the isotropic areas, providing some isotropic droplets and a matrix containing spheres. Fig. 8 shows the change of anisotropic content on blending. PVCP-3 (prepared at 420° C for 30 min) increased the isotropic content more sharply than PVCP-6. Both pitches can dissolve mesophase components of MP-B to show an isotropic appearance, higher solubility of the molecules in MP-B being suggested.

3.4. Spinning and oxidation of pitch fibres from MP-A and its blends

MP-A and its blends with 10 and 20% PVCP-6 were spun smoothly at 345 to 370° C for several minutes without any filament breakage, indicating good spinnability.

Fig. 9 shows the photomicrographs of polished surfaces of pitch fibres prepared from MP-A and its blends with PVCP-6 (20%). Anisotropic flow textures run parallel to the fibre axis as shown in Fig. 9, while random orientation was observed in the surface sectioned perpendicular to the fibre axis. The pitch fibres spun from the blended pitches showed some flexibility when they were shaken by hand, being different from the very stiff fibres obtained from MP-A alone. However, the tensile strength and the Young's modulus of the former were essentially the same as those of the latter, as shown in Table III although accurate

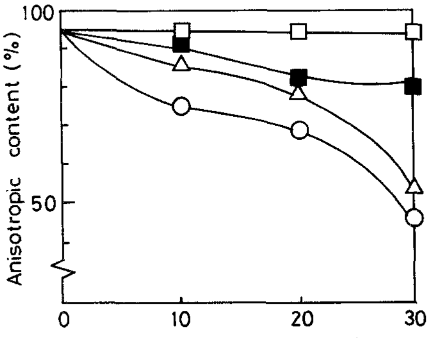


Figure 5 Change of anisotropic content of MP-A by blending of PVC pitches. (○) PVCP-1, (□) PVCP-6, (△) PVCP-2, (■) PVCP-7.

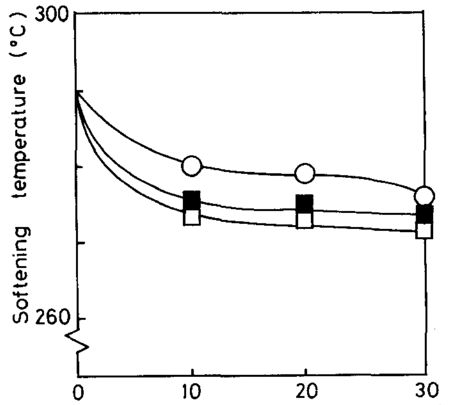


Figure 6 Change of softening temperature by blending of PVC pitches. (○) PVCP-1, (■) PVCP-7, (□) PVCP-6.

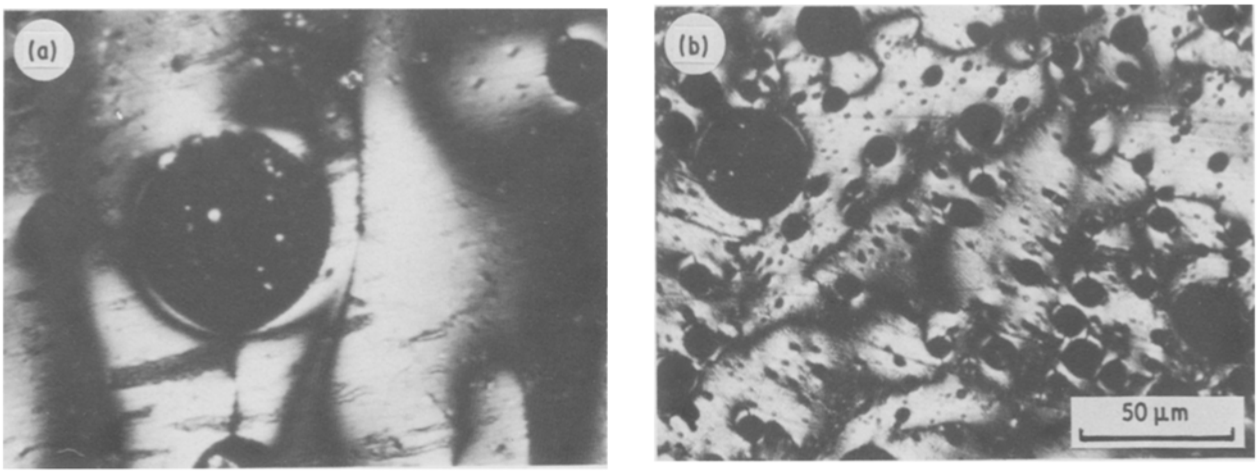


Figure 7 Optical photomicrographs of blends of MP-B with PVCP-6. Amount of blended PVCP-6: (a) 10 wt %, (b) 20 wt %.

measurement was very difficult because of the very low strength of the pitch fibres.

The microanalyses of pitch fibres oxidized at 250° C for 2 h are included in Table IV. The oxidation increased the oxygen content and decreased slightly the atomic H/C ratio as shown in Table IV. Fig. 10 compares the infrared spectra of the pitch and oxidized pitch fibres. The oxidation produced the absorbance bands at 1700 and 1450 cm^{-1} which were identified as calbonyl C=O and aromatic C=C stretching vibrations, respectively [11, 12]. Such increases of oxygen content and intensities of the bands were more marked with the fibres from the blend, despite the same oxidation conditions. These results may suggest the higher reactivity of the blend with oxidation at 250° C.

3.5. Carbonization of oxidized fibres

Photomicrographs of the carbon fibres prepared from the oxidized pitch fibres are shown in Fig. 11, where the carbonization was performed at 1300° C, for 1 h at a heating rate of 10° C min^{-1}. The fibres from MP-A alone cohered through their partial fusion when the oxidation was performed for 2 h at 250° C. It was found that 3 h was required to achieve sufficient infusibility before the carbonization.

In contrast, the fibres from the blend showed no fusion during carbonization by oxidation for 2 h at 250° C. The anisotropy in both fibres became more distinct and no skin–core structure was observed, indicating that the oxidation was just sufficient. The pitch infusibility does not affect the uniaxial orientation of aromatic planes in the fibre during carbonization.

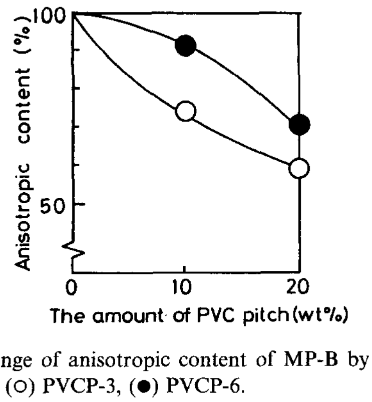


Figure 8 Change of anisotropic content of MP-B by blending of PVC pitches. (○) PVCP-3, (●) PVCP-6.

Fig. 12 shows scanning electron micrographs of carbon fibres prepared from MP-A and its blend after similar oxidations except for a longer oxidation with the former. Both fibres showed similar profiles of excellent density with least voids and random orientation in the fractured surface, and a smooth surface parallel to the fibre axis.

The tensile properties of the carbon fibres (carbonized at 2500° C) are summarized in Table V. The dispersion of the observed values was fairly large; nevertheless, the blends can be concluded to give carbon fibres of slightly better strength than the mesophase pitch alone.

4. Discussion

Extensive studies on the preparation of pitch-based carbon fibres have revealed the problems of its commercial production as described in Section 1. Some of the problems are found to be solved by modifying the nature of the mesophase pitch as the precursor of the

TABLE III Mechanical properties of pitch fibres

Sample	Tensile strength (kg mm^{-2})	Young's modulus (10^3 kg mm^{-2})
MP-A	4	0.3
MP-A/PVCP-6 (10 wt %)	4	0.4
MP-A/PVCP-6 (20 wt %)	4	0.4

TABLE IV Elemental analyses of pitch fibres before and after oxidation

Sample	Element (wt %)				
	H	C	N	O[†]	H/C
MP-A	3.8	94.1	1.1	0.9	0.49
Ox. MP-A[*]	3.4	90.8	1.0	4.6	0.45
MP-A/PVCP-6 (20 wt %)	4.0	93.9	0.8	1.1	0.52
Ox. MP-A/PVCP-6 (20 wt %)	3.6	90.6	0.8	4.9	0.48

[*] Oxidized pitch fibre.
[†] By difference.

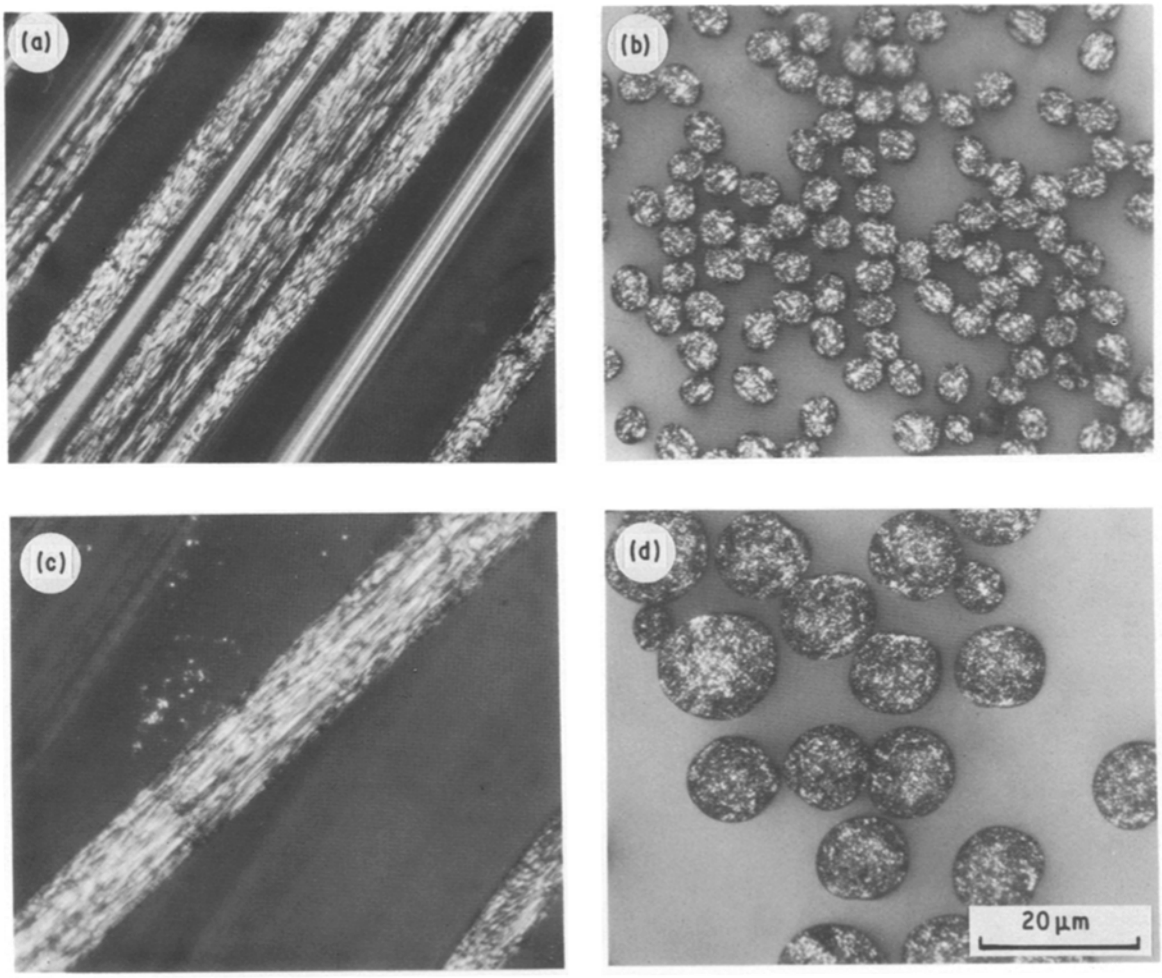


Figure 9 Optical photomicrographs of the pitch fibres from (a), (b) MP-A, and (c), (d) its blends with PVCP-6 (20 wt %).

fibre, through blending. As the mesophase pitch consisted of very complex molecular mixtures, blending, within certain limitations, can improve a particular nature without deteriorating the favourable natures as suggested from a pragmatic understanding of its thermotropic behaviour in relation to its compositional distribution [9, 13]. The blending reagents are strictly required to have a structure compatible with the mesophase components.

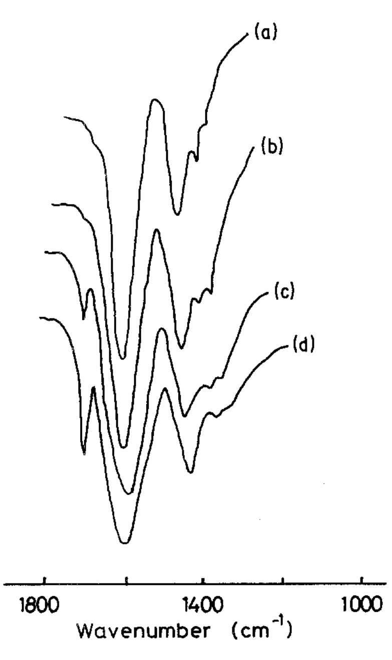


Figure 10 Infrared spectra of pitch and oxidized pitch fibres. (a) MP-A, (b) blended MP-A (PVCP-6 20 wt %), (c) oxidized MP-A (5° C min^{-1}, 250° C, 2 h), (d) oxidized blended MP-A (5° C min^{-1}, 250° C, 2 h).

Blending of PVC pitch prepared under rather severe heat-treatment conditions was found, in the present study, to allow good spinnability of the coal tar-derived mesophase pitch without any decrease of optical anisotropy. Improvement of the tensile properties of pitch fibres expected by blending was not observed in the present study, although the fibres certainly appeared more flexible than the fibres without blending. Unfortunately, the characteristics of PVC pitch as a polymer are not sufficient to improve the tensile strength of blended pitch fibres. More linear linkages between the aromatic nuclei are supposed to be necessary.

TABLE V Mechanical properties of carbon fibres

Sample	Tensile strength (distribution) (kg mm^{-2})	Young's modulus (distribution) (10^3 kg mm^{-2})
MP-A	190 (139–240)	48.8 (43.0–54.6)
MP-A/PVCP-6 (10 wt %)	235 (189–281)	46.3 (41.8–50.7)
MP-A/PVCP-6 (20 wt %)	200 (157–243)	61.7 (43.0–80.5)

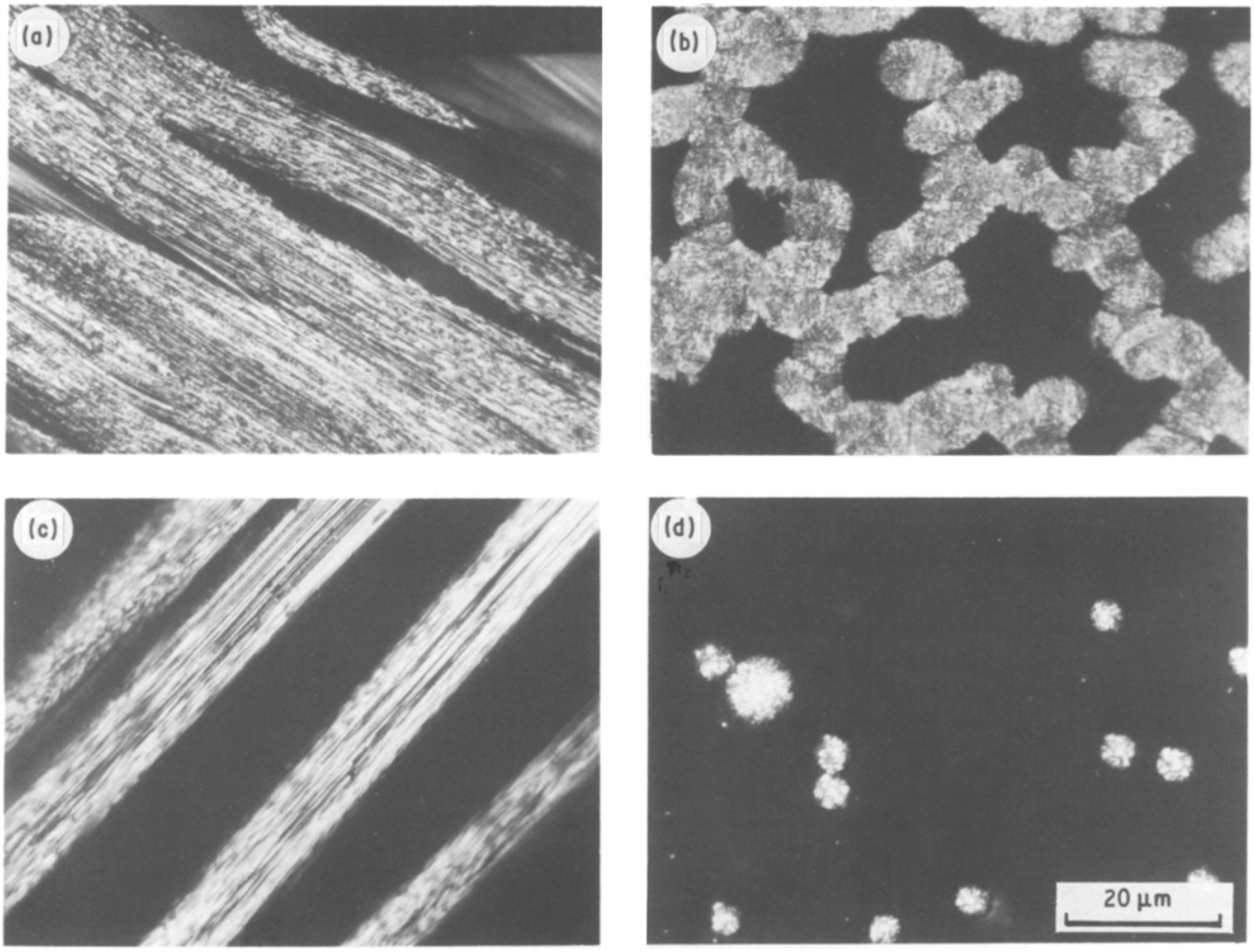


Figure 11 Optical photomicrographs of carbon fibres from (a), (b) MP-A, and (c), (d) its blends with PVCP-6 (20 wt %). Oxidation conditions: 5° C min^{-1}, 250° C, 2 h. Carbonization conditions: 10° C min^{-1}, 1300° C, 1 h.

It should be noted that the blending enhanced the oxidation reactivity, shortening the time for the stabilization. PVC pitch can trigger the oxidation of whole blended fibres because its blending by 20% enhanced the stabilization of the whole pitch, although an understanding of the stabilization reaction is far from complete [11, 12, 14–16].

Such favourable influences of PVC pitch blend are correlated to its structure. According to the present analyses and the literature [2], components of PVCP-6 are assumed to have a representative structure as shown in Fig. 13. Longer chains of rather small aromatic nuclei and rich naphthenic hydrogens may cause the initiation of oxidation easily by modifying the mesophase pitch favourable as a precursor.

Compatibility of mesophase pitches and PVC pitches appears to depend very much on their structure. Low aromaticity of PVC pitches which is due to mild heat-

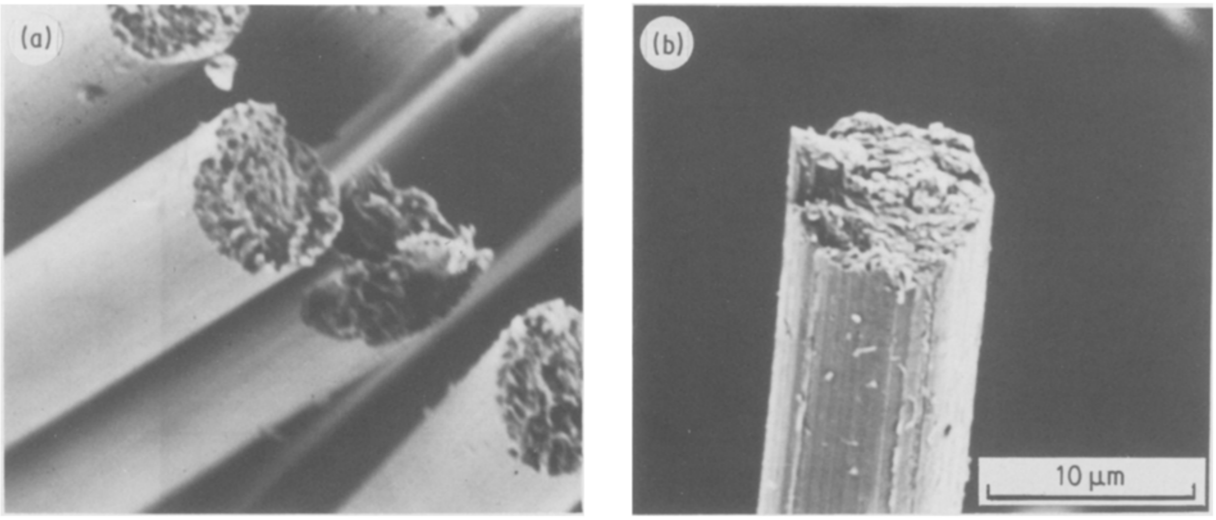


Figure 12 Scanning electron micrographs of carbon fibres from (a) MP-A, and (b) its blends with PVCP-6 (20 wt %). Oxidation conditions: MP-A, 5° C min^{-1}, 250° C, 3 h, blended pitch A, 5° C min^{-1}, 250° C, 2 h. Carbonization conditions: 10° C min^{-1}, 1300° C, 1 h.

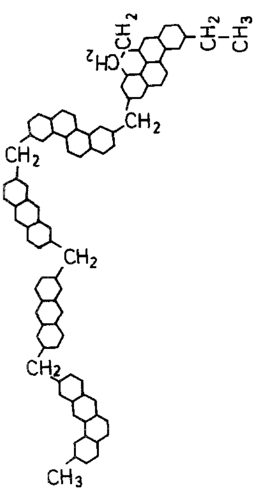


Figure 13 Schematic model structure of PVCP-6.

treatment appears unfavourable for its compatibility in the mesophase pitch. Because PVC pitches of low aromaticity had a larger molecular weight, excess original methylene bonds may remain in the pitch, causing lower compatibility. Petroleum-derived mesophase pitch is definitely inferior to coal tar-derived mesophase pitch in its compatibility with the PVC pitch subjected to severe heat-treatment to give isotropic droplets, suggesting the importance of aromaticity of the mesophase components in accommodating the less aromatic molecules in their anisotropic layer structure.

References

1. S. OTANI, K. OKUDA and H. S. MATSUDA, "Carbon Fibre" (1983) p. 231.
2. S. OTANI, *Carbon* **3** (1965) 31.
3. *Idem, Molec. Cryst. Liq. Cryst.* **63** (1981) 249.
4. S. CHWASTIAK, UK Patent Application GB 2005298 A (1979).
5. D. RIGGS and R. J. DIEFENDORF, US Patent 4208267 (1980).
6. S. OTANI, K. OKUDA and H. S. MATSUDA, "Carbon Fibre" (1983) p. 246.
7. S. OTANI, K. OKUDA and H. S. MATSUDA, *ibid.* p. 139.
8. S. OTANI and A. OYA, "Carbon Fibre Nyumon" (1983) p. 71.
9. I. MOCHIDA and Y. KORAI, *J. Fuel Soc. Jpn* **64** (1985) 802.
10. I. MOCHIDA, Y. SONE, Y. D. PARK and Y. KORAI, *J. Mater. Sci.* **20** (1985) 3177.
11. I. MOCHIDA and Y. KORAI, Japan Carbon Society, 11th Annual Meeting, Kyoto, Extended Abstracts (1984) p. 138.
12. T. KASU and H. MARSH, Japan Carbon Society, 12th Annual Meeting, Tokyo, Extended Abstracts (1985) p. 60.
13. Y. KORAI and I. MOCHIDA, *Carbon* **23** (1985) 97.
14. W. C. STEVENS and R. J. DIEFENDORF, Proceedings of 4th International Conference, Baden-Baden, July (1986) p. 37.
15. J. L. WHITE and P. M. SHEAFFEER, 17th Biennial Conference on Carbon, Lexington, Kentucky, Extended Abstracts (1985) p. 161.
16. Y. KORAI and I. MOCHIDA, 13th Annual Meeting, Tsukuba, Extended Abstracts (1986) p. 12.

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