JOURNAL OF MATERIALS SCIENCE 25 (1990) 4898–4905

Solubility of heat-resisting polymers in mesophase pitches at their spinning temperatures

ISAO MOCHIDA, HIROSHI TOSHIMA, YOZO KORAI
Institute of Advanced Material Study, Kyusho University, Kasuga, Fukuoka 816, Japan

Solubilities of two thermoresisting polymers (polyethylene telephthalate *p*-hydroxybenzoate, a liquid crystal polymer and polyethylene naphthalate) in mesophase pitches (MP) derived from coal tar (C1) and petroleum residues (P1 and P2) were examined to prepare blended fibre as the better precursor for the high-performance carbon fibre. MP-C1 and MP-P1 of high aromaticity dissolved 5 wt% of both polymers on mixing at 360° C for 3 h, maintaining 100 vol% anisotropy which the parent mesophase pitches exhibited, although only MP-C1 did so at 340° C. In a marked contrast, a number of isotropic droplets from both polymers dispersed in MP-P2 after the blending under the same conditions. The blends of MP-C1 with polymers were spinnable at around 370° C into fibres of 10 to 20 μm diameter although their spinnability was slightly inferior to that of the pitch alone. The blended fibre exhibited slightly higher stabilization reactivity at 270 to 300° C than that of the parent mesophase pitch fibre. Structural factors of the mesophase pitch which influence their dissolving ability are discussed. Thermal stability of the polymers is also briefly examined.

1. Introduction

Mesophase pitch-based carbon fibre has been recognized to be an excellent filler for the advanced composites [1]. However, its high cost restricts its broad application in spite of the great impact expected in its utilization [2]. The difficulty in the handling of the pitch fibre before its stabilization is one of the most sincere problems to be solved [3]. This difficulty comes from the restricted molecular size and disc-like form of the mesophase pitch components which carry no polymer effects on the strength of their fibre form [4]. The problem may be solved either by increasing the molecular size of the components up to the level where the polymeric interaction among them is expected or by blending reinforcing substances. The low reactivity for the oxidative stabilization is another problem [5–7].

We have reported previously [8] that polyphenylene oxide (PPO) could be blended to be spun into fibres together with a coal tar pitch-derived mesophase pitch. PPO became dispersed as a number of small droplets in the mesophase pitch like a polymer alloy at the spinning temperature, and was spun into very thin fibre forms ($< 1\ \mu$m) in the major matrix of the mesophase pitch fibre. It certainly reinforced the physical properties of the as-spun fibre although the increased strength was still limited.

In the present study, some other heat-resisting polymers were examined as the blending substances which were expected to be miscible with the mesophase pitches at the spinning temperature. A liquid crystal polymer, polyethylene telephthalate *p*-hydroxybenzoate (Rod Run), and thermoresisting polymer, polyethylene naphthalate (PEN), were selected because of expectations that their dissolution in the mesophase pitch would form molecular alloys. Because the former can be in liquid crystal state in the temperature range 220 to 320° C, a mixed liquid crystal state with mesophase pitch may be expected to be formed. The latter polymer carried the naphthalene units which are expected to assist its solubility in the highly aromatic moiety of the mesophase pitch molecules.

2. Experimental procedure

2.1. Materials

2.1.1. Mesophase pitches

Three kinds of mesophase pitches used in the present study were prepared from a coal tar and petroleum residues of fluidized catalytic cracking decant oils (FCC-DO). A coal tar-derived mesophase pitch (MP-C1) was prepared by the heat treatment under rapid nitrogen flow from a QI-free (Quinoline insoluble) coal tar which was hydrotreated with a Ni–Mo/Al_2O_3 catalyst [9]. Petroleum-derived mesophase pitches of MP-P1 and MP-P2 which were distributed from petroleum companies were prepared through the heat treatment from two FCC-DOs whose chemical structures were thought to be extensively different [10].

Three kinds of mesophase pitches were analysed by elemental analyses, softening point, anisotropic content, solubilities and ^{1}H-NMR spectroscopy to clarify their detailed structure. Softening points of the pitches were measured using a hot stage (Leitz 1350) attached to the polarized light microscopes (Leitz Orthoplan, Poland). Solubilities of the pitches were measured by

0022–2461/90 $03.00 + .12 © *1990 Chapman and Hall Ltd.*

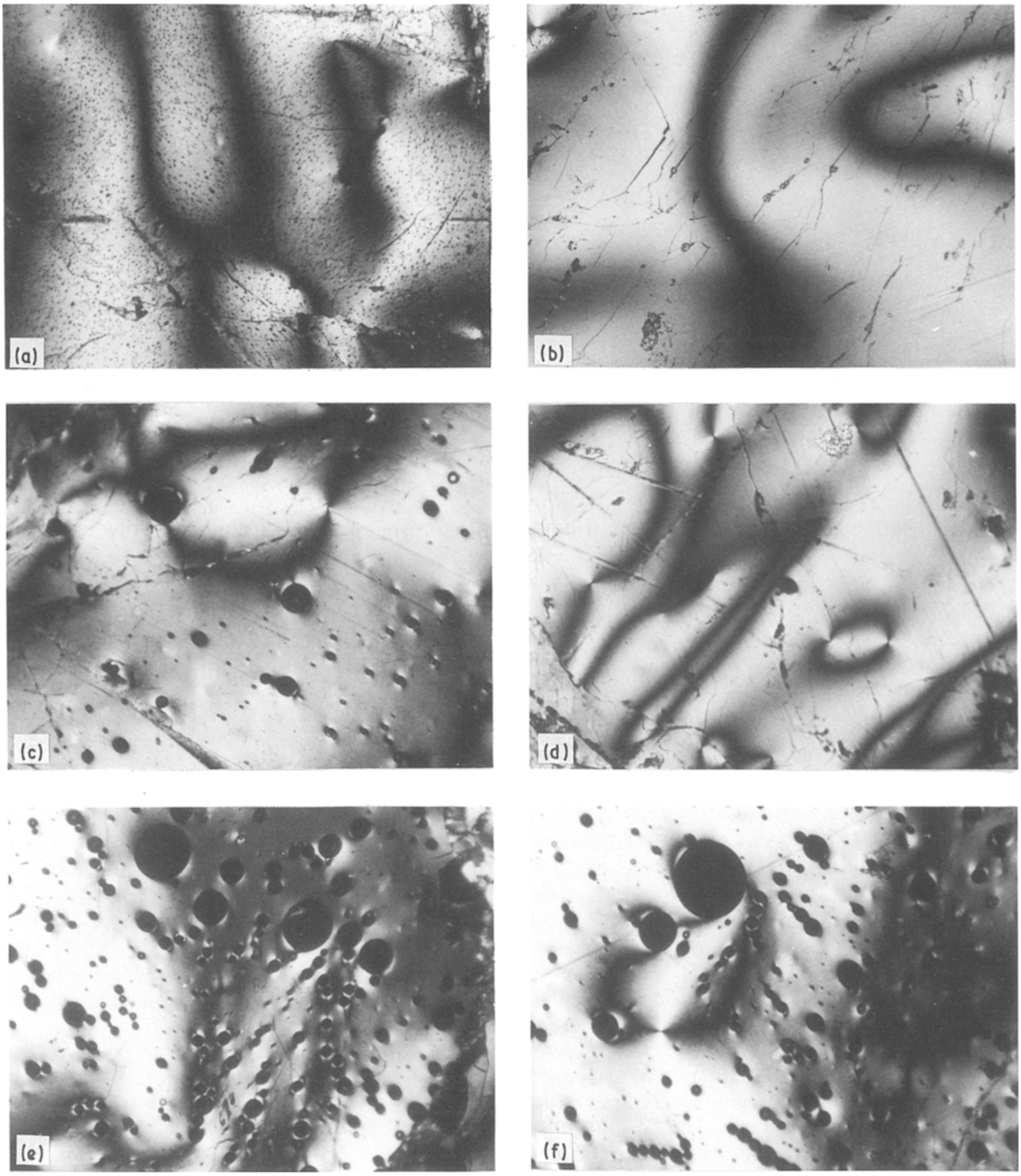

Figure 1 Optical microphotographs of the mesophase pitches blended with 5 wt % PEN. (a, b) MP-C1, (c, d) MP-P1, (e, f) MP-P2. Blending conditions: (a, c, e) 340° C, 3 h, (b, d, f) 360° C, 3 h.

using the Sohxlet apparatus. Benzene soluble (BS) and benzene insoluble–pyridine soluble (BI–PS) fractions were further analysed by ^{1}H-NMR (Jeol, FX-100) to clarify the hydrogen distributions and to obtain some analytical parameters according to the Brown–Ladner method [11].

2.1.2. Polymers

Thermoresistive polymers used in the present study were polyethylene naphthalate (PEN) and polyethylene telephathalate *p*-hydroxybenzoate (Rod Run NC3000), supplied by Mitsubishi Gas Chemical Co. Ltd and Unichica Co. Ltd, respectively. The former is a crystalline thermoresistive polymer and the latter is a thermotropic liquid crystal polymer in an elevated temperature range (220 to 350° C), according to the producers.

2.2. Blending, spinning, stabilization and carbonization

2.2.1 Blending polymers in the mesophase pitches

Two kinds of polymer (5 wt %) were blended into the mesophase pitches with vigorous agitation (600 r.p.m.) at 340 and 360° C for 10 min and 3 h under a nitrogen atmosphere. The heating rate to the above temperatures was controlled at 5° C min^{-1}. The blended pitches were re-annealed at the same temperatures

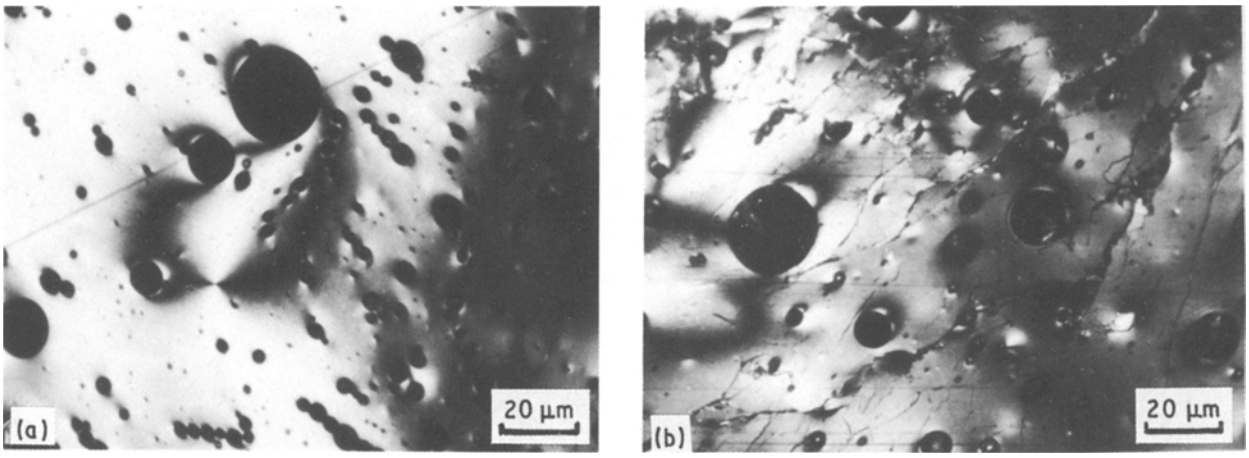

Figure 2 Optical microphotographs of the mesophase pitches blended with 5 wt % PEN. Blending conditions: 5° C min^{-1}, 360° C, 10 min. (a) MP-C1, (b) MP-P1.

to observe optical textures and to count the anisotropic content of the blends under the polarized-light microscope.

2.2.2. *Spinning of the blends*

The blended pitches were spun into fibres from a steel spinneret using pressurized nitrogen (1.2 kg cm^{-2}). The cone-type spinneret, whose length (L) and nozzle diameter (D) were both 0.4 mm, was used for spinning. The winding rate was around 400 m min^{-1}.

2.2.3. *Stabilization and carbonization of the pitch fibres*

Bundles of the pitch fibres ($\sim$0.2 g) were stabilized by oxidative thermosetting in the atmosphere at 270 to 300° C for variable periods of time. Heating was begun at room temperature and proceeded at the controlled rate of 5° C min^{-1} to the stabilization temperatures.

The stabilized pitch fibres were further carbonized under a nitrogen flow at 600° C for 1 h. The heating rate to this temperature was 10 to 30° C min^{-1}. After mounting in the polyester resin and conventionally polishing, the morphology and optical textures of the carbonized fibres sectioned perpendicular to the fibre axis were observed using a polarized light microscope (Leitz Orthoplan, Poland) to check that stabilization had occurred.

3. Results

3.1. Miscibility of PEN in the mesophase pitch

Fig. 1 shows the optical microphotographs of the blends of PEN (5 wt %) and mesophase pitches mixed vigorously at 340 and 360° C for 3 h. MP-C1 (coal tar-derived mesophase pitch) was almost completely miscible with 5 wt % PEN at 340° C, no separate phase being found in the domain anisotropy derived from the mesophase of coal tar molecules. In contrast, a large number of isotropic droplets of variable sizes (5 to 20 μm diameter) was observable in the mesophase pitch from an FCC-DO (MP-P1). Many more isotropic droplets of larger sizes were observable in another petroleum-derived mesophase pitch (MP-P2), the miscibility of PEN being certainly inferior to that in MP-P1 and MP-P2.

Annealing at a higher temperature of 360° C enhanced the miscibility. No droplets were found in MP-P1 nor in MP-C1 while a number of droplets were still present in the blend of MP-P2, although the number was certainly less.

Fig. 2 shows the optical microphotographs of the blends of MP-C1 and MP-P1 after annealing for 10 min at 360° C. A certain number of large droplets were present, indicating that PEN in the mesophase pitch required some time at the annealing temperature before its dissolution.

3.2. Miscibility of Rod Run in mesophase pitches

Fig. 3 shows the optical microphotographs of Rod Run (5 wt %) blended in MP-C1 and MP-P1 after annealing at 360° C. No droplets were found in both mesophase pitches annealed for 3 h, beautiful flow domain textures being developed.

Mixing for 10 min was insufficient in these cases because a number of isotropic droplets was found after annealing. However, MP-C1 certainly showed fewer droplets.

3.3. Spinning and stabilization of blended pitches

Mesophase pitches MP-C1 and MP-P1 blended with 5 wt % PEN were spun at around 370° C into fibres of 10 to 20 μm diameter. The spinning was continued for a few minutes with both pitches, although spinability of the blends was certainly inferior to those of the parent mesophase pitches because of some gas evolution which was probably due to the partial decomposition of PEN.

Optical microphotographs of the carbonized fibres from MP-C1 and its blend with 5 wt % PEN (PEN-5) after stabilization at 270° C for 40 to 60 min are shown in Fig. 4, where the heating rates for the stabilization and carbonization are 5 and 10° C min^{-1}, respectively. MP-C1 fibre required 60 min to achieve no deformation nor adhesion between fibres while the blend with PEN-5 required 40 min.

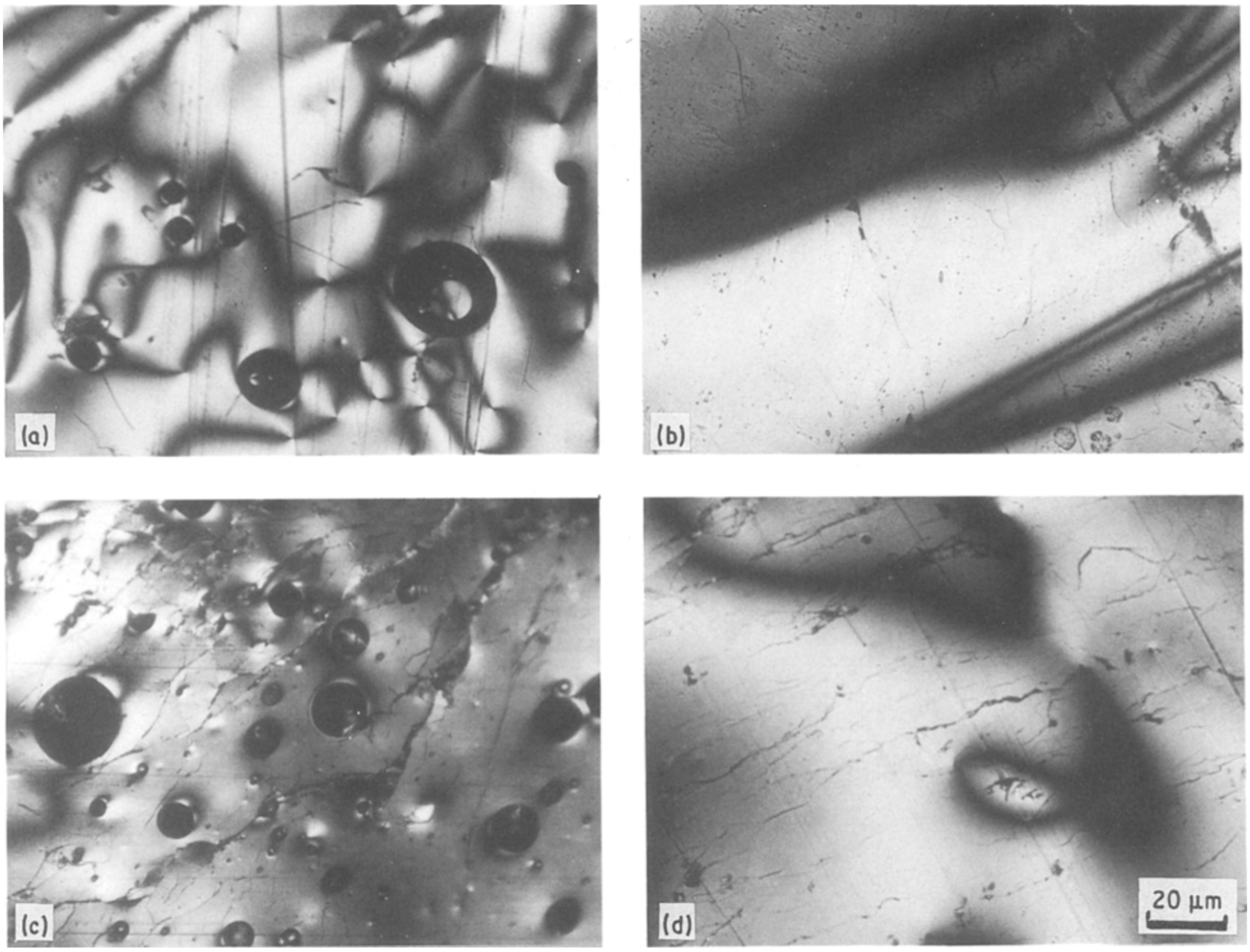

Figure 3 Optical microphotographs of the mesophase pitches blended with 5 wt % Rod Run. (a, b) MP-C1, (c, d) MP-P1. Blending conditions: (a, c) 360° C, 10 min, (b, d) 360° C, 3 h.

The rapid heating at the carbonization enhanced the adhesion between fibres as shown in Fig. 5. MP-C1 fibres stabilized at 270° C for 60 min adhered to each other at a heating rate of 20° C min^{-1} while the blended fibre, stabilized under the same conditions, showed no adhesion even at a carbonization rate of 30° C min^{-1}.

A higher stabilization temperature shortened the thermosetting time required for no adhesion of the carbonized fibres to occur. MP-C1 and the blend (PEN-5) were sufficiently stabilized by 30 and 20 min at 280° C and 12 and 10 min at 300° C, respectively, as shown in Table I.

Thus, the blending of PEN with the mesophase pitch certainly enhanced the stabilization reactivity of the whole pitch fibre which is one of the most important requirements in the production of pitch-based carbon fibre.

TABLE I Stabilization time required for complete thermosetting

Sample	Stabilization time (min) at ST*		
	270° C	280° C	300° C
MP-C1	60	30	12
MP-C1/PEN(5%)	40	20	10

*Stabilization temperature. Heating rates of stabilization and carbonization were 5 and 10° C min^{-1}, respectively.

3.4. Thermal stability of polymers

Thermal stabilities of the present polymers at 360° C were examined by thermogravimetric analysis (TGA) and their solubility in pyridine, because their thermal decomposition is reported by the producer to begin at 370 to 400° C.

Fig. 6 illustrates the weight loss of PEN during heat treatment at 340 and 360° C. Weight loss due to partial decomposition began to take place at 30 and 10 min at 340 and 360° C, respectively. Weight loss of PEN at 360° C is found to be much more marked (reaching 22 wt % over 3 h) than that at 340° C. Rod Run showed almost the same trend of weight loss as the case of PEN.

62 wt % PEN and 32 wt % Rod Run became soluble in pyridine after heating at 360° C for 3 h, although both polymers before heating were completely pyridine-insoluble, suggesting some depolymerization under these conditions.

The infrared spectrum of PEN after heat treatment at 360° C for 3 h is illustrated in Fig. 7. The bands at 1791 and 1699 cm^{-1}, which are ascribed to the carboxylic and carbonyl C=O bonds, respectively, were found to be very intensified. Very sharp bands at 1136 to 1294 and 1089 cm^{-1} (carboxylic or aldehyde, and ether C–O bonds, respectively), were also observable as shown in Fig. 7, suggesting that the skeletal structure of PEN may still be maintained.

The ^{1}H-NMR spectrum of the PS fraction in PEN

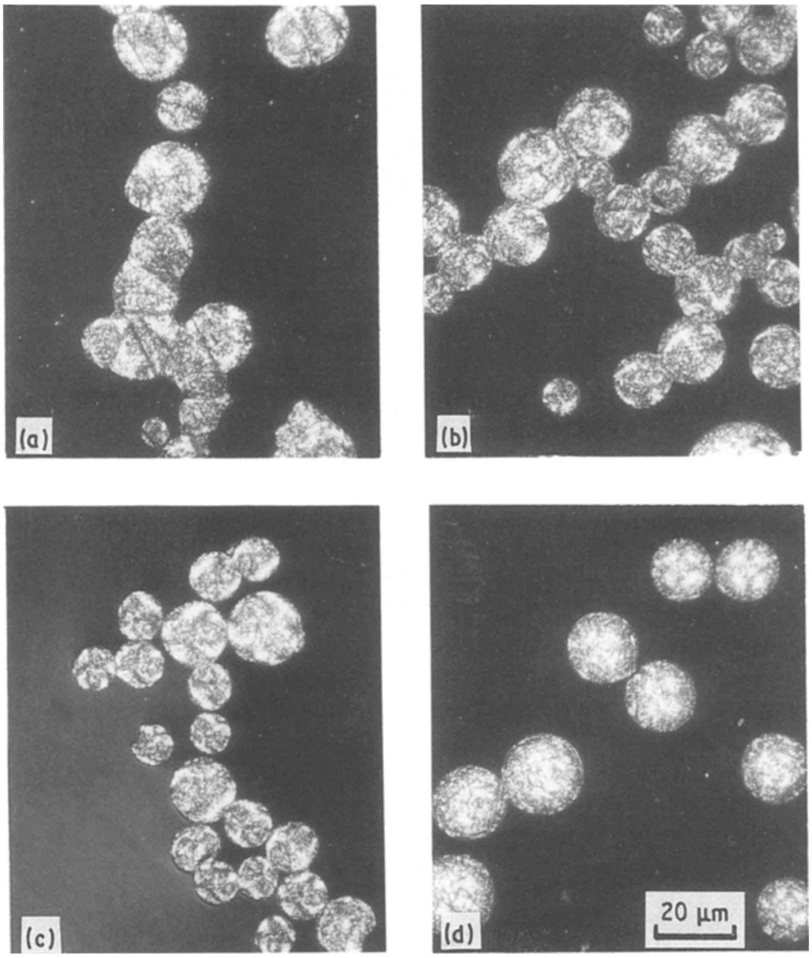

Figure 4 Optical microphotographs of the carbonized fibres. Stabilization conditions: 5° C min^{-1}, 270° C, in air. Carbonization conditions; 10° C, 600° C, 1 h, in nitrogen. (a to c) MP-C1, (d) PEN-5. Stabilization time: (a, d) 40 min, (b) 50 min, (c) 60 min.

after the heat treatment is illustrated in Fig. 8. The doublets at 8.0 to 8.5 p.p.m. and triplets at 7.0 to 7.5 p.p.m. may indicate that the fraction carried the 2,6-naphthalate group. The molecular weight of the PS fraction in the heat treated PEN obtained by GPC was distributed from 100 to 10 000. The content of molecular weight between 1000 and 10 000 was 42%, and between 100 and 1000 and 58% (the molecular weight was obtained using a polystrene standard) while that of PEN before heat treatment was expected to be around 25 000 from the reported intrinsic viscosity in phenol/tetrachloroethane (6/4). Hence, the skeletal structure of 2,6-naphthalate is suggested to be maintained, although the depolymerization is certainly proved at the heat treatment temperature to produce substances of lower molecular weight and which are pyridine soluble.

3.5. Some analytical data of the mesophase pitches

Although the softening temperatures of the three kinds of mesophase pitches were all 250° C as shown in Table II, their solubilities in benzene, pyridine and quinoline were different, their solubilities in benzene, pyridine and quinoline were different, their solubility and H/C ratio increasing in the order MP-C1 < MP-P1 < MP-P2.

Table III summarizes some analytical date of BS and BI–PS fractions in the three mesophase pitches. The aromaticity of both fractions increased markedly in the order MP-C1 > MP-P1 > MP-P2. In turn, the numbers of alkyl substitution and naphthenic ring increased in the reverse order; MP-C1 < MP-P1 < MP-P2.

It is thus obvious that the present mesophase

TABLE II Some properties of mesophase pitches

Sample	Elemental analyses (wt %)				H/C	A.C.§ (vol %)	S.P.¶ (° C)	Solubilities (wt %)			
	H	C	N	Diff.				BS	BI–PS	PI–QS	QI
MP-C1*	3.9	94.6	0.8	0.7	0.50	> 98	250	26	31	11	32
MP-P1†	4.3	95.4	0.1	0.2	0.54	100	250	25	23	30	22
MP-P2‡	4.7	94.4	0.2	0.7	0.60	100	250	36	19	21	24

*MP-C1: Coal tar-derived mesophase pitches.
†MP-P1: Petroleum-derived mesophase pitches.
‡MP-P2: Petroleum-derived mesophase pitches.
§Anisotropy content.
¶Softening point measured by hot stage.

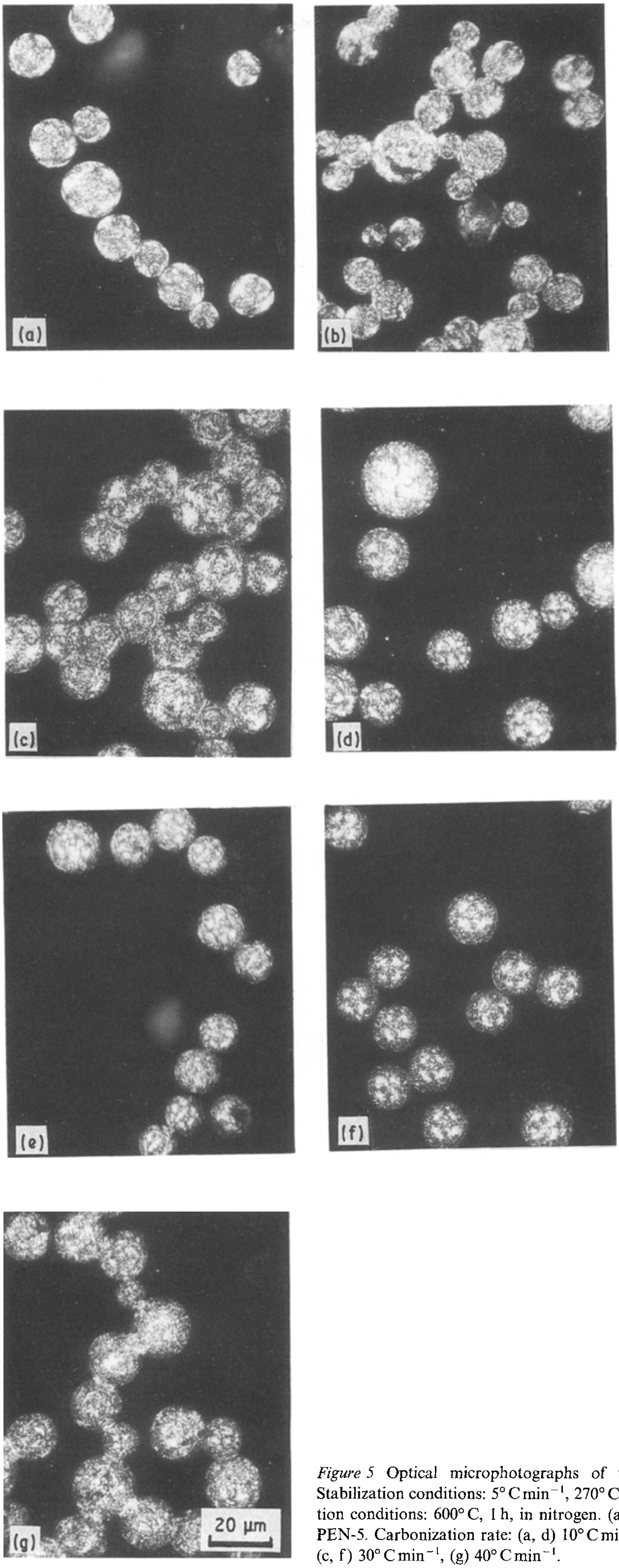

Figure 5 Optical microphotographs of the carbonized fibres. Stabilization conditions: 5° C min^{-1}, 270° C, 1 h, in air. Carbonization conditions: 600° C, 1 h, in nitrogen. (a to c) MP-C1, (d to g) PEN-5. Carbonization rate: (a, d) 10° C min^{-1}, (b, e) 20° C min^{-1}, (c, f) 30° C min^{-1}, (g) 40° C min^{-1}.

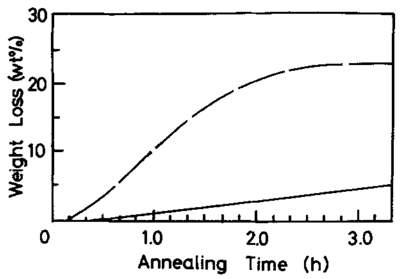

Figure 6 TGA curve of PEN during heat treatment at 340 and 360° C. (——) 340° C, (– –) 360° C.

pitches were very different in their structure and structure distribution, probably reflecting their different origins and preparation procedures [10, 12].

4. Discussion

The present study revealed that two thermoresistive polymers were miscible with particular mesophase pitches. The blends of such pitches maintained 100 vol % anisotropy without any phase separation and were spinnable by melt spinning into fibre form of 10 to 20 μm diameter. Although the spinnability was certainly inferior to those of the mesophase pitches alone because of gas evolution during spinning, the determination of more appropriate conditions for spinning at a lower temperature, appling a higher pressure, would be of value.

The fibre from the blend appeared harder to break before stabilization. Its reactivity for stabilization was enhanced, slightly shortening the time required for complete stabilization, although part of the polymers may be decomposed during blending, suggesting that the oxygen in PEN may play an important role in this step. Thus, the blending of a better combination of a mesophase pitch and a thermoresistive polymer may appear promising to provide a better precursor for the carbon fibre in terms of handling and stabilization of the as-spun fibre. A kind of molecular alloy is expected to solve the problems in the carbon fibre manufacture.

It is of value to discuss the different dissolution abilities of the mesophase pitches used in the present study. The ability of the mesophase pitches to dissolve definitely decreased in the order MP-C1 > MP-P1 > MP-P2. This order coincides with that of increasing aromaticity (f_a) or decreasing atomic H/C ratio and the number of alkyl side chains. The considerably sized aromatic planes in the mesophase pitch may dissolve

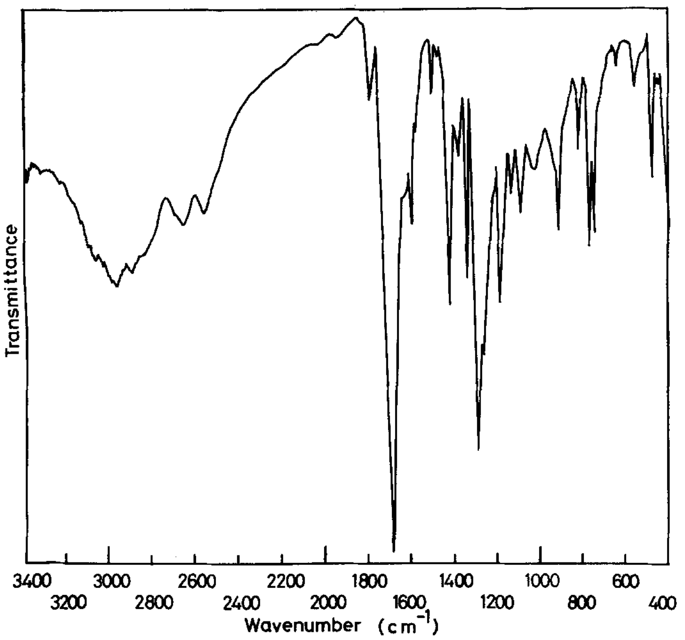

Figure 7 FTIR spectrum of PEN heat treated at 360° C for 3 h.

TABLE III Analytical data of soluble fractions in the mesophase pitches

Sample	H/C	Hydrogen distribution (%)				f_a	Structural parameters		
		H_{ar}	H_α	H_β	H_γ		σ_{al}	C_{alus}	R_{nus}
MP-C1									
BS	0.58	76.1	13.0	8.7	2.2	0.93	0.08	5.74	1.55
BI-PS	0.52	90.5	6.3	3.2	0	0.98	0.03	1.73	1.28
MP-P1									
BS	0.62	69.3	21.9	7.1	1.7	0.91	0.13	5.01	0.95
BI-PS	0.55	74.0	19.6	4.8	1.6	0.93	0.11	8.91	3.95
MP-P2									
BS	0.66	57.9	28.0	11.0	3.1	0.86	0.19	6.45	1.47
BI-PS	0.57	62.1	28.5	7.5	1.9	0.89	0.17	15.76	7.03

Notes:
H_{ar} = aromatic hydrogen; H_α = α-position hydrogen; H_β = β-position hydrogen; H_γ = γ-position hydrogen.
f_a = aromaticity of carbon. σ_{al} = number of alkyl substitution group per unit structure, C_{alus} = number of aliphatic carbons per unit structure. R_{nus} = number of naphthenic carbons per unit structure.

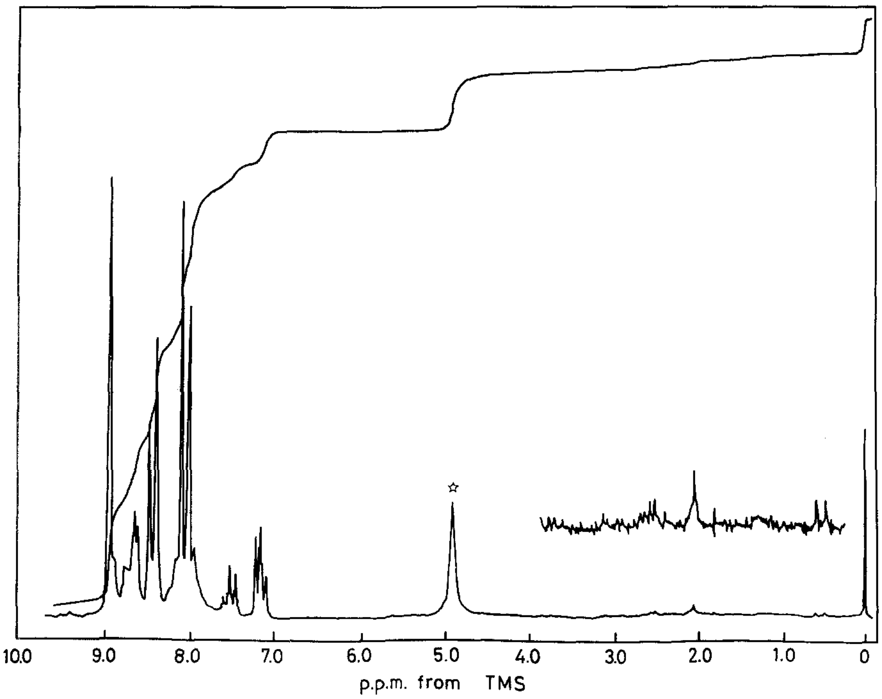

Figure 8 ^{1}H-NMR spectrum of the PS fraction in PEN heat treated at 360° C for 3 h. (☆) impurity in d_5-pyridine.

and accommodate the polymers which have some aromaticity in the ordered stacking of aromatic planes, to show complete anisotropy [13]. The contact method was not useful in the present study because rapid agitation during blending was necessary to dissolve the polymer in the mesophase pitches. More detail study on the origins of the mutual miscibility and interaction between a variety of polymers and mesophase pitches is required to clarify the dissolving ability of the carbonaceous mesophase. Such a study may be promising to find a better precursor for the pitch-based carbon fibre.

References

1. S. OTANI, K. OKUDA and H. S. MATSUDA, "Carbon Fibre" (Kindai Henshusha, 1983) p. 231.
2. K. KAWATA, S. UMEKAWA and K. KOBAYASHI, "Composites '86: Recent Advances in Japan and the United States" (Kokon Shoin, Tokyo, 1986) p.1.
3. S. OTANI and A. OYA, "Carbon Fibre" (Nyumon, Ohmusha, 1983) p. 84.
4. I. MOCHIDA and Y. KORAI, *J. Fuel Soc. Jpn* **64** (1985) 796.
5. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. MATSUMOTO, *Chem. Lett.* **11** (1987) 2279.
6. *Idem, J. Mater. Sci.* **23** (1988) 670.
7. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. HINO, *ibid*, in press.
8. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. NAITO, *ibid* **23** (1988) 678.
9. T. MATSUMOTO *Pure and Appl. Chem.* **57** (1985) 1553.
10. I. MOCHIDA, T. OYAMA, Y. KORAI and Y. Q. FEI, *Fuel* **67** (1988) 1171.
11. J. K. BROWN and W. R. LADNER, *ibid.* **39** (1960) 79.
12. I. MOCHIDA, Y. Q. FEI, T. OYAMA, Y. KORAI and H. FUJITSU, *Mater. Sci.*, in press.
13. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. MATSUMOTO, *ibid.* **24** (1989) 57.

Received 6 June
and accepted 23 October 1989