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Modification of mesophase pitch by blending

Part 2 *Modification of mesophase pitch fibre precursor with thermoresisting polyphenyleneoxide (PPO)*

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Polyphenyleneoxide was blended in amounts of 5 or 10 wt% into petroleum-derived mesophase pitch to reinforce the pitch fibre before the oxidative stabilization to achieve better handling properties. Although polyphenyleneoxide was fusible but hardly soluble in the mesophase pitch even at a spinning temperature of ~350° C, blended pitch could be smoothly spun into pitch fibre 10 μm diameter, as could the parent pitch. Fibrous polyphenyleneoxide of less than 1 μm diameter was homogeneously dispersed in the pitch fibre, being arranged along the fibre axis. Such fibrous polyphenyleneoxide reinforced the pitch fibre considerably. The fibrous substances at the centre of the fibre disappeared in the carbonized fibre at 1300° C after oxidation at 250° C, although some short ones were observed in the skin region of the fibre, suggesting that polyphenyleneoxide was co-carbonized to be assimilated with mesophase pitch at the centre of the fibre, where the effects of oxidation may be rather limited. The oxidation reactivity and its mechanical strength after carbonization were slightly lower in comparison with those of the parent mesophase pitch.

1. Introduction

High-performance mesophase pitch-based carbon fibre has been studied as a strategic material of the next generation [1, 2]. Although the principles of its production have been established [3–6], there still remain several serious problems to be solved to balance its production cost/performance ratio [7, 8]. One such problem is the difficulty of handling pitch fibre just after spinning, before the oxidative stabilization, because of its extraordinary low mechanical strength [8]. The mesophase pitch of diskotic liquid crystal consists essentially of planar aromatic hydrocarbons of moderate molecular weight [9–11].

In the present study, polyphenyleneoxide (PPO, m.p. = 250° C) was blended into petroleum-derived mesophase pitch to reinforce its pitch fibre. PPO is known as a thermoresisting polymer [12, 13] so that it can be stable at the spinning temperature where it can fuse or may be partly soluble in the mesophase pitch. Because its spinning is recognized to be very difficult and it is usually moulded with thermoplastic polystyrene [12], its spinning in the matrix of the mesophase pitch was the largest target in the present study. The oxidative stabilization and carbonization properties of the blended pitch were compared with those of the parent pitch. Mechanical properties of carbonized fibres were briefly studied.

2. Experimental details

Polyphenyleneoxide (PPO, Mitsubishi Chemical Industry), was used as a polymer to blend the petroleum-derived mesophase pitch in the present study. Some analyses of the mesophase pitch are summarized in Table I. After blending in their pyridine solution, the blended pitch was obtained by evaporating the solvent. The blended pitch was annealed at 350° C for 10 min at a heating rate of 5° C min^{-1} in a vertical electric furnace. A block of blended pitch was observed under a polarized-light microscope (Leitz) to define their mutual solubility after the conventional mounting in the resin and polishing. The pitch was also observed at 360° C on the hot-stage (Leitz) under an optical microscope.

The blended pitch was spun into pitch fibre form, from a nozzle (0.5 mm diameter) attached to a container (amount of sample ~ 10 g) by applying a nitrogen pressure (0.2 to 1.0 kg cm^{-2}). The spinning rate was about 400 m min^{-1}.

The mesophase and its blend pitch fibres were oxidized at 250° C in the atmosphere under flowing air. The heating rate to the oxidation temperature was 5° C min^{-1}. The properties of oxidized pitch fibres were analysed by elemental analyses and FT-IR (Jeol, JIR-03F).

The oxidized pitch fibres were further carbonized into their respective carbon fibres at 1300° C for 1 h in a horizontal electric furnace. The heating rate to the carbonization temperature was 10° C min^{-1}.

The tensile strengths of pitch and carbon fibres were measured using a single yarn strength tester (Toyo Seiki, Strograph M-100). The strength of 30 single yarns (length 25 mm) was measured in this study to obtain an average value.

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TABLE I Microanalyses of mesophase pitch

Element (wt %)				f_a^*	$R_{nus}^{\dagger}$	s.p.[‡] (°C)	Solubilities (wt %)		
H	C	N	H/C				BS[″]	BI-QS[§]	QI[¶]
4.7	94.1	0.1	0.60	0.86	1.22	270	41	30	29

[*] Carbon aromaticity.

[†] Number of the naphthenic ring in the unit structure.

[‡] Softening point.

[″] Benzene, soluble.

[§] Benzene, insoluble–quinoline, soluble.

[¶] Quinoline, insoluble.

3. Results

3.1. Optical texture of blended pitch

The photomicrographs of the mesophase pitch and its blends with 5 and 10% PPO after annealing are shown in Fig. 1. The mesophase pitch showed flow domain textures over the whole area (Fig. 1a). In contrast, isotropic droplets of various sizes (5 to 30 μm) were dispersed in the blended pitch. The number and volume of the droplets increased with increasing PPO content.

The optical textures of the blends (10% PPO) at a spinning temperature of 360° C are illustrated in Fig. 2. The mesophase pitch retained anisotropy over its whole region at this temperature, although the pitch became mobile. PPO fused but provided isotropic droplets, which exhibited deformed or diffused shapes with some coalesced forms at an annealing time of zero. The isotropic area was much larger than that observed at room temperature, as shown in Fig. 1. A considerable amount of fused PPO may float on the surface of the mesophase pitch. The deformation and diffusion became much more marked at 30 min, indicating its slight dissolution or intimate wetting in the mesophase pitch.

3.2. Spinning of pitch

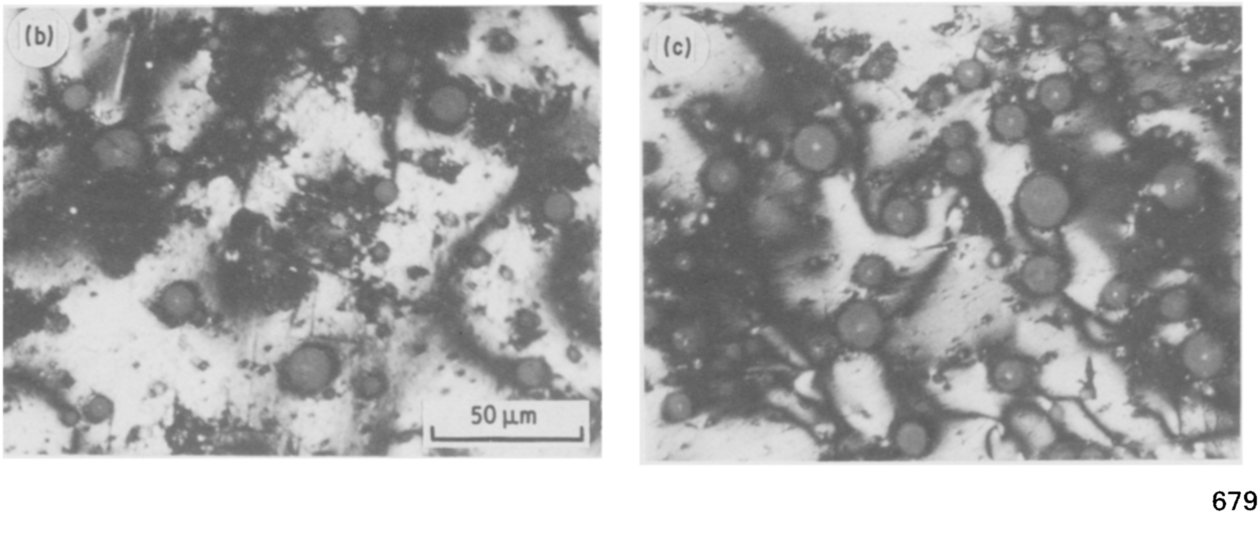
Fig. 3 shows softening and spinnable temperatures of the mesophase pitch and its blends with PPO. The softening temperature of the pitch tended to rise slightly on blending PPO from 270° C of the parent pitch with a 10% addition at 285° C.

The spinnable temperatures are also illustrated by the hatched area in Fig. 3. The mesophase pitch showed excellent spinnability, allowing continuous spinning at 345° C for times longer than 20 min with our primitive spinning instrument. The addition of 5 and 10% PPO increased the spinnable temperatures to 350 to 365° C, and 350 to 370° C, respectively. These blends could still be smoothly spun for longer than 20 and 10 min into pitch fibres of 10 μm diameter at 355 and 360° C, respectively. A small amount of decomposition of PPO may begin to take place at the latter temperature, somewhat disturbing the spinning.

3.3. Texture and properties of pitch fibre

Optical photomicrographs of the mesophase pitch and its blend pitch fibres are shown in Fig. 4. Anisotropic flow textures run parallel to the fibre axis, while random orientation is observable in the surface sectioned perpendicular to the fibre axis. PPO was not detectable in the surface parallel to the blend pitch

Figure 1 Optical photomicrographs of mesophase pitch and its blends with 5 and 10% PPO. (a) Mesophase pitch, (b) 5% PPO, (c) 10% PPO.



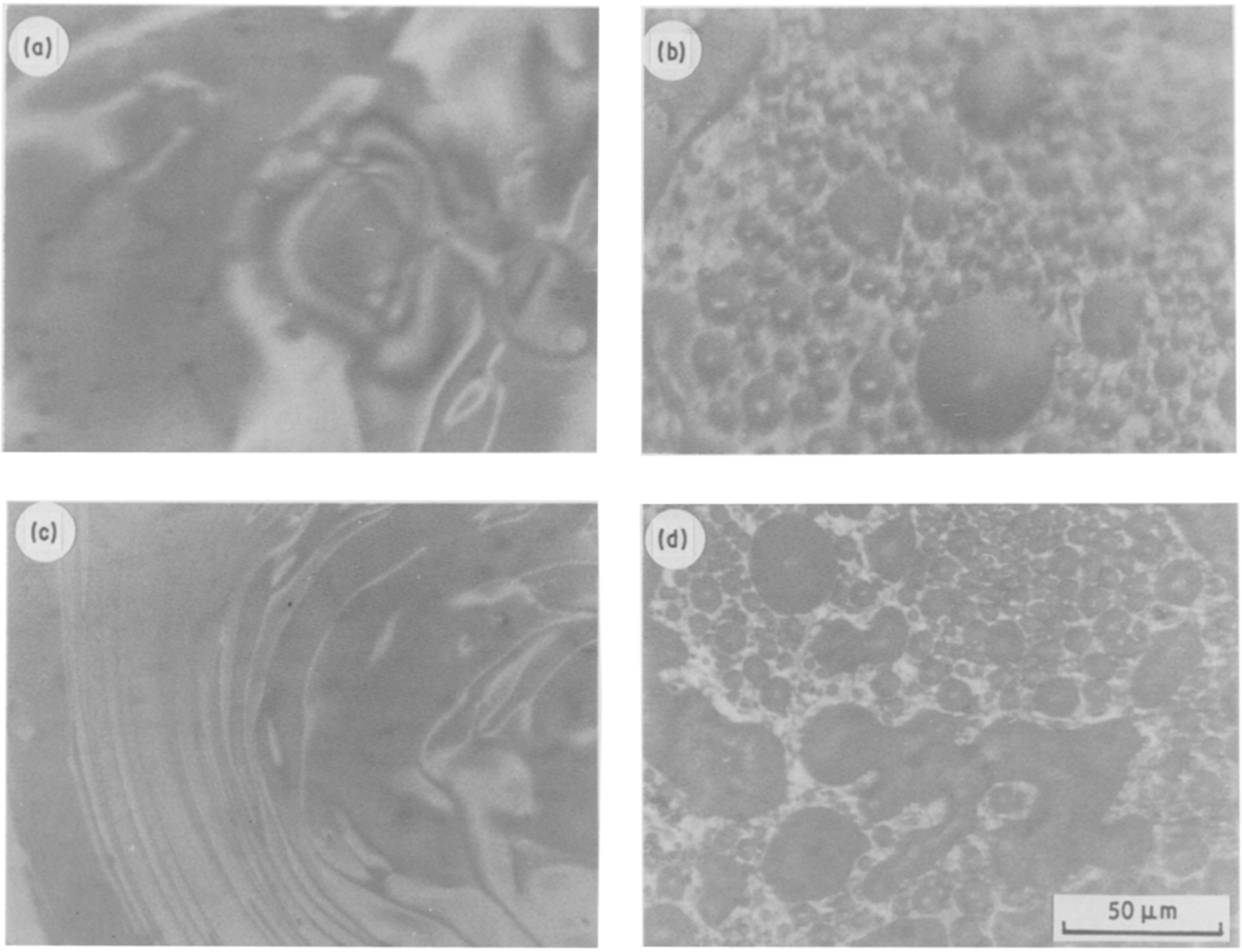


Figure 2 Optical textures of mesophase pitch and its blends (10% PPO) at a spinning temperature of 360° C. (a) Mesophase pitch (360° C, 0 min), (b) with 10% PPO (360° C, 0 min), (c) mesophase pitch (360° C, 30 min), (d) with 10% PPO (360° C, 30 min).

fibre axis at × 1200; however, some isotropic droplets less than 1 μm were definitely observable in the surface perpendicular to the fibre axis.

Scanning electron micrographs of mesophase and its blend pitch fibres were shown in Fig. 5. Both surfaces (A and B) of the mesophase pitch fibres were flat as shown in Fig. 5a. In contrast, a number of fine fibrous substances, very probably PPO, smaller than 1 μm were unfissioned in the fractured area of the blended pitch fibres (PPO 10%, Fig. 5b), although the surface along the fibre axis was quite smooth. The thin fibres were dispersed homogeneously in the pitch fibre, running along the fibre axis. PPO fibres were fissioned, emerging in random lengths from the flat surface of the fractured mesophase pitch (Figs 5c and d). Some fibres carried some flakes of pitch substances (Fig. 5c). Thus, the majority of the PPO remained insoluble, to be smoothly spun together with the mesophase pitch even at the spinning temperature but fusible in the pitch.

Table II summarizes the mechanical strength of pitch fibres. The addition of 10% PPO increased both the average tensile strength and Young's modulus of the pitch fibres by 30% and 8%, respectively. Although the values scattered considerably as indicated by the highest and lowest ones, the highest values suggest that the addition of PPO improved the mechanical properties of the pitch fibres by about twice as much.

3.4. Stabilization reactivity of pitch fibres

Fig. 6 shows a series of photomicrographs of the sectioned surfaces of pitch fibres carbonized at 600° C for 1 h at a heating rate of 10° C min^{-1} after the oxidation at 250° C for variable times. The oxidation for 30 min allowed adhesion of both fibres during the

TABLE II Mechanical properties of pitch fibres

Sample	Av. σ* (kg mm^{-2})	Av. E† (kg mm^{-2})	σ (kg mm^{-2})		E (kg mm^{-2})	
			min.	max.	min.	max.
Meso. pitch	3.8	480	1.8	5.0	440	530
Meso. pitch/10% PPO	4.9	520	2.8	9.6	360	1200

*Tensile strength.
†Young's modulus.

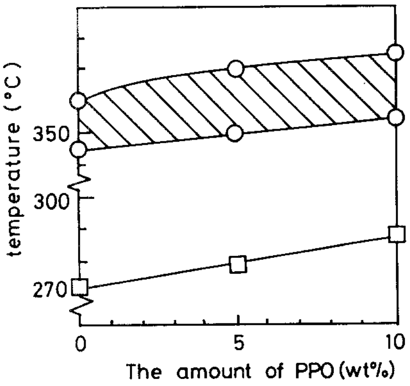


Figure 3 Changes of softening and spinnable temperatures of mesophase pitch blended with PPO. (□) Softening temperature, (○) spinning temperature. Hatched area indicates spinnable temperatures.

carbonization. The mesophase pitch fibres showed a homogeneous fine mosaic anisotropy over the whole surface, whereas the blended pitch fibres (10% PPO) showed a skin–core texture, where the skin and core areas consisted of fine and coarse mosaic textures, respectively, indicating that the pitch is still fusible at the core to increase its optical texture size during carbonization. Oxidation for 50 min was still insufficient to obtain good stabilization of both fibres, although the skin areas increased considerably in the blended pitch fibre. Both fibres stayed as single strands during carbonization after oxidation for 70 min, although the centres of both fibres still showed some areas of coarse mosaic texture.

Scanning electron micrographs of the pitch fibre after oxidation for 120 min are shown in Fig. 7. No change was observable after oxidation in the number of fibrous substances of less than 1 μm in the blended pitch fibre.

The oxidation increased the oxygen content considerably while hydrogen and carbon contents decreased slightly in similar manners with both pitches. Infrared spectra of fibres indicated the appearance and/or increased intensity of absorption bands at 1700 (carbonyl), 1600 (aromatic C–C), and around 1200 cm^{-1} (very broad, aryl–aryl ether) by oxidation as shown in Fig. 8. The oxidative stabilization brings about dehydroaromatization as well as oxygenation. The blended pitch provided a band at 1200 cm^{-1} which was ascribed to the ether bond in PPO. The oxidation decreased its intensity along with the oxidation time. The oxygen content of both fibres increased almost proportionally to the oxidation time; the contents of hydrogen and carbon showed reverse trends. Both pitch fibres after oxidation at 250° C for 70 min, which remained as a single strand after carbonization, had an oxygen content of 6.4 to 6.9%. Some authors [14, 15] reported similar contents necessary for stabilization.

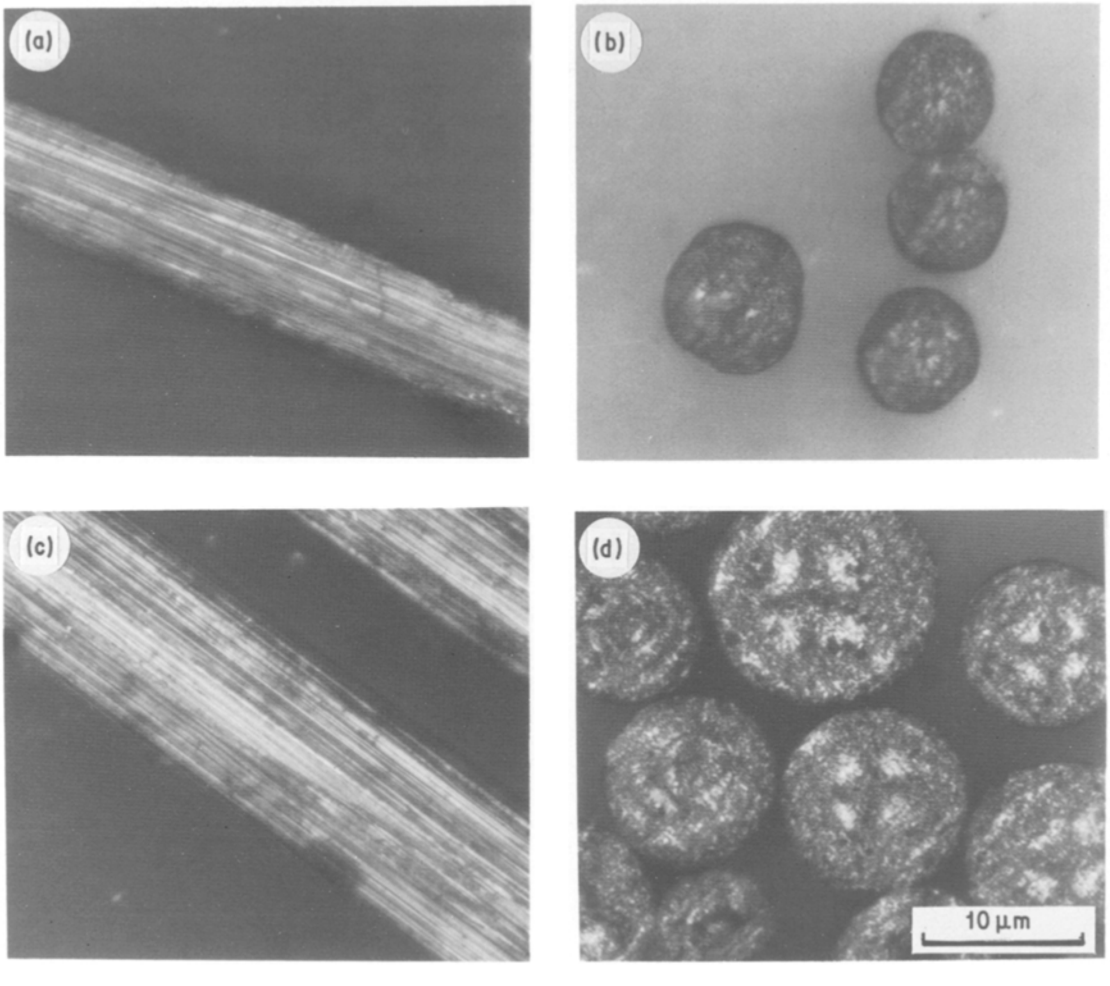


Figure 4 Optical photomicrographs of mesophase and its blend pitch fibres. (a), (b) Mesophase pitch fibre, (c), (d) blend pitch fibre (10% PPO).

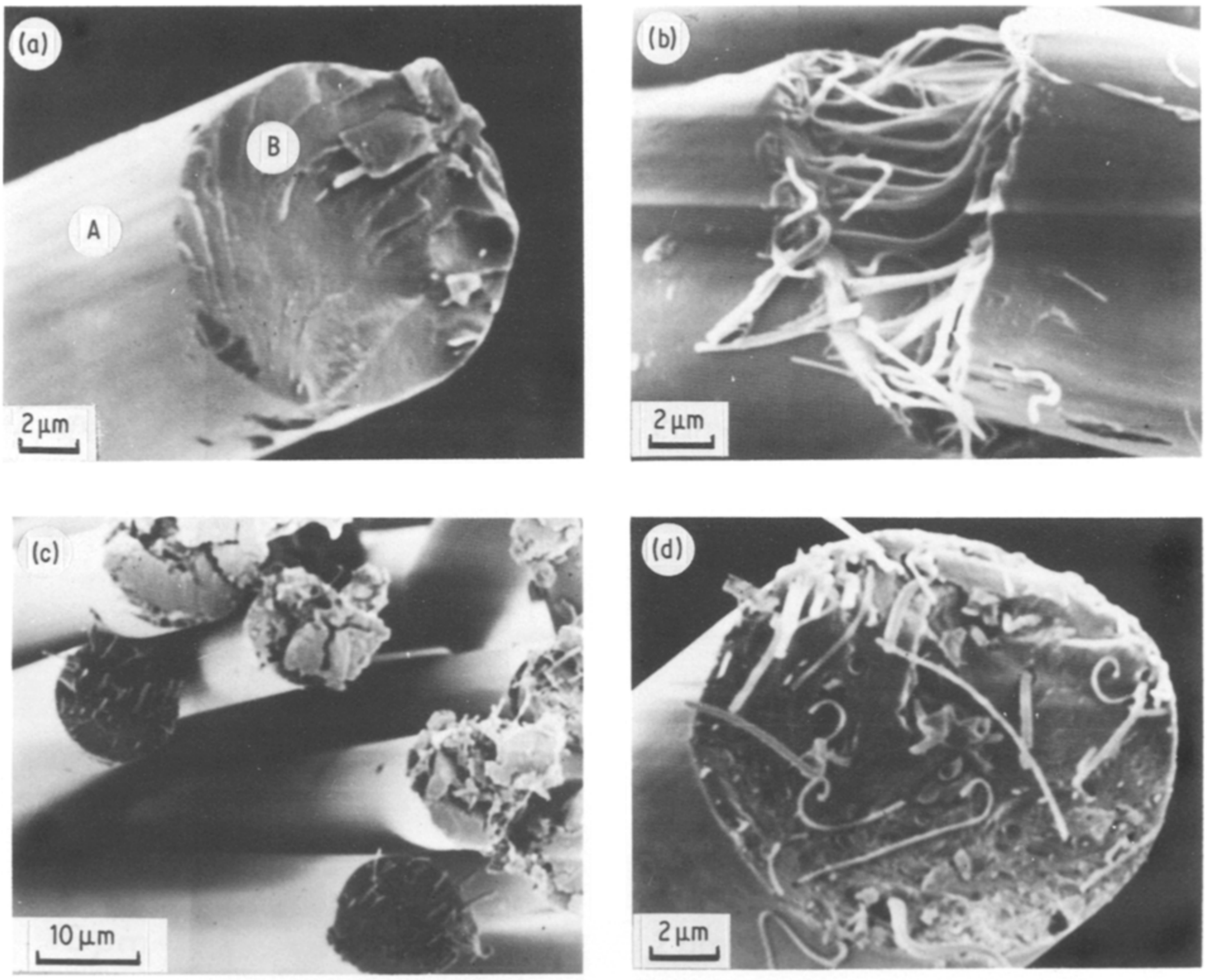


Figure 5 Scanning electron micrographs of mesophase and its blend pitch fibres. (a) Mesophase pitch fibre, (b) blend pitch fibre (10% PPO), (c) blend pitch fibre (10% PPO), (d) blend pitch fibre (10% PPO).

3.5. Carbonized fibre

Fig. 9 shows the photomicrographs of the carbonized fibres at 1300° C after oxidation at 250° C for 120 min. Both fibres showed excellent uni-axial flow texture along the axis. It should be noted that more homogeneous spherical units of anisotropy were observable over the whole areas of sectioned surface of both fibres. The sizes of the anisotropic units in the centre of blended pitch fibres appeared slightly larger than those of mesophase pitch fibre. Some isotropic droplets of less than 1 μm diameter were still observable in the outer areas of the sectioned surface of the blended carbon fibre.

Scanning electron micrographs of carbon fibres are shown in Fig. 10. Very short fibrous substances smaller than 1 μm remained only in the outer surface in the blended pitch carbon fibre. More voids were formed in the carbon fibre from the blended pitch than from mesophase pitch alone.

The mechanical properties of carbon fibres (carbonized at 1500° C) are summarized in Table III. Addition of 10% PPO decreased slightly the mechanical strength when the values of 30 filaments were averaged, although the Young's modulus was slightly increased. It is noted that dispersions of the strength values of carbon fibres from the blend were much larger than those from mesophase pitch alone.

4. Discussion

The blending of PPO was found to reinforce the mesophase pitch fibre before oxidative stabilization through its small fibrous forms distributed along the fibre axis in the pitch fibre which consist of diskotic molecules. Although the majority of PPO was fusible,

TABLE III Mechanical properties of carbon fibres

Sample	Av. σ* ($\mathrm{kg\,mm^{-2}}$)	Av. E† ($\mathrm{t\,mm^{-2}}$)	σ ($\mathrm{kg\,mm^{-2}}$)		E ($\mathrm{t\,mm^{-2}}$)	
			min.	max.	min.	max.
Meso. pitch	210	22.0	160	250	20.0	24.0
Meso. pitch 10% PPO	170	25.0	110	240	22.0	27.0

*Tensile strength.
†Young's modulus.

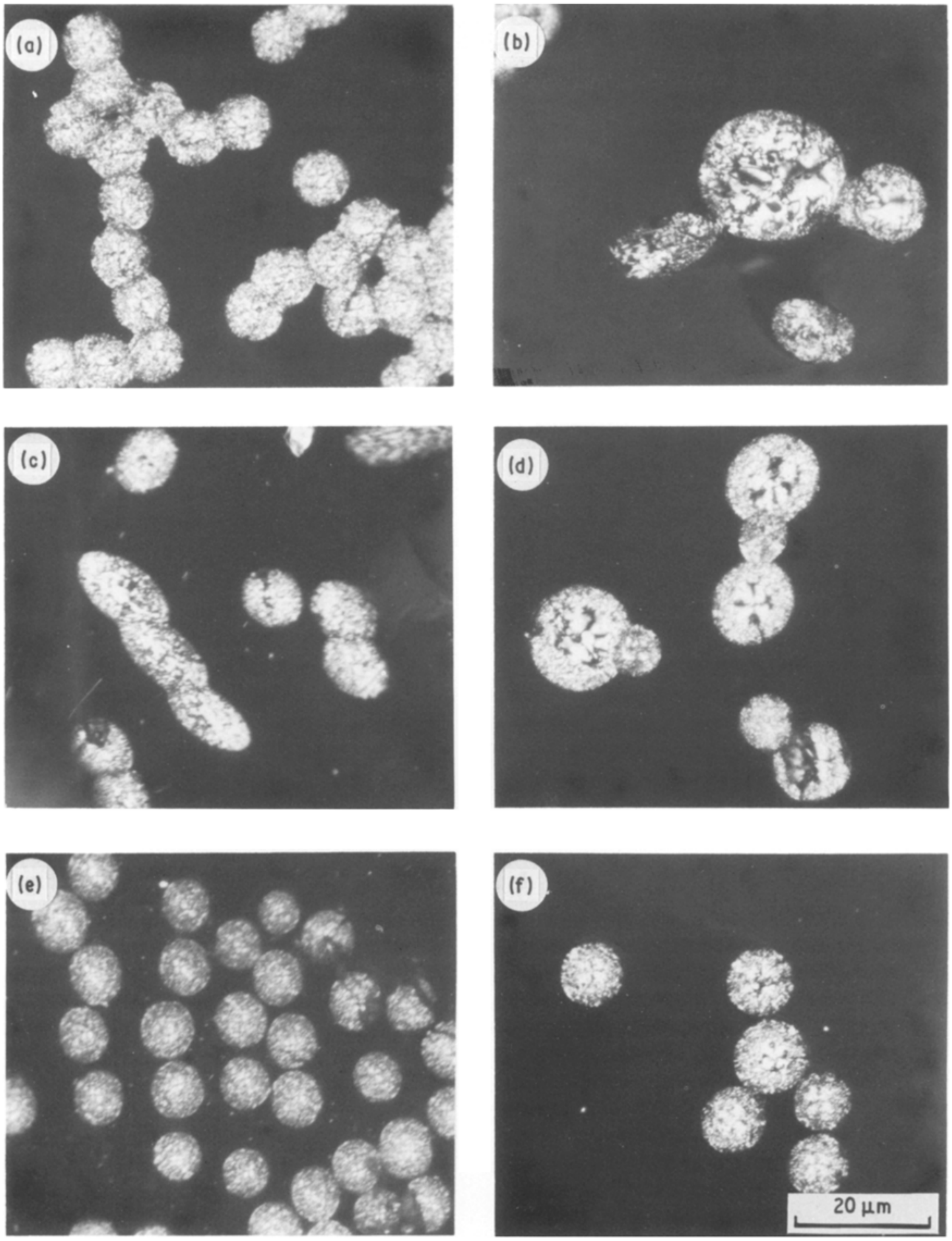


Figure 6 Optical photomicrographs of carbon fibres from mesophase and blend pitch fibres (10% PPO). Oxidation conditions, 5° C min^{-1}, 250° C, 30 min (a) mesophase carbon fibre, (b) blend carbon fibre; – 50 min (c) mesophase carbon fibre, (d) blend carbon fibre; – 70 min (e) mesophase carbon fibre, (f) blend carbon fibre. Carbonization conditions, 10° C min^{-1}, 600° C, 60 min.

but scarcely soluble and remained isotropic in the mesophase pitch, it was spun with the mesophase pitch into small fibrous forms ($< 1\,\mu$m) and distributed homogeneously in the mesophase pitch fibre.

Models of blended pitch and carbon fibres are illustrated in Fig. 11. Such fibrous forms of PPO of a linear polymer may cause the increased strength of the pitch fibre by adhering intimately to the pitch components, as shown in Fig. 11a.

It should be noted that the spinning of PPO from the fused phase is known to be very difficult. Nevertheless, the blended pitch was smoothly spun into excellent anisotropic fibre of $10\,\mu$m diameter, just like the parent mesophase pitch. PPO fused in the mesophase pitch at the spinning temperature, indicating their intimate wetting and very homogeneous dispersion in the mesophase pitch. They are spun together without any discontinuous viscoelasticity, giving fine fibrous forms of PPO in a pitch fibre of $10\,\mu$m, although its solubility in the mesophase pitch is very limited as observed under hot-stage microscopy (Fig. 2d).

The blended pitch fibre was oxidatively stabilized and carbonized in the same manner as those of the

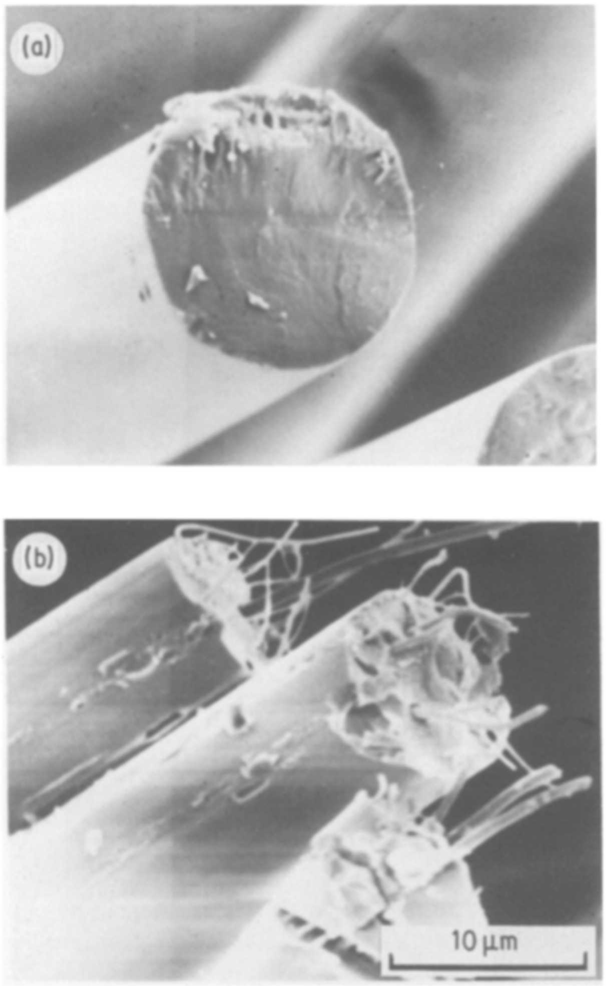


Figure 7 Scanning electron micrographs of pitch fibres after oxidation (5° C min^{-1}, 250° C, 120 min). (a) Mesophase pitch fibre, (b) blend pitch fibre.

parent pitch fibre except that the ether bonds in PPO were lost during oxidation. It is worthwhile to discuss the carbonization behaviour of PPO in the blended fibre. PPO was certainly dispersed homogeneously in the pitch fibre; however, PPO or its derivatives were principally found in the skin area of the fibre after carbonization, as shown in Fig. 11b. PPO or its derivatives should be assimilated into mesophase-derived

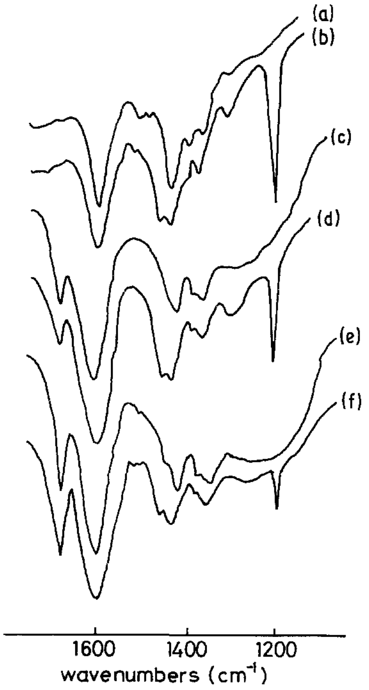


Figure 8 FT–IR spectra of pitch and oxidized pitch fibres. (a) Mesophase pitch fibre, (b) blend pitch fibre (10% PPO), (c) oxidized mesophase pitch fibre (5° C min^{-1}, 250° C, 30 min), (d) oxidized blended pitch fibre (5° C min^{-1}, 250° C, 30 min), (e) oxidized mesophase pitch fibre (5° C min^{-1}, 250° C, 70 min), (f) oxidized blended pitch fibre (5° C min^{-1}, 250° C, 70 min).

carbon through a kind of co-carbonization during the carbonization at the centre of the fibre where the influence of oxidation may be minimum. The mesophase component of high aromaticity with the least oxidative cross-linkage may dissolve PPO-derived molecules during carbonization [16]. In contrast, the mesophase components at the skin of the oxidized fibres cannot assimilate PPO, probably because they are extensively oxidized to be cross-linked together, losing their fusibility [17, 18]. Such observations may indicate the way to define the progress of oxidation in the radial direction of the fibre.

Thus, the blending of PPO into mesophase pitch may solve one of the most severe problems of carbon

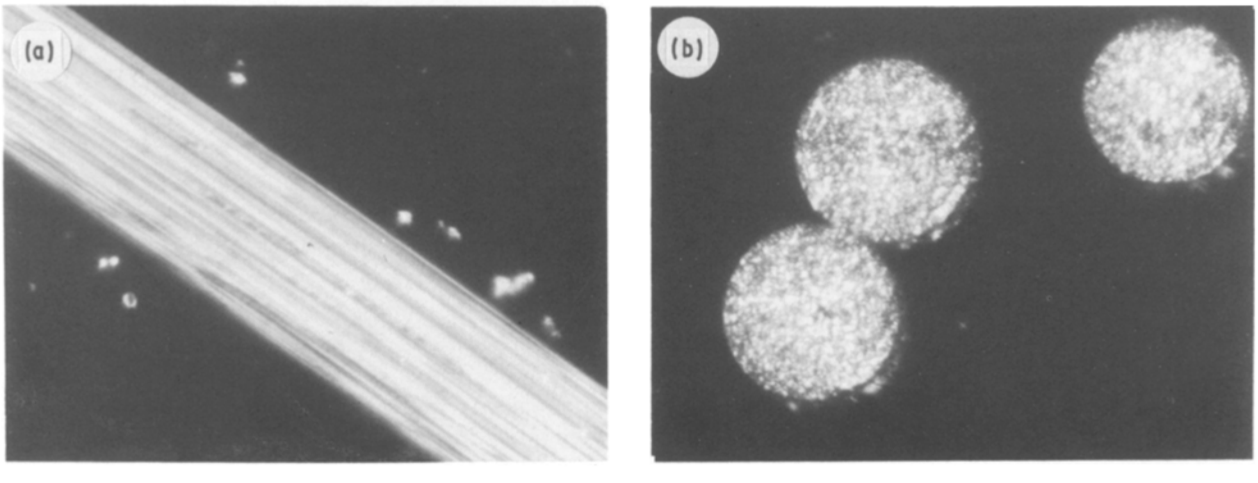


Figure 9 Optical photomicrographs of carbon fibres from (a), (b) mesophase pitch and (c), (d) blended pitch (10% PPO). Oxidation conditions 5° C min^{-1}, 250° C, 120 min. Carbonization conditions 10° C min^{-1}, 1300° C, 60 min.

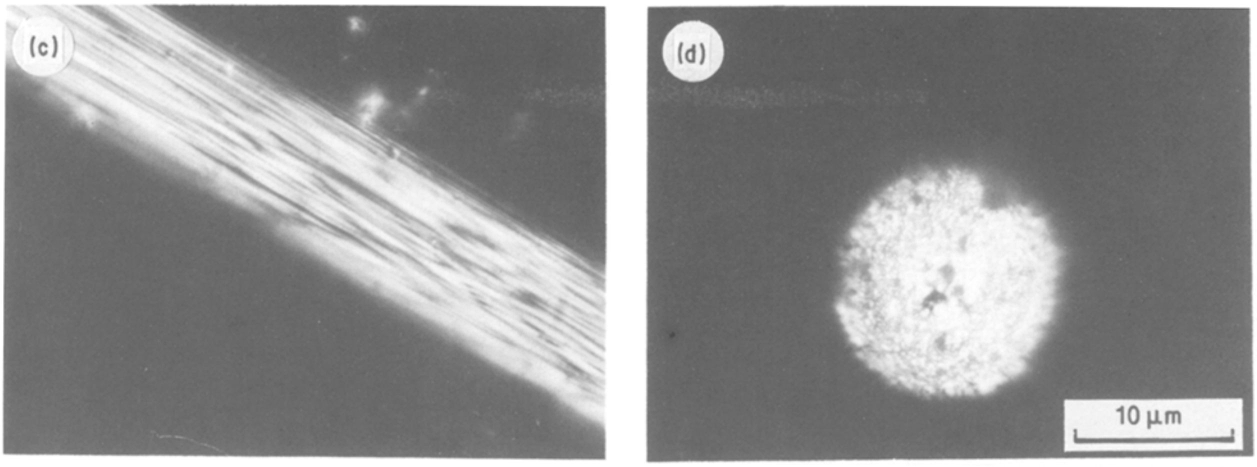


Figure 9 Continued.

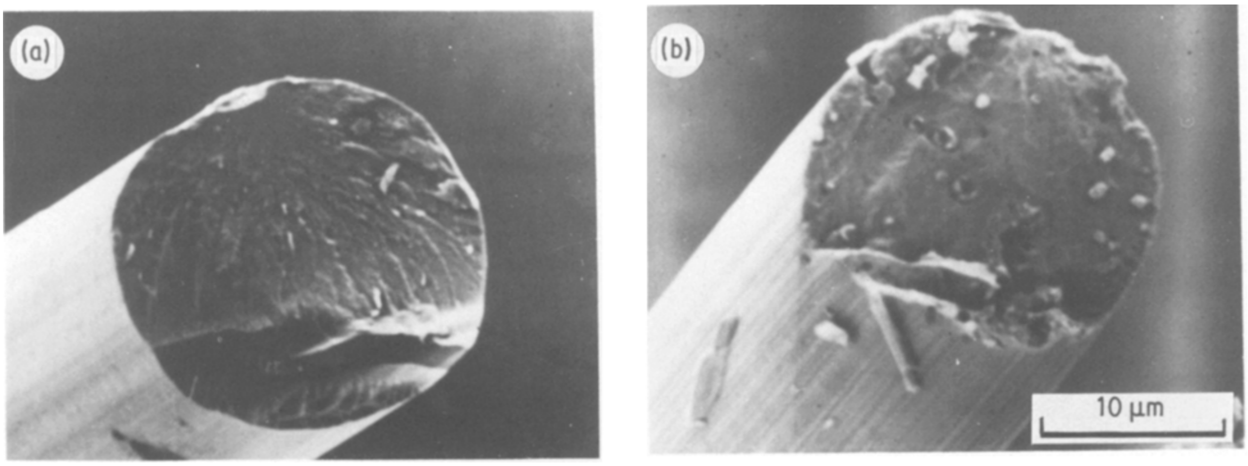


Figure 10 Scanning electron micrographs of carbon fibres from (a) mesophase pitch, and (b) blended pitch (10% PPO). Oxidation conditions 5° C min^{-1}, 250° C, 120 min. Carbonization conditions 10° C min^{-1}, 1300° C, 60 min.

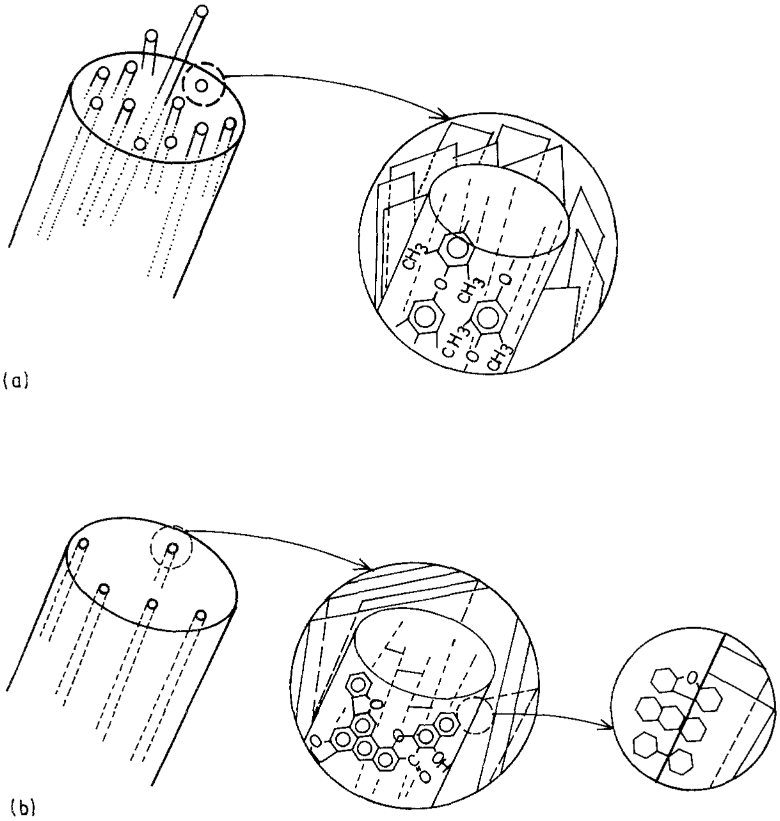


Figure 11 Models of two-phase pitch and carbon fibres. (a) pitch fibre, (b) carbon fibre.

fibre production: improving the handling properties of the pitch fibres.

Unfortunately, the mechanical strength of the resultant carbon fibre was slightly decreased by blending. Many pores formed due to the partial decomposition of PPO on spinning, may deteriorate the mechanical properties of the resultant carbon fibre. Better atomization of PPO and spinning at a lower temperature may solve the problems. It is also worthwhile to search for better polymers.

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