The Creation of a Skin-Core Structure in Petroleum Derived Mesophase Pitch Based Carbon Fiber

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Stabilization of a petroleum-derived mesophase pitch (P-MP) fibers was investigated in order to create a skin-core structure in the carbonized fibers. The pitch fibers were either oxidatively stabilized at 270 °C in air or 10 vol% O_2 for short periods, or oxidized in air for 15 min and successively extracted by tetrahydrofuran (THF) for 30 min. A skin-core structure could be observed in the carbonized fibers under a polarized-light microscope or SEM. The relationship between the oxidative reactivity of P-MP fiber and creation of a skin-core structure, and the effect of solvent extraction for the creation are discussed according to the results.

Mesophase pitch-based carbon fiber has been recognized to be a prominent filler for advanced composites.[1–3] However, problems concerning its quality and cost still remain.

There may be several lines of approach to solve these problems. The present authors have reported that[4–7] carbonization under strain of a coal tar-based mesophase pitch fiber significantly improved the mechanical strength of the carbon fiber when the stabilization was controlled in such a way that the fiber central area was fused to form a core, whereas the fiber surface area was sufficiently stabilized so as not to adhere to each other during carbonization. Such a manner of stabilization reflects a steep gradient of oxidation along the fiber radius, leading to a skin-core structure in the carbonized fiber, where the skin and the core exhibit a mosaic and a domain texture, respectively, under a polarized-light microscope.

An oxidation gradient has been introduced by rapid heating and a short stabilization period at higher temperatures, such as 350 °C,[4] by stabilization in a lower oxygen concentration,[5,6] and by two-step stabilization, short oxidation, and solvent extraction.[7]

In the present study, by controlling the stabilization conditions, the creation of a skin-core structure was attempted into petroleum (FCC-decant oil) derived mesophase pitch, which is practically believed to be a more suitable precursor than that derived from coal tar.[3,8–13] The pitch has been reported to show a higher reactivity for oxidative stabilization due to its greater number of alkyl and naphthenic groups.[14,15] Higher reactivity may be favorable for creation when competition between the diffusion of oxygen and oxidation governs the oxidative gradient along the pitch fiber radius. However, higher reactivity may lead to rapid oxidation into the core of a thin fiber (ca. 10 μm in diameter) within a short period. No fusion is allowed at the core, even if an oxidation gradient is established.

Table 1. Properties of the Petroleum Derived Mesophase Pitch (P-MP)

Pitch	H	C	N	Diff.	H/C	S.P.[b]	A.P.[c]	Solubilities/%[d]		
	wt%					°C	%	BS	BI-PS	PI
P-MP	4.6	93.9	0.2	1.3[a]	0.59	250	100	42	12	46

a) Ash: 0.2, Sulfur 0.7. b) Softening point by hot stage. c) Anisotropic percentage. d) BS: Benzene soluble. BI-PS: Benzene insoluble/pyridine soluble. PI: Pyridine insoluble.

Table 2. Proton and Carbon Distribution by ^{1}H NMR and ^{13}C NMR

Pitch	Haro	H_α	H_β	H_γ	Fa(H)[a]	
P-MP	62	25	12	1	0.88	
Caro 4.1	Caro 4.2	Caro 4.3	Caro 3	Cali 2	Cali 1	Fa(C)[b]
3.7	13.1	23	52.6 (23.6)	3	5	0.92

a) Proton distribution by ^{1}H NMR. b) Carbon distribution by ^{13}C NMR. Aromatic carbon. Caro 4.4: Internal benzonaphtenic carbon (150.1—138.0 ppm). Caro 4.2: Substituted carbon (138.0—132.1 ppm). Caro 4.3: Internal carbon (132.1—127.0 ppm). Caro 3: Unsubstituted carbon (127.0—116.9 ppm). Aliphatic carbon. Cali 2: Methylene carbon (54.2—21.9 ppm). Cali 1: Methyl (21.9—8.5 ppm).

Experimental

Some properties and structural parameters (NMR) of the petroleum derived mesophase pitch (P-MP) used in the present study are summarized in Tables 1 and 2, respectively.

The pitch was spun into pitch fibers at 315 °C, at which temperature its viscosity was 500 poise. The pitch fibers were oxidatively stabilized at 270 °C for various periods in air or in a diluted oxygen atmosphere (10 vol% O_2) at a heating rate of 5 °C min^{-1}. After oxidative stabilization, some fibers were successively extracted with tetrahydrofuran (THF) in Soxhlet for 30 min.[7] The stabilized fibers were carbonized at 600 °C for 1 h and, subsequently, calcined at 1300 °C for 1 h. The heating rates for both steps were 10 °C min^{-1}.

The oxygen uptake in the stabilized fibers was calculated according to elemental analyses. The oxygen distribution along the radius of thick fiber (30 μm in diameter) was measured by EPMA (Shimadzu, electron probe microanalyzer EPM-810).[16] The fibers stabilized at 270 °C for a holding time of 0 or 45 min were mounted in the polypropylene resin at 200 °C for 1 min. The mounted fibers were carefully cut with a sharp knife at room temperature to obtain a flat cross-sectional surface. The fiber surface was coated with carbon using a high-vacuum evaporator (Hitachi, HVS-5GB). The electron beam accelerated by a voltage of 15 kV was irradiated to such a surface by scanning along the fiber diameter with a step of 1 μm. The sample electric current due to the irradiation was 0.05 μA. The intensity of the characteristic X-rays due to oxygen (2.3608 nm wavelength) was recorded as counts for 10 sec at 30 points along the fiber diameter. The counts were then converted into the average oxygen content based on elemental analyses.

After mounting in a polyester resin and conventional polishing, carbonized fibers were observed under a polarized-light microscope (LEITZ Othoplan) in order to examine the adhesion and texture of the filaments. The cross-sectional morphology of the carbonized fiber was observed by SEM (JEOL-25S).

Results

Oxidative Stabilization of P-MP Fiber in Air. Figures 1 (a) to (c) show the microphotographs of the carbonized P-MP fibers after stabilization at 270 ° for 15, 20, and 30 min, respectively. A short holding time of 15 min left a few adhesions among the filaments; they exhibited a distinct skin-core structure (Fig. 1 (a)). The adhesion was reduced by increasing the holding time to 20 min. The skin-core structure could still be observed in most of the filaments (Fig. 1 (b)). A further increase in the time to 30 min completely eliminated the adhesion, leading to a disappearance of the skin-core structure (Fig. 1 (c)).

Figures 2 (a) to (c) show cross-sectional morphologies of the fibers oxidatively stabilized, carbonized and further calcined at 1300 °C. All filaments show a radial-like cross-sectional morphology in the skin, where a marked increase in its thickness with the stabilization time could be observed. During the initial stage of stabilization (15 min) carbon planar sheets were densely stacked, forming a broad core (3.5—4.0 μm in diameter), as shown in Fig. 2 (a). A fusion of mesogens during carbonization is suggested. However, the diameter of the core was reduced to 2.5—3.0 μm by increasing the stabilization time to 20 min (Fig. 2 (b)); finally, almost no difference between the skin and the core was observed in Fig. 2 (c), where stabilization had come to completion. Thus, creation was possible only whithin a narrow range of stabilization times under the specified conditions.

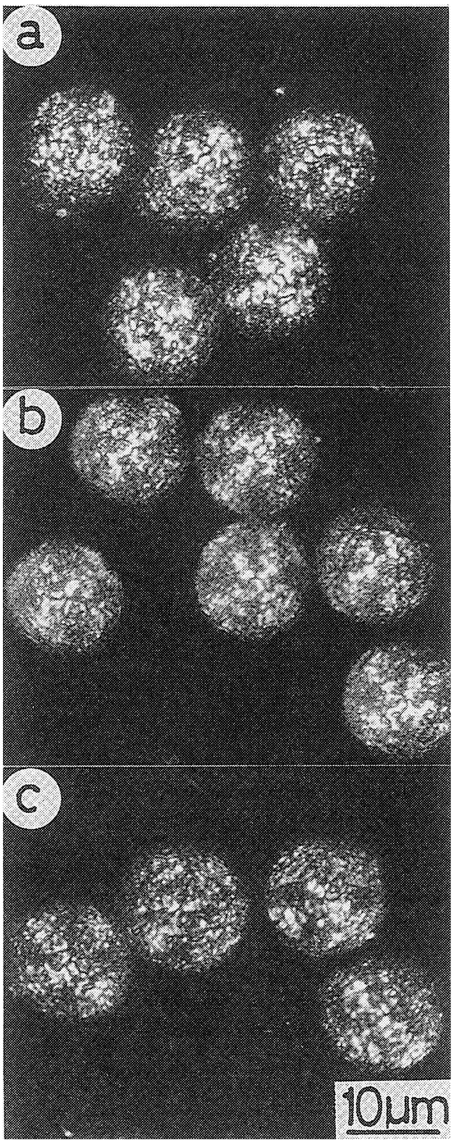

Fig. 1. Microphotographs of carbonized P-MP fibers. Stabilization: 5 °C min^{-1}, 270 °C in air for (a) 15, (b) 20, and (c) 30 min. Carbonization: 10 °C min^{-1}, 600 °C, 1 h.

Oxidative Stabilization in 10 vol% O_2. The pitch fibers were oxidatively stabilized in 10 vol% O_2 at 270 °C for 25 and 45 min. Figures 3 (a) and (b) show cross-sectional morphologies of the carbonized fibers.

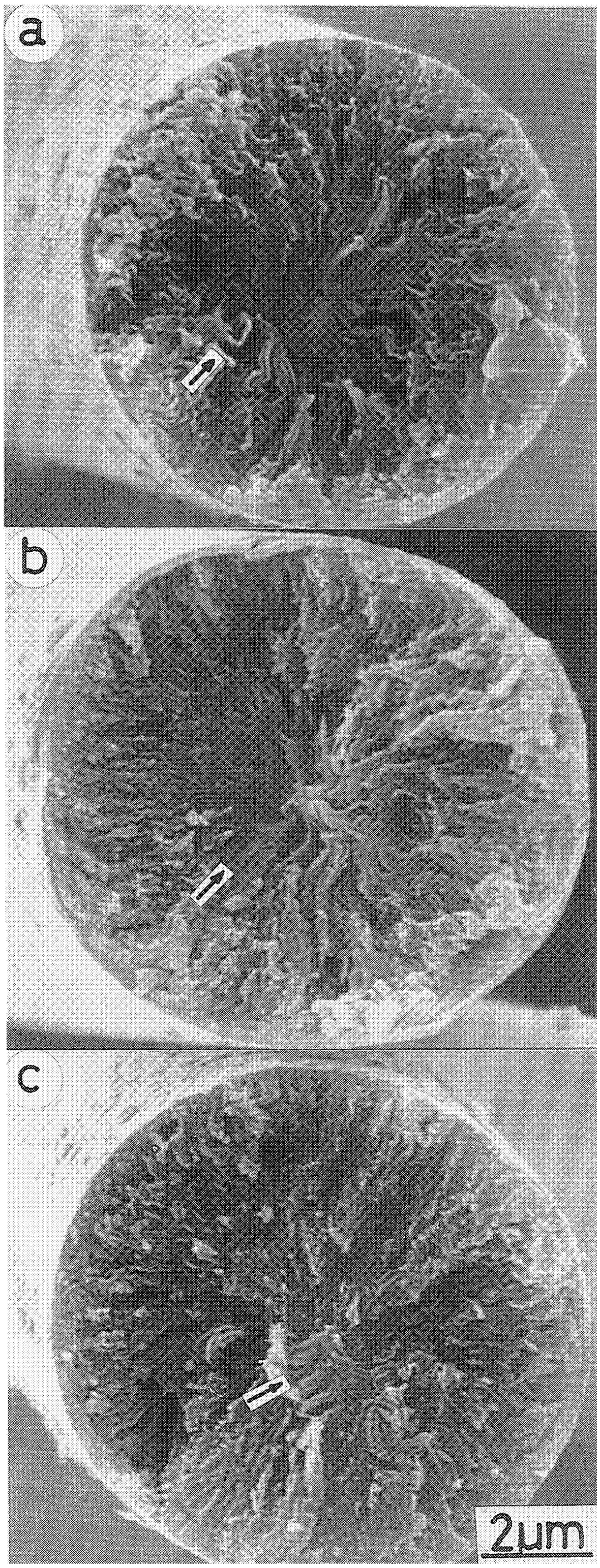

Fig. 2. Cross-sectional morphologies of carbonized P-MP fibers. Stabilization: 5 °C min^{-1}, 270 °C in air for (a) 15, (b) 20, and (c) 30 min. Carbonization: 10 °C min^{-1}, 600 °C, 1 h. Calcination: 10 °C min^{-1}, 1300 °C, 1 h.

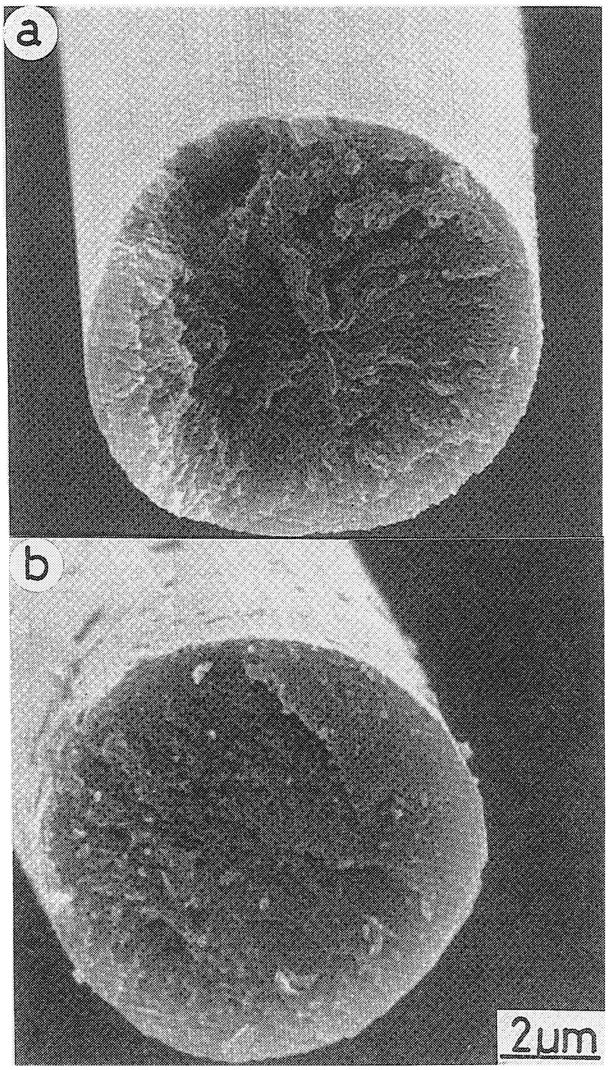

Fig. 3. Cross-sectional morphologies of carbonized P-MP fibers. Stabilization: 5 °C min^{-1}, 270 °C in 10% O_2 for (a) 25 and (b) 45 min. Carbonization: 10 °C min^{-1}, 600 °C, 1 h. Calcination: 10 °C min^{-1}, 1300 °C, 1 h.

The skin-core structure could be created in the fibers without filament adhesion by using 25 min stabilization (Fig. 3 (a)); however, no skin-core structure was observed after the time was prolonged to 45 min (Fig. 3 (b)). Thus, even if in a diluted oxygen atmosphere, the creation of a skin-core structure in P-MP fibers proved to be difficult.

Oxidation and Solvent Extraction Stabilization. The P-MP fibers that oxidatively stabilized at 270 °C for 15 min in air were further extracted with tetrahydrofuran (THF) for 30 min in a Soxhlet. Figure 4 shows microphotographs of the carbonized fibers. A slight adhesion of filaments was observed without extraction (Fig. 4 (a)); however, extraction completely removed the adhesion, leaving a distinct domain texture in the core (Fig. 4 (b)).

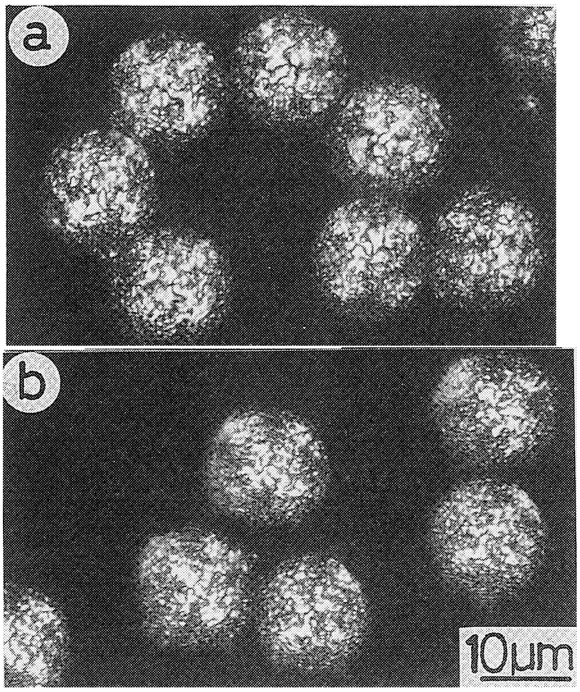

Fig. 4. Microphotographs of carbonized P-MP fibers. Stabilization: (a) 5 °C min^{-1}, 270 °C, 15 min in air without extraction. (b) after successive extraction in THF for 30 min. Carbonization: 10 °C min^{-1}, 600 °C, 1 h.

Figures 5 (a) to (d) show typical morphologies of the carbonized fibers after oxidation and extraction stabilization. All filaments exhibited a distinct skin-core structure. The morphological feature of those fibers revealed difference in the orientation and the size of carbon planar sheets between the skin and the core. Larger carbon planar sheets (around 0.5 µm in width) could be observed in the core (3.5—4.0 µm in diameter). In contrast, very small sheets (less than 0.1 µm) were found in the skin area (2.0—2.4 µm). The sheets in the core became radially oriented in most cases with some folded ones, whereas all of sheets in the skin became oriented radially. The different fusibilities during carbonization at the skin and the core may be responsible for these sheet orientations. It should be noted that a crack running paralled to the fiber axis, which was introduced by the solvent extraction, did not propagate further upon carbonization.

Oxygen Uptake and Distribution in Stabilized Pitch Fibers. Figure 6 shows the oxygen and hydrogen contents in the pitch fibers after stabilization at 270 °C for 10, 15, and 45 min in air. The oxygen and hydrogen contents increased and decreased, respectively, upon increasing the stabilization time. The oxygen content was around 6 wt% after 30 min of stabilization, when the stabilization of the pitch fiber was completed. Such a rapid oxygen uptake may reflect its more naphthenic natures, as revealed in Table 2.

Figure 7 show the distribution of oxygen along the radius of thick fibers (30 µm in diameter) after stabilization at 270 °C for 0 and 45 min in air, and the calculation result for a thin fiber (10 µm). During the initial step of oxidation (270 °C, 0 min), the fiber exhibited a small gradient of oxygen distribution along the radius. In the skin zone (5 µm), the oxygen content was 4 wt% at the surface and 2 wt% at 5 µm from the surface, respectively. The oxygen content at the central zone (beyond 5 µm from the surface) was identical, around 2 wt%.

A steep gradient was introduced in the skin zone within 7 µm from the surface after 45 min stabilization, where the oxygen contents at surface and point 7 µm deep were 6.0 wt% and around 3 wt%, respectively. The oxygen content at the skin zone within 5 µm from surface, on average, increased by 2 wt% for 45 min stabilization, whereas that in the core (beyond 5 µm) only increased by 1 wt%.

When oxygen is assumed to diffuse similarly in the thin fiber (10 µm in diameter), the oxygen content in the center is estimated to be over 4.5 wt% by the time when the skin is sufficiently stabilized by taking up 6.3 wt% of oxygen, and no fusion is expected any more. The diffusion of oxygen to the center from the two surfaces of the fiber should be expected to increase the oxygen content there.

The thick fibers (30 µm in diameter) after EPMA observation were carbonized at 600 °C for 1 h. The pitch fiber which stabilized without a holding time fused completely during carbonization, with no fibrous form being retained at all. The fibers stabilized for 45 min showed a distinct skin-core structure, as shown in Fig. 8. The skin area (5.8—6.7 µm) prohibited any deformation in the fiber form during carbonization, suggesting a sufficient stabilization of the skin. The mesogens fused in the center to give a large domain texture. Thus, thick petroleum fiber provided rather easily the skin-core structure. By comparing the texture along the fiber radius with the oxygen content, their relation could analyzed.

Discussion

The desired skin-core structure was introduced into reactive petroleum mesophase pitch (P-MP) based carbon fibers by selecting very narrow conditions for oxidative stabilization in air or a reduced oxygen concentration (10 vol% O_2), and readily through two-step stabilization by oxidation and solvent extraction. The thermal introduction to the P-MP fiber was possible only in a much narrower range of oxidative conditions to satisfy both no adhesion of the filaments and fusion of the core during carbonization than to the coal tar derived pitch fiber.[4—7]

It may be worthwhile to discuss why the oxidative stabilization alone suffers a narrow window for

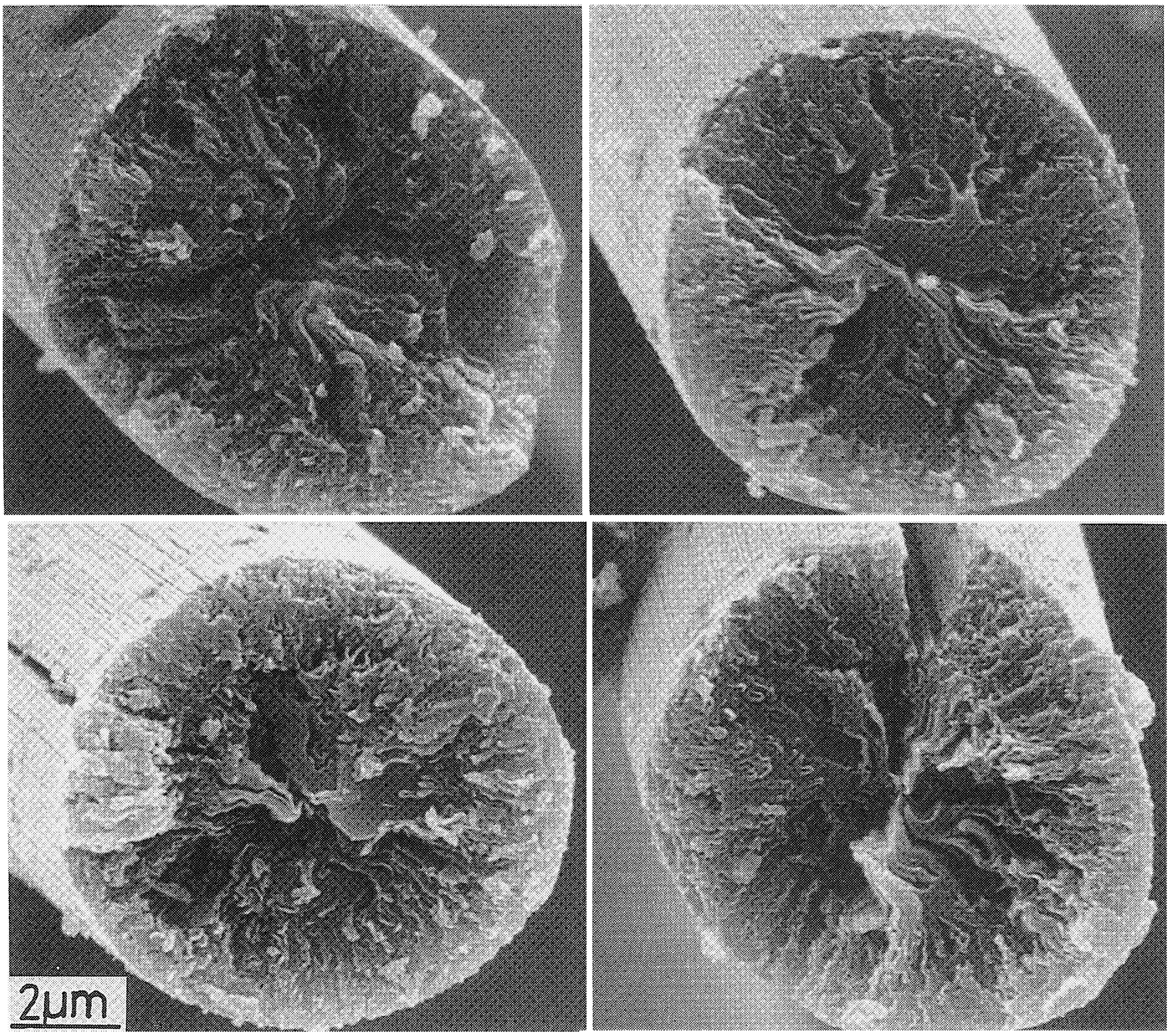

Fig. 5. Cross-sectional morphologies of carbonized P-MP fibers. Stabilization: 5 °C min^{-1}, 270 °C, 15 min in air extraction in THF for 30 min. Carbonization: 10 °C min^{-1}, 600 °C, 1 h. Calcination: 10 °C min^{-1}, 1300 °C, 1 h.

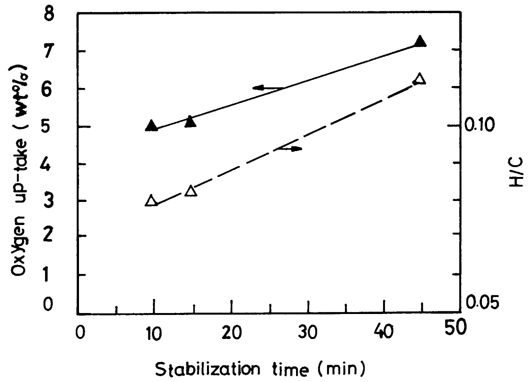

Fig. 6. Oxygen uptake during the stabilization. Stabilization: 5 °C min^{-1}, 270 °C in air.

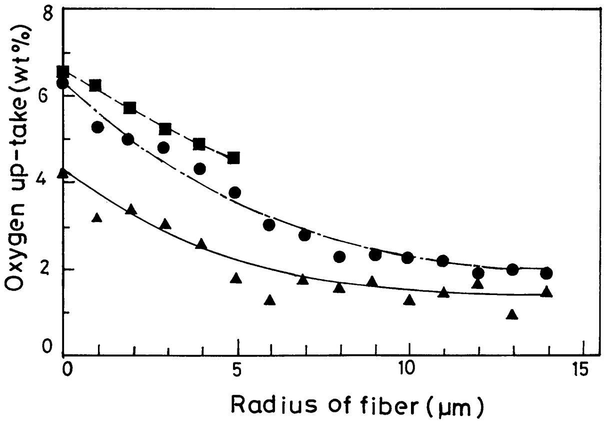

Fig. 7. The distribution of oxygen uptake along the radius of stabilized pitch fibers. ▲: 30 μm fiber, 270 °C—0 min. ●: 30 μm fiber, 270 °C—45 min. ■: calculation oxygen distribution in 10 μm fiber.

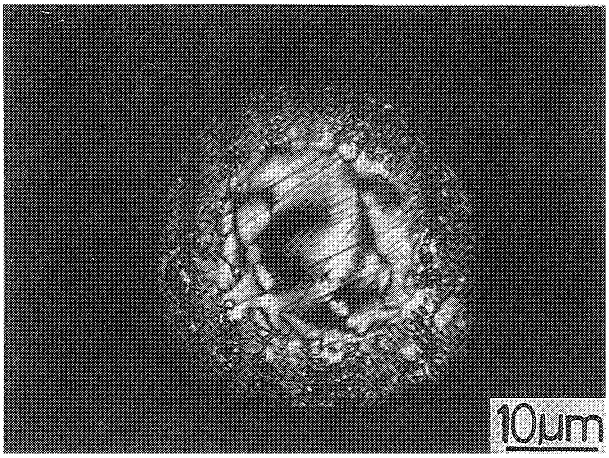

Fig. 8. Microphotographs of the thick (30 μm in diameter) carbonized P-MP fibers. Stabilization: 5 °C min^{-1}, 270 °C for 45 min in air. Carbonization: 10 °C min^{-1}, 600 °C, 1 h.

creating a skin-core structure in thin petroleum fiber in spite of its high oxidation reactivity. The petroleum fiber exhibited more rapid oxygen uptake and complete to the stabilization than a coal tar fiber at the same temperature.[15] The EPMA of the stabilized thick fiber (30 μm in diameter) revealed that such a rapid oxygen uptake led to a steeper gradient of the oxygen concentration in the skin zone (within 5 μm from the surface) along the fiber radius, whereas the oxidation extent was flat in the center (beyond 5 μm). Thus, a definite skin-core structure could easily be introduced in the thick fiber.

The gain in oxygen and loss of hydrogen contents have been attributed to a series of reactions which take place at the naphthenic and alkyl side chain groups uni- or bi-molecularly during stabilization. Oxygenation, oxidation, dehydrogenation as well as cross-linkage formation are assumed.[17–21] The P-MP carries a greater number of aliphatic hydrogen in naphthenes and alkyl side chains (Table 2); in another word, it carries a larger number of reaction sites to tie up oxygen, allowing a rapid increase in the oxygen content, even at the core of the fiber within the stabilization period. Thus, the skin-core structure is obtained only by a very short range of stabilization periods.

In contrast, two-step stabilization could control the fusibilities of the skin and the core separately. Only thin skin is slightly oxidized to be differentiated from the core, and successive extraction by solvent could further complete the stabilization to surround a broad core of unoxidized mesogens. Hence, the skin-core structure can be designed by the oxidation extent, and the adhesion is removed by extracting the fusible components from the skin. Such a stabilization procedure is expected to be very useful for obtaining a skin-core structure in the fiber of higher reactive mesogens derived from naphthenic feedstocks.

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