

A microscopic study on the oxidative stabilization of a coal-tar-based mesophase pitch and its blends with PVC pitch

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Coal-tar-based mesophase pitch and its blends with PVC pitch at 5 or 10 wt% were oxidatively stabilized at 230, 270 and 300°C for variable periods to clarify the progress of stabilization and the effects of the blending with PVC pitch on the stabilization reactivity. PVC pitch which was prepared from PVC by heat-treatment at 420°C for 2 h enhanced the stabilization reactivity of whole pitch fibres to shorten the stabilization time to a half of that for mesophase pitch alone. PVC pitch carrying considerable amounts of aliphatic components and large molecular weight may initiate, as a trigger, the stabilization reactions of mesophase constituent molecules. Carbonized fibres of 30 µm diameter after stabilization at 270 and 300°C exhibited a skin-core structure, while fibres of 10 µm diameter showed no skin-core structure, indicating a homogeneous progress of stabilization in the radial direction of the latter fibres. Lower stabilization temperatures provoked no skin-core structure even in the thick fibres. The rate of core diminishing became relatively slower in the later stage of the stabilization, even when the reactivity of the pitch fibres was enhanced by blending with PVC pitch and using a higher stabilization temperature. The diffusion of the oxidant and stabilization reactivity of the pitch fibres are discussed comparatively.

1. Introduction

The preparation of pitch-based carbon fibres (PBCFs) of high performance has been extensively investigated as being a strategic material in the near future [1, 2]. Although the manufacturing principles have been established [3-6], their practical use is now encountering several problems in the attempt to reduce the cost to an acceptable one for wide application [7]. The tedious procedure and low yield in the preparation of precursor pitch, unstable spinning, and slow stabilization of pitch fibres are most critical [8, 9]. The stabilization has been performed by the air-oxidation of pitch components [9-12]. The rate is very slow because of the low reactivity of high aromatic constituents at the oxidation temperature, which is restricted by the softening point of the pitch [12-14]. It is most desirable to accelerate this step, based on its mechanistic understanding. White and Sheaffer [15], Stephens and Diefendorf [16] and some other authors [17] have studied the problem by determining the required content of oxygen for complete stabilization and the influence of oxygen diffusion on the progress of stabilization. However, recent practical preparations of the fibres indicate a significant difference in the stabilization time required for petroleum- and coal-tar-based mesophase pitches, suggesting the importance of chemical reactivity in the step.

The present authors have reported some merits of

blending the foreign pitch with polymeric substances for the improvement of spinnability and the strength of the as-spun pitch fibre [13, 17].

In the present study, the authors intended to accelerate the stabilization reactivity of coal-tar-based mesophase pitch by blending with polyvinylchloride (PVC) pitch, which was freely miscible with the parent mesophase pitch, maintaining its liquid crystal nature [13]. Since the PVC pitch carries more aliphatic structures than mesophase pitch as reported previously [14], a higher reactivity during oxidation was expected as a result of the blending.

The mechanism of the stabilization reaction was also studied microscopically along the radius direction of the pitch fibre by varying the stabilization temperature, time and composition of the pitch as well as its diameter (10 to 30 µm). The formation of skin-core structure and the diffusion of the oxidant through the skin are discussed on the basis of the results.

2. Experimental procedure

Coal-tar-based mesophase pitch used in the present study was prepared from a (Quinoline Insoluble fraction) QI-free coal-tar pitch after heat-treatment with tetrahydroquinoline (THQ). PVC pitch, which was completely miscible with coal-tar-based mesophase pitch, was prepared by the heat-treatment of a

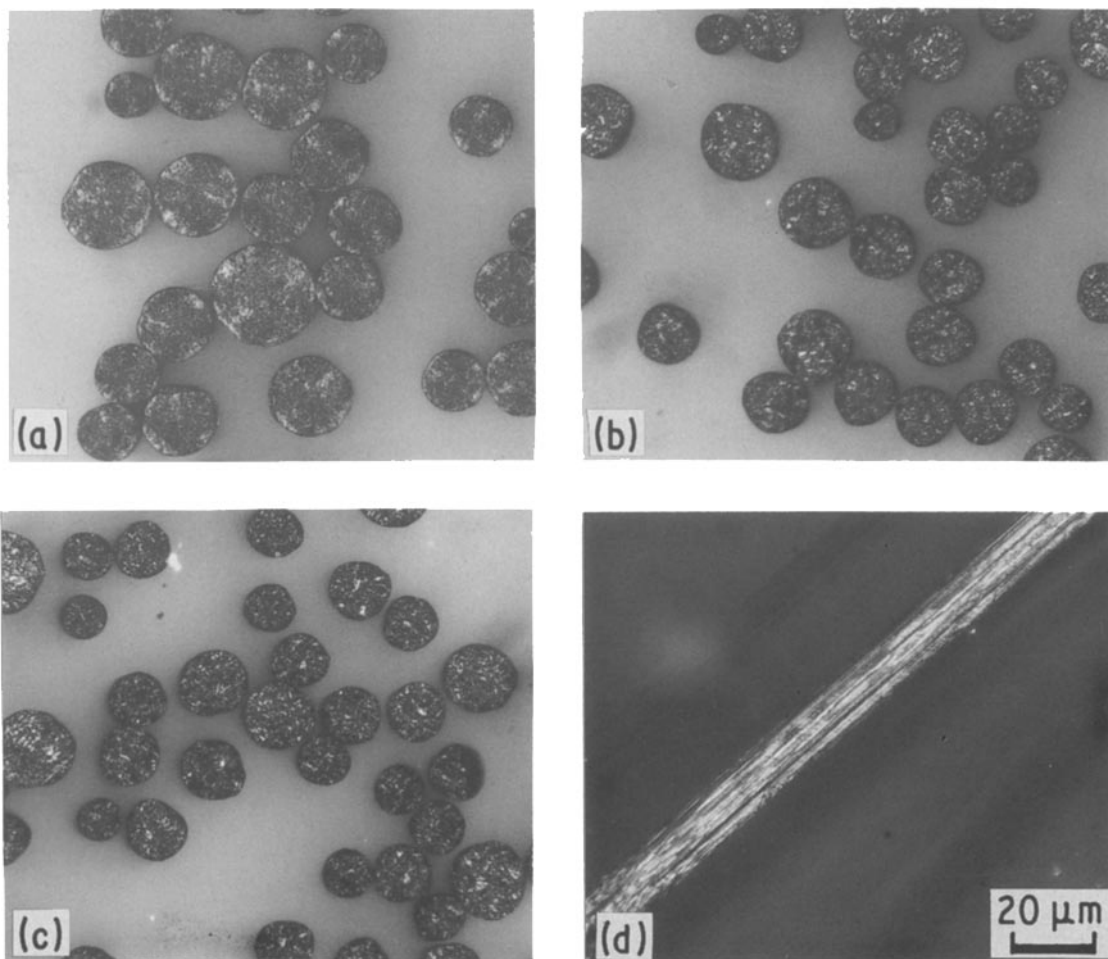


Figure 1 Optical microphotographs of mesophase and its blends with pitch fibres: (a) MP, (b) PVC-5, (c) PVC-10, (d) MP (longitudinal section).

commercial-grade PVC at 420°C for 2 h with a heating rate of 10°C min⁻¹ [13, 14].

Mesophase pitch (MP) and PVC pitch (PVC-P) were blended at 360°C for 10 min with a heating rate of 5°C min⁻¹ in a glass container (30 mm diameter, 300 mm length) heated in a vertical electric furnace.

Mesophase pitch and its blends with PVC pitch at 5 or 10 wt % were spun into fibres from the spinneret ($L/D = 1$, $D = 0.4$ mm where L and D are the length and diameter of the spinneret, respectively) by applying pressurized nitrogen (0.1 to 0.3 kg cm⁻² G).

Bundles of pitch fibres from the mesophase pitch and its blends (the amount of pitch is ca. 0.2 g) were stabilized under an air flow at 230, 270 and 300°C for variable periods. The heating rate to the stabilization temperature was 5°C min⁻¹.

Stabilized fibres were further carbonized to form carbon fibres under a nitrogen flow at 600°C for 1 h with a heating rate of 10°C min⁻¹ in a glass container (30 mm diameter, 600 mm length) heated in a vertical electric furnace.

After mounting in a resin and conventional polishing, pitch, stabilized and carbonized fibres were observed under a polarized-light microscope (Leitz) to examine the changes of shape and adhesion of the fibres during stabilization and carbonization. The morphology of fibres carbonized at 1300°C for 1 h with a heating rate of 10°C min⁻¹ was also observed

in detail with a scanning electron microscope (Jeol JSM-25S).

3. Results

3.1. Spinning of mesophase pitch and its blends with PVC pitch

Although the diameter of the fibres fluctuated from 10 to 30 μm, MP and its blends with PVC-P at 5 and 10 wt % (PVC-5 and 10, respectively) were smoothly spun at 350°C. Figs 1a to c show transverse sections of as-spun fibres from MP and its blends. Regardless of the blending, the fibres showed mosaic anisotropy (the unit size was about 0.5 μm in diameter), of which the reflectance was rather weak. The orientation of anisotropic units was difficult to distinguish.

Fig. 1d exhibits a longitudinal section of the MP fibre, where anisotropic lines were beautifully oriented along the fibre axis.

3.2. Stabilization reactivity of MP and its blends

Fig. 2 shows microphotographs of transverse sections of fibres stabilized at 270°C for 60 and 120 min. The reflectance of oxidized fibres is certainly strengthened over that of parent pitch fibres; however, it is difficult to estimate the progress of the stabilization at the respective stages.

Fig. 3 exhibits transverse sections of fibres (dia-

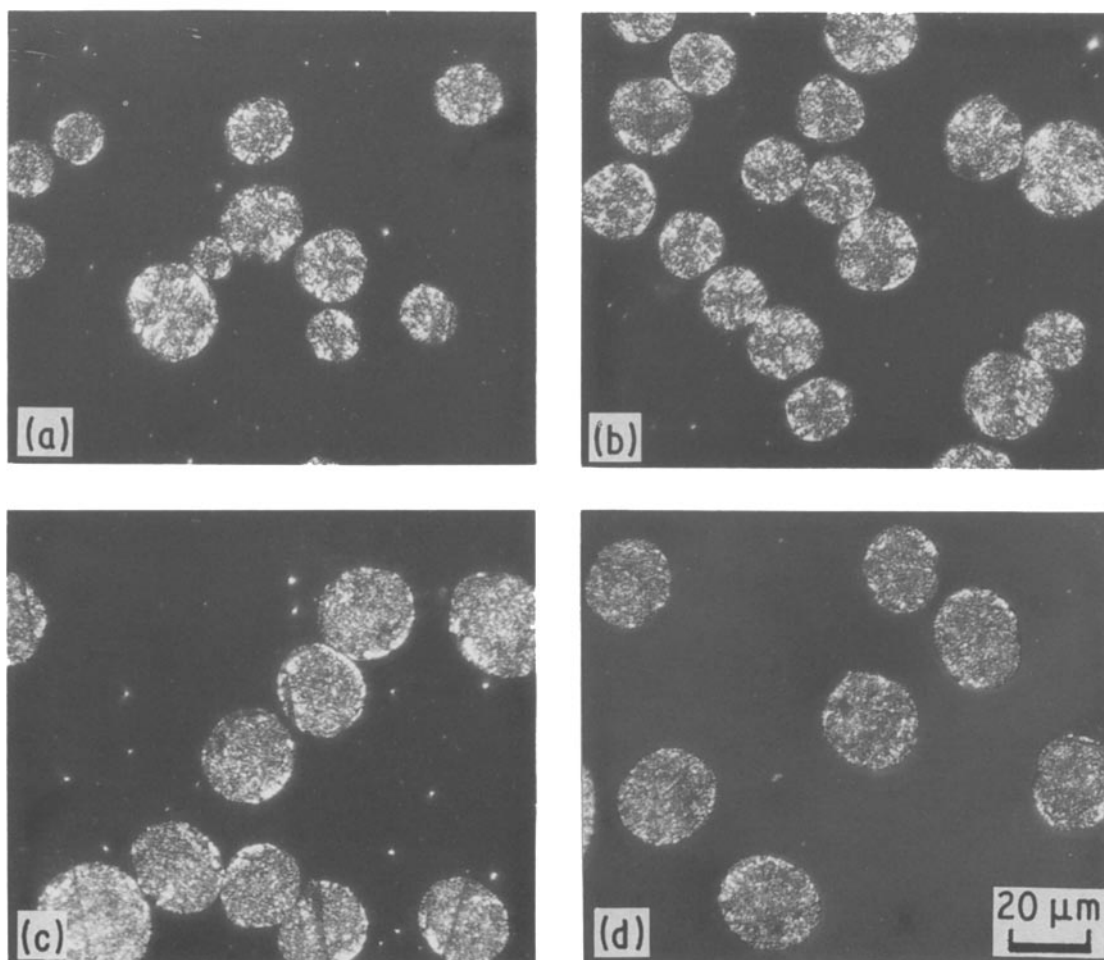


Figure 2 Optical microphotographs of stabilized fibres. Stabilization conditions $5^{\circ}\text{C min}^{-1}$, 270°C . (a) MP, 60 min; (b) MP, 120 min; (c) PVC-10, 60 min; (d) PVC-10, 80 min.

meter 10 to $20\ \mu\text{m}$) carbonized at 600°C for 1 h (heating rate $10^{\circ}\text{C min}^{-1}$) after stabilization at 230°C for various periods of time, where the heating rate was fixed at $5^{\circ}\text{C min}^{-1}$. The mesophase pitch fibres fused completely to give a lump coke of mosaic and flow textures on carbonization, even after stabilization at 230°C for 3 h. The stabilization for 9 h allowed the fibres to keep their fibrous shapes. Fibres fused or adhered with each other for a stabilization time shorter than 9 h, although the mosaic texture of the pitch fibres was maintained even after carbonization.

The addition of PVC pitch at 10 wt % accelerated the stabilization. Fibres kept their fibrous forms almost completely after stabilization at 230°C for 5 h, and perfectly for a time of 6 h.

The higher temperatures of 270 and 300°C accelerated the stabilization reaction to shorten the time required for complete stabilization, as shown in Table I. At 270°C the MP was perfectly stabilized after 120 min, while the addition of PVC pitch at 5 or 10 wt % further shortened the oxidation time required for perfect stabilization, 80 and 60 min being enough to maintain the fibre form of the respective blend. At 300°C , stabilization times of 15 and 12 min for MP and PVC-10, respectively, were satisfactory to prevent their adhesion during carbonization. It should be noted that the central parts of the fibres of large diameter exhibited a coarse mosaic texture after carbonization. The coalescence of anisotropic units

through their fusion must take place even after the stabilization.

In any case, PVC pitch certainly enhanced through its blending the stabilization reactivity of whole fibres which principally consisted of coal-tar-based mesophase pitch. It may play the role of a trigger in oxidative stabilization.

3.3. Stabilization of fibres of different diameters

The carbonized fibres from MP of about 10, 20 and $30\ \mu\text{m}$ in diameter after stabilization at 230°C for 6 and 9 h exhibited a uniformly mosaic texture regardless of the diameter, indicating the homogeneous progress of oxidation in the radial direction of the fibre.

Carbonized fibres of about $30\ \mu\text{m}$ after stabilization at 270°C showed a skin-core texture as shown in

TABLE I Time required for complete stabilization

Stabilization temperature ($^{\circ}\text{C}$)	Material	Time
230	MP	9 h
	PVC-10	6 h
270	MP	120 min
	PVC-5	80 min
	PVC-10	60 min
300	MP	15 min
	PVC-10	12 min

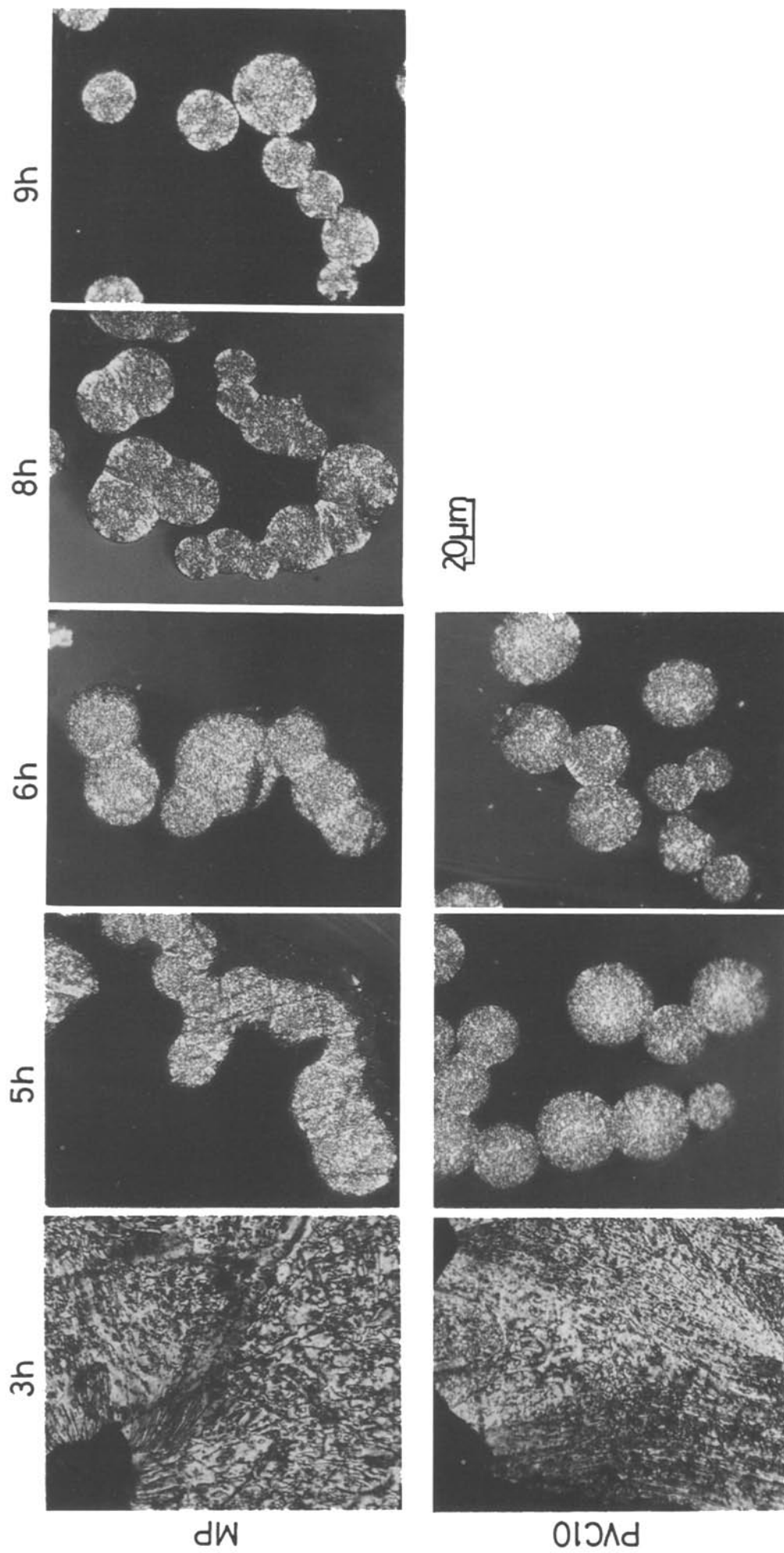


Figure 3 A series of optical microphotographs of carbonized fibres. Stabilization conditions $5^{\circ}\text{C min}^{-1}$, 230°C ; carbonization conditions $10^{\circ}\text{C min}^{-1}$, 600°C , 1 h.

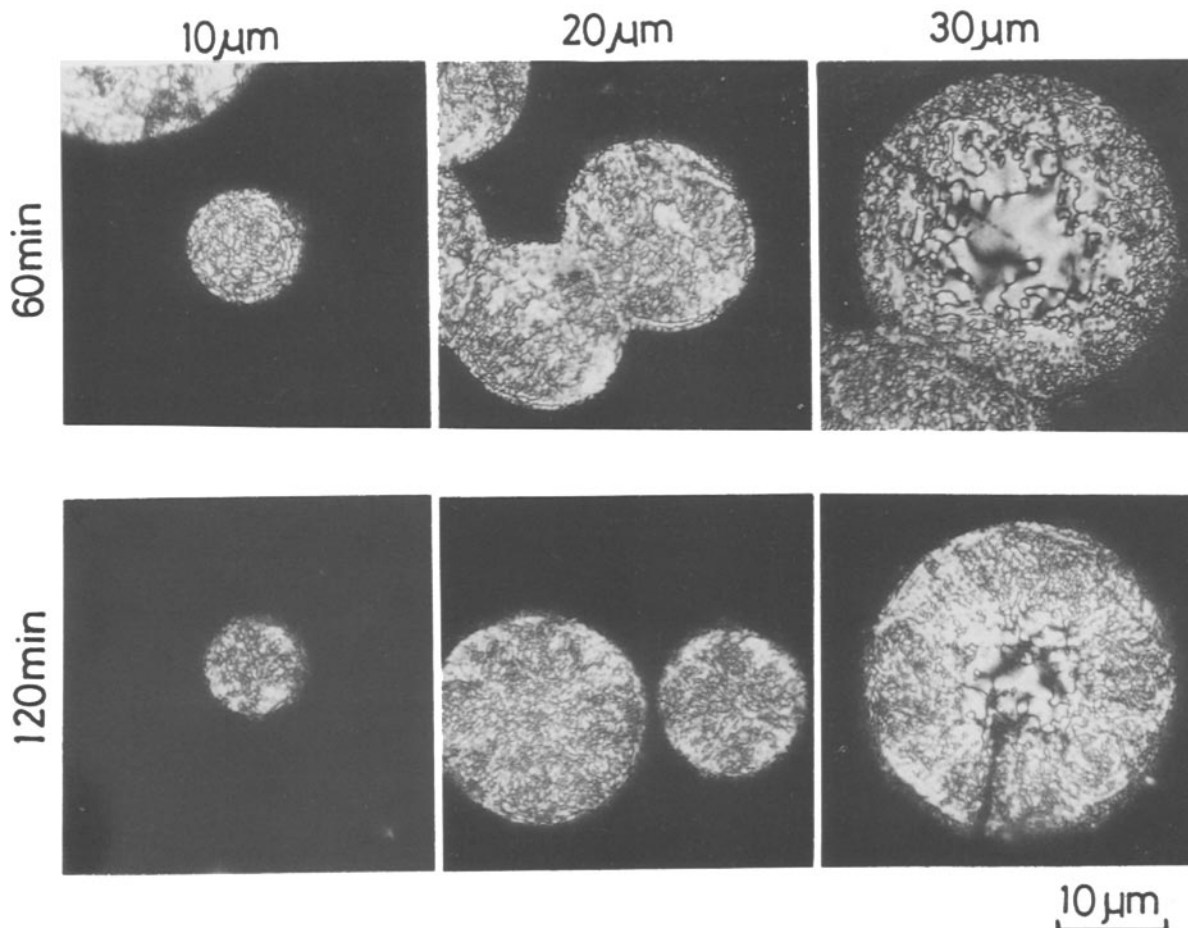


Figure 4 Optical microphotographs of carbonized MP fibres. Stabilization conditions $5^{\circ}\text{Cmin}^{-1}$, 270°C ; carbonization conditions $10^{\circ}\text{Cmin}^{-1}$, 600°C , 1 h.

Fig. 4, where a coarse mosaic texture was observed in the centre of the fibre, while a fine mosaic texture was seen in the skin. Although the longer stabilization time of 2 h (when adhesion among the fibres no longer took place) decreased the area of the coarse mosaic in the centre, an area of about $10\ \mu\text{m}$ diameter still remained. In contrast, fibres of smaller diameters ($< 20\ \mu\text{m}$) showed a homogeneous mosaic texture all through the transverse section.

The carbonized fibres after stabilization at 300°C showed more or less skin-core structure, the area of core and the size of its anisotropic unit being larger with fibres of larger diameter. The largest size of the anisotropic unit indicates complete fusion and reorientation of mesophase constituent molecules in the centre of the fibre to allow their coalescence, although the fibrous shape was maintained. Stabilization at 300°C for 15 min prevented the adhesion of the fibres during carbonization; however, complete stabilization in the whole fibre bundle was not necessarily achieved.

Fig. 5 shows scanning electron microphotographs of MP fibres carbonized at 1300°C . The thinner fibres (about $10\ \mu\text{m}$ in diameter) clearly exhibited a radial structure, with some cracks running along the fibre axis. The thicker fibres (about $20\ \mu\text{m}$ in diameter) exhibited a radial structure in the skin and irregularly oriented flakes of large size in the core, where the coalescence of anisotropic units may take place. It must be noted that the reflected-light polarized microscope had insufficient resolution to distinguish the precise orientation of anisotropic units in the trans-

verse sections of the fibres, even if $1250\times$ magnification was applied.

Fig. 6 shows micrographs of carbonized fibres of the blend PVC-10 after stabilization at 230°C . A definite skin-core structure was found in the fibre of about $30\ \mu\text{m}$. As described above, the fibres from MP alone of the same diameter showed a homogeneous texture. Domain texture was observable in the core (about $20\ \mu\text{m}$ in diameter) of fibres stabilized for 12 min at 300°C . Although the filaments had been stabilized so as not to adhere with other filaments, a skin-core structure was still found in thick filaments.

Thus, the addition of PVC pitch tends to allow skin-core structure in the carbonized fibres of larger diameter, although PVC pitch certainly enhanced the stabilization reaction of whole pitch fibres.

3.4. The rate of stabilization progress in the fibre

The skin thickness is plotted against the time of stabilization in Fig. 7. The skin thickness of MP increased linearly with the time of stabilization at 270°C . The stabilization progressed from the surface at the centre of the fibre at the same rate regardless of the location in the fibre or the extent of stabilization. Similar plots are also illustrated in Fig. 7 for cases where MP and PVC-10 fibres were stabilized at 300 and 270°C , respectively. The skin thickness increased linearly until the skin reached a certain thickness and then the progress became definitely slow. There must be some barriers in the skin to slow down the pene-

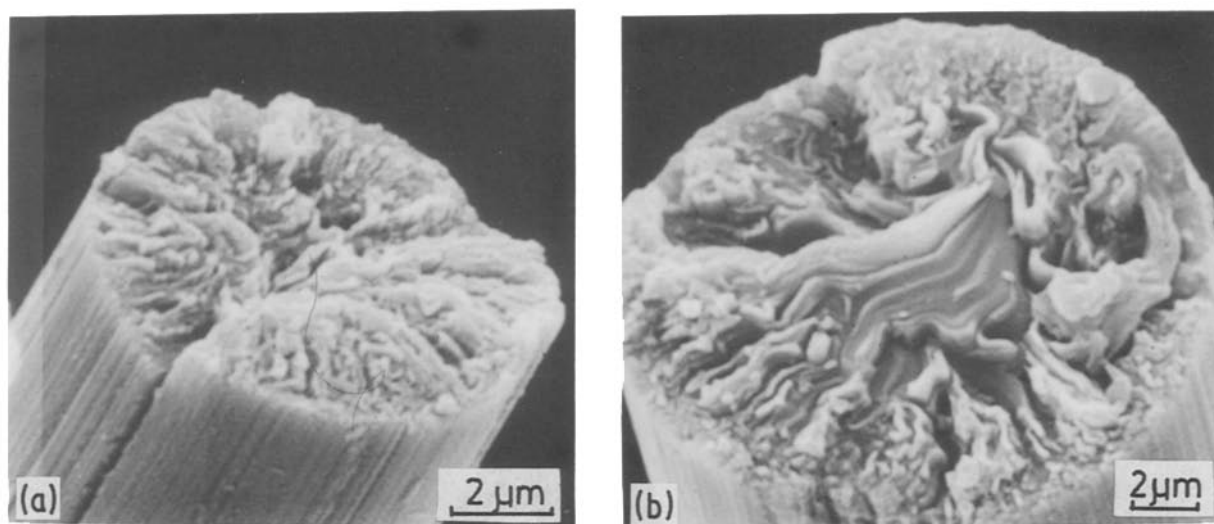


Figure 5 Scanning electron micrographs of carbonized MP fibres of diameter (a) 10 μm , (b) 20 μm . Stabilization conditions 5° C min⁻¹, 270° C, 2 h; carbonization conditions 10° C min⁻¹, 1300° C, 1 h.

tration of the oxidant and the progress of stabilization under such conditions.

4. Discussion

The stabilization of pitch fibres is assumed to be achieved through oxidative condensation, oxygenation and oxidative dehydrogenation of the pitch components of a highly aromatic nature [18] which may remove their fusibility, and/or dissolving ability and maintain their fibrous shape during carbonization. The rates of such chemical reactions are influenced by the partial pressure or concentration of oxidant

within the fibre filaments and the reactivity of the components.

Since the present study as well as some previous reports [11, 13, 14] revealed that the rate of stabilization is strongly influenced by the pitch precursor, the diffusion rate of oxygen was not the sole influence on the rate of stabilization. The micropore structure of the pitch fibre can be assumed to be much the same regardless of the precursor. The chemical role of the additive during the stabilization process is not yet fully clarified in the present study. Nevertheless, the increased aliphatic components and larger molecular

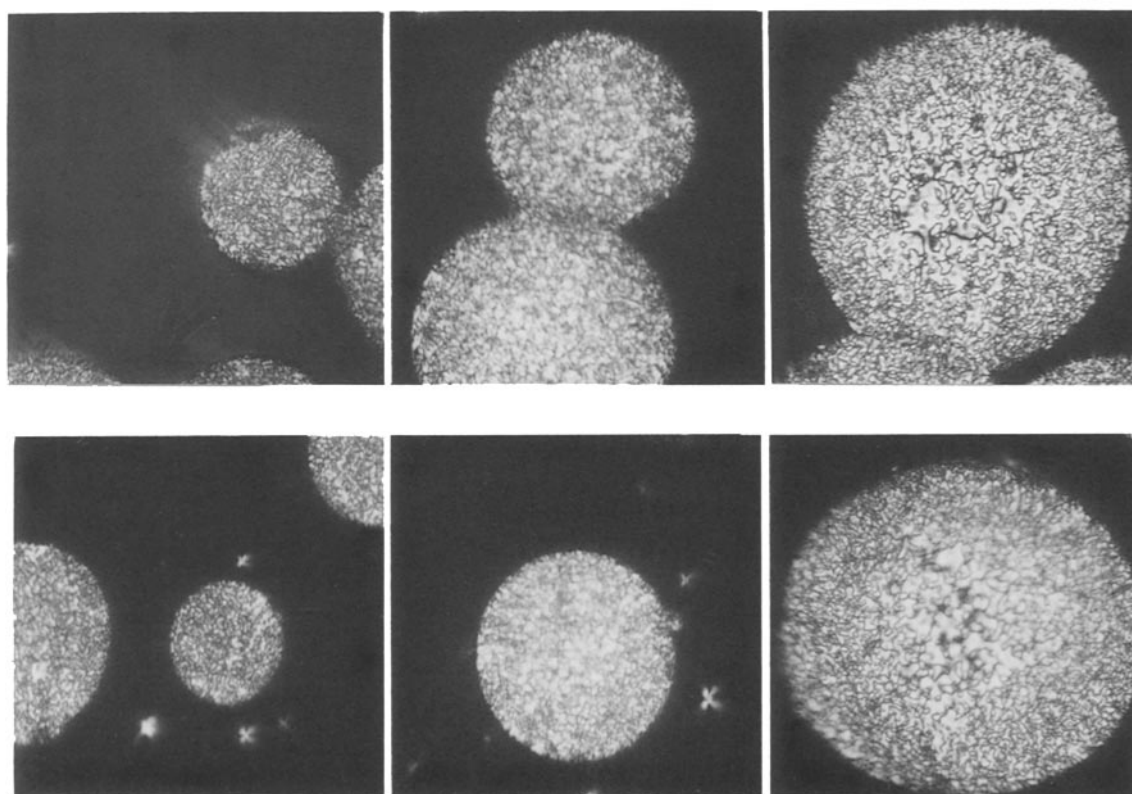


Figure 6 Optical microphotographs of carbonized PVC-10 fibres. Stabilization conditions 5° C min⁻¹, 230° C; carbonization conditions 10° C min⁻¹, 600° C, 1 h.

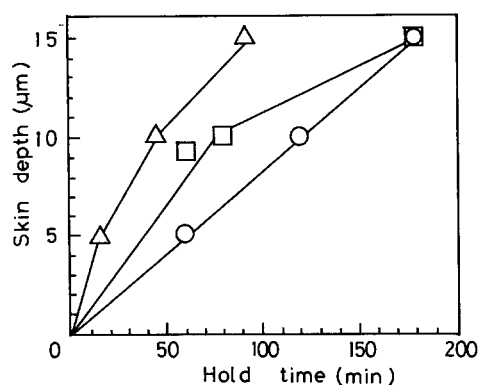


Figure 7 Changes of skin thickness in carbonized fibres. (O) MP carbon fibre stabilized at 270°C; (Δ) PCV-10 stabilized at 270°C; (□) MP stabilized at 300°C.

size of PVC pitch [13] may provide a high reactivity in oxidative stabilization to shorten the time of stabilization. PVC pitch components are well dispersed in the mesophase pitch components, so they can initiate the oxidation of the latter components or react with the latter components in the surroundings to achieve a high stabilization reactivity of the whole pitch components in the fibre through their coupling reactions. More reactive additive can further accelerate the stabilization.

The present study revealed the formation of skin-core structure in carbonized fibres when the stabilization was not sufficiently performed in the centre of the filament. The core of such a fibre appears to fuse, and its anisotropic units coalesce to produce larger anisotropic units surrounded by fine mosaics in the skin, while the skin stays unchanged in its texture. Such a skin-core structure suggests that the oxidative reaction takes place first at the surface of the fibre and penetrates into the core. The diffusion of oxygen may influence the reaction rate, especially in the centre region of a thick fibre.

The area of the core observed in non-adhered fibres tends to be larger when the stabilization temperature is high or reactive PVC pitch is added. In other words, a thin skin is enough to hold the fibrous shape, suggesting its deep stabilization. Whether skin-core structure is formed or not is dependent basically upon the relative rates of diffusion and oxidative reactivity, of which the activation energies are usually very different (the energy of the latter reaction is much larger than that of the former). Hence the skin-core structure tends to be formed at higher stabilization temperatures where the latter reaction becomes more rapid. The higher reactivity provoked by PVC pitch leads to the same trend.

High reactivity in the skin at high temperatures or by blending may cause more consumption of oxygen and extensive stabilization in the skin, to send less oxygen to the core. Extensive stabilization may remove the adhesion ability of a fibre even if the skin is thin and the core is still fusible during the carbonization. In contrast, the oxidation is slow enough at a low temperature of 230°C even when PVC pitch is added, so that a skin-core structure is never observable regardless of the diameter of the fibre.

Skin-core structure is never observed in thin fibres of diameter less than 10 μm, under any stabilization conditions examined in the present study. Thus, the oxygen appears to penetrate freely into this depth of fibre. Some diffusion barriers may be formed to prevent the penetration of oxygen beyond this depth, since skin-core structure is observable in fibres of 20 μm diameter according to the conditions. The second point relates to the reduced rate of disappearance of core at the latter stage of stabilization as shown in Fig. 7. The reduction is definite when MP and blended pitch are stabilized at 300 or at 270°C, respectively. Their extensively oxidized structure which contains firm cross-linkages may retard the diffusion of oxygen.

5. Conclusions

The principal conclusions on the stabilization of mesophase pitch-based fibres obtained in the present study are as follows:

1. The rate of the stabilization was strongly influenced by the composition of the pitch and the temperature. Blended PVC pitch accelerated the stabilization of the whole pitch fibres.
2. Restricted stabilization at the surface of a fibre allowed maintenance of the fibre shape during carbonization of the stabilized fibre, forming a skin-core structure in the carbonized fibre.
3. The rates of oxidation and oxidant diffusion competed when the reactivity of the pitch and the stabilization temperature were both high, tending to give a skin-core structure in the carbonized fibre.
4. The oxidant diffusion become much slower at the centre of a thick fibre, providing a skin-core structure in the carbonized fibre.

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