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Oxygen distribution in the mesophase pitch fibre after oxidative stabilization

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The oxygen distribution in the transverse section of 30 μm diameter mesophase pitch fibres after oxidative stabilization was measured by using EPMA (electron probe X-ray micro-analyser) to clarify the progress of the oxidative reaction and diffusion of the oxidant during the stabilization. Oxygen was distributed in shallow gradients regardless of the stabilization time from the surface to the centre of the mesophase pitch (MP) fibres stabilized at 230° C, suggesting sufficient diffusion of the oxidant to the centre of the fibre at this temperature. In contrast, steeper gradients of distribution were observed in the MP fibres stabilized at 270° C although oxygen up-take of the centre increased steadily with the longer stabilization time to decrease the gradient. Much steeper gradients of the oxygen distribution were observed in the cross-sectioned surface of the fibres stabilized at 300° C for 15 and 30 min. The gradient became much steeper with longer stabilization, suggesting some barriers in the deeply oxidized zone which may block the oxygen diffusion. The PVC-10 fibres, whose reactivity was enhanced by blending PVC pitch of 10 wt %, showed steeper distributions of oxygen after the stabilization at 270° C comparing to those of the MP fibres stabilized under the same conditions. It showed steeper gradient with the longer stabilization time. In conclusion, stabilization at a lower temperature (230° C) allows relatively rapid diffusion of the oxidant into the centre of the MP fibre during rather slow stabilization but, a higher temperature of stabilization (at 300° C) and/or higher reactivity of the mesophase pitch accelerates the oxidation much more rapidly than the diffusion, providing a blockade zone for the oxygen diffusion near the fibre surface. The extensive oxidation may cross-link three dimensionally the mesophase molecules thus allowing no diffusion of oxygen among the molecules. Such diffusion control tends to provide skin–core structure in the carbonized fibre.

It should be noted that fibre thinner than 10 μm showed no skin–core structure. Diffusion within 5 μm from the surface may be rapid under any conditions.

1. Introduction

Although pitch based carbon fibres (PBCF) are expected to be a strategic material in the near future because of their high performance for its weight [1, 2], there remain some severe problems to be solved in order for production on a large scale to be carried out and balance their cost/performance for their broad applications [3]. The stabilization process, which oxidizes the pitch fibre to the thermosetting polymer to prohibit the adhesion and deformation of the filaments during the successive carbonization, is so slow that it is one of the most inefficient steps in the fibre production [4, 5]. This step is also recognized as a strong influence on the performance of the resultant carbon fibres [6]. Hence, an extensive study of this process is most desirable. Diefendorf *et al.* reported that oxygen diffusion was the rate-determining step of the stabilization process, revealing the required content of oxygen for sufficient stabilization [7]. White *et al.* revealed that the skin formation in the stablized fibres was due to the progress of the oxidative reactions from the surface to the core in the radial direction of the fibre [8]. Mochida *et al.* reported some chemical changes of the pitch fibres during stabilization to clarify the functional groups, optimum oxygen content and solubility of the stabilized fibres [5, 9, 10]. Kowbel and Don recently observed the oxygen distribution in the stabilized pitch particles which depends upon their stabilization conditions [11]. The present authors also reported that blending PVC pitch enhanced the reactivity of the coal tar derived mesophase pitch to shorten the stabilization time significantly. They suggested, on the basis of microscopic observation and some chemical analyses, that the reactivity of the fibre components was also an important factor which controls the stabilization process of the pitch fibre [12–14].

In the present study, oxygen distribution in the

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thick fibres was measured after the oxidative stabilization at 230 to 300° C by EPMA to clarify the oxygen up-take at each depth in the fibre and to discuss the influences of the oxygen diffusion under different stabilization conditions. The change of oxygen distribution due to the blending of PVC pitch, which certainly enhanced the stabilization reactivity [12–14], was also observed to clarify the influence of enhanced reactivity on the oxygen diffusion. Comparison of the microscopic feature of carbonized fibre with the oxygen distribution of the stabilized fibre may reveal the roles of fixed oxygen in the stabilization of molecular orientation during carbonization.

2. Experimental procedure

A coal tar derived mesophase pitch and PVC pitch were used in the present study [12–15]. Their analyses and properties are summarized in Table I [12–14]. The parent mesophase pitch (MP) and its blend with PVC pitch of 10 wt % (PVC-10) were spun at 350° C into pitch fibres from a steel spinneret ($D = 0.4$ mm, $L/D = 1$, where L and D mean the length and diameter of the nozzle, respectively) by applying pressurized nitrogen (0.2 kg cm^{-2} G^{-1}). The diameter of the fibre was controlled to be 30 μm per analytical convenience.

MP and PVC-10 pitch fibres were stabilized in air flow at 230, 270 and 300° C for several periods [12–14]. The heating rate to the above temperature was 5° C min^{-1}.

The stabilized fibres were further carbonized at 600° C for 1 h. The heating rate was 10° C min^{-1}.

2.1. Measurement by EPMA (electron probe X-ray microanalyser)

Stabilized fibres of 30 μm in diameter were observed with an EPMA (Shimadzu, electron probe microanalyser EPM-810) to obtain the oxygen distribution in the cross-section surface of the thick fibre (30 μm in diameter). After mounting the stabilized fibre in the polypropylene resin at 200° C for 1 min, the mounted fibre was cross-sectioned carefully at room temperature with a sharp knife to obtain a flat surface. The flat surface of the stabilized fibre was coated with carbon using a high vacuum evaporator (Hitachi, HVS-5GB). The electron beam, accelerating voltage, sample electric current and electron beam irradiation time were 1 μm in diameter, 15 kV, 0.05 μA, and 10 sec, respectively. The intensity of a characteristic X-ray due to oxygen (the wavelength is 2.3608 nm) was quantified for 10 sec at 30 points in a line analysis along the diameter on the cross-section surface of the fibre.

2.2. OM and SEM observation of the carbonized fibre

Carbonized fibres were observed under polarized-light (Leitz) and scanning electron (JEOL, JSM-25S) microscopes. The thick carbonized fibres of 30 μm in diameter which showed the skin–core structures [13] were compared to the oxygen distributions by EPMA to define the progess of the stabilization reaction at each temperature. The structure of thinner fibre was also observed for comparison after stabilization and carbonization [13].

3. Results

3.1. Microscopic structure of carbonized fibre (30 μm in diameter)

Fig. 1 shows the optical microphotographs and scanning electron micrographs of carbonized fibres of 30 μm in diameter. As previously reported [13, 14], it took 9 h at 230° C to stabilize completely and remove the adhesion of the mesophase pitch fibre of this thickness. The mosaic texture in the transverse section of the fibre was almost maintained during the carbonization by stabilization for 6 h, suggesting that the fusibility of the constituent molecules was almost removed by this level of stabilization, although many filaments extensively adhered at their surfaces. It took 20 h at 230° C to maintain the mosaic texture tightly in the transverse section of the fibre, suggesting its very low reactivity at this temperature.

The carbonized fibres which had been stabilized at 270 and 300° C tended to show some skin–core structure in the transverse section where the area of core clearly indicated some fusion, suggesting obstacles for oxygen diffusion into the centre of fibre. The skin-thickness of MP carbon fibre stabilized at 270° C increased proportionally with the stabilization time, and no skin–core structure was still present in the fibre after stabilization for 180 min.

Stabilization at 300° C for 15 min allowed skin–core structure, where the skin thickness was 5 μm. No adhesion among the filaments was found after the carbonization. The skin thickness increased very slowly with the stabilization time to reach 9 μm after 30 min and 15 μm (no skin–core structure) after 90 min. Thus, the stabilization in the filament of the surface 5 μm was very rapid at this temperature, however, the stabilization at its centre was much slower [13].

The skin thickness of 10 μm was observable in the PVC-10 carbon fibre when the stabilization time was 60 min at 270° C. It was twice as thick as that of MP carbon fibre after stabilization under the same

TABLE I Some properties of pitches

Sample	wt %				H/C	fa[2]	Rnus[3]	s.p.[4] (° C)	Solubility (wt %)			
	H	C	N	O[1]					BS	BI-PS	PI-QS	QI
Mesophase pitch	3.9	94.1	1.0	1.0	0.50	0.97	0.55	290	6	41	11	42
PVC pitch	5.9	94.0	0.1	0	0.75	0.81	0.80	200	69	13	16	2

[1] By difference.

[2] Carbon aromaticity.

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

[4] Softening point.

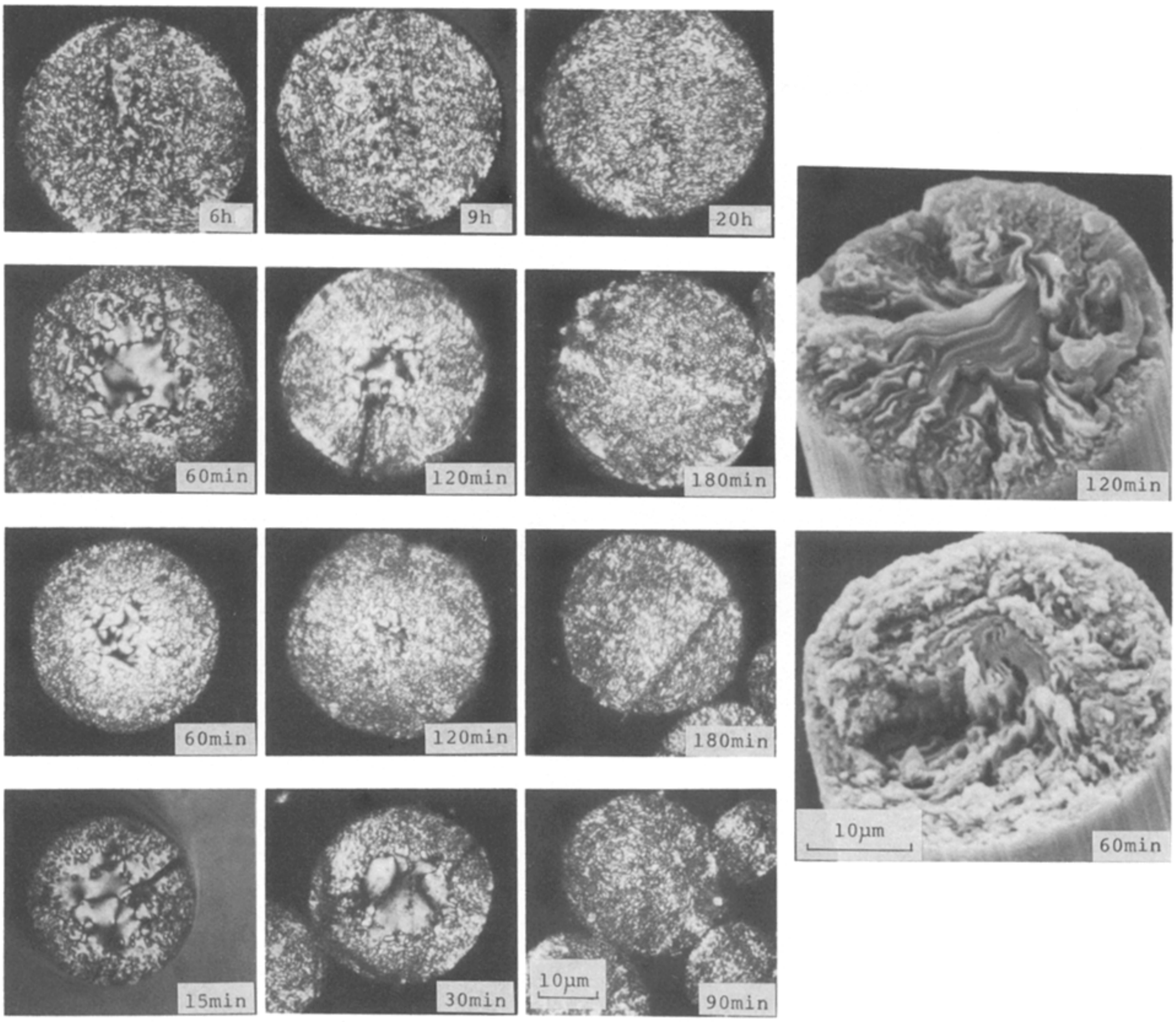

Figure 1 Optical microphotographs and scanning electron micrographs of carbonized fibres of 30 μm in diameter.

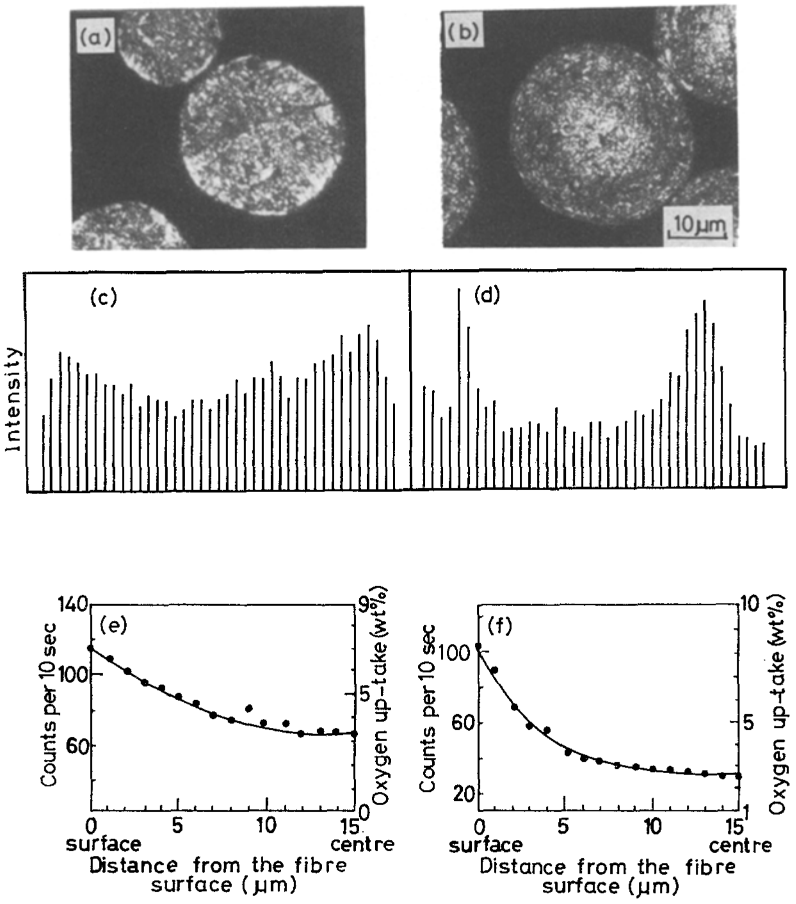

Figure 2 Optical microphotographs and EPMA data of stabilized MP fibres of 30 μm in diameter. (a), (c), (e), Stabilization condition 5° C min^{-1}, 230° C, 4 h (b), (d), (f), Stabilization condition 5° C min^{-1}, 300° C, 15 min.

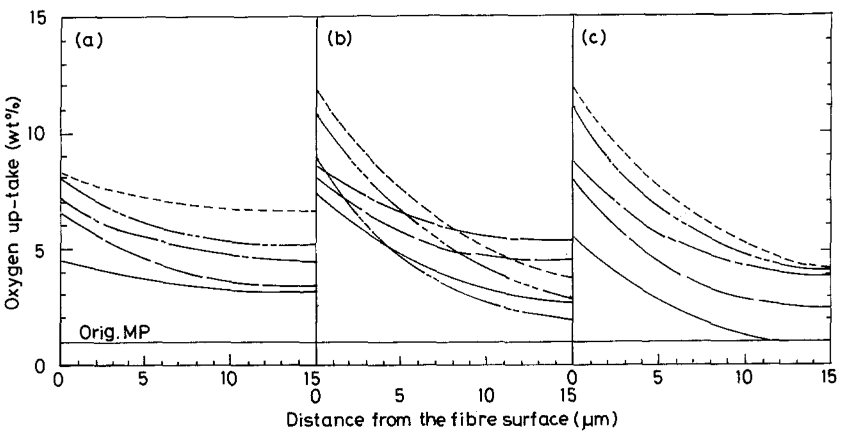

Figure 3 Oxygen distributions in the radius direction of stabilized fibres by EPMA. Stabilization conditions; (a) 5° C min^{-1}, 230° C, (MP —— 2 h, — — 4 h, - - - 8 h, -·-·- 10 h, - - - 20 h) (b) 5° C min^{-1}, 270° C (MP —— 60 min, — — 120 min, - - - 180 min, PVC-10 -·-·- 60 min, ---- 120 min, - - - 180 min) (c) 5° C min^{-1}, 300° C (MP —— 0 min, — — 15 min, - - - 30 min, ---- 75 min, - - - 105 min).

conditions. However, it took 180 min to remove the skin–core structure in the PVC-10 fibre. It is suggested that the stabilization reactivity of the core of the blended fibre was apparently much the same as that of the MP alone, although the surface of the fibre was stabilized more rapidly. Thus, the higher stabilization reactivity at the higher stabilization temperature as well as blending tends to provide skin–core structure in the thick fibre.

3.2. Oxygen distributions in thick fibres by EPMA

Fig. 2 illustrates the optical microphotographs (Figs 2a and b) of stabilized fibres and their EPMA profiles (Figs 2c and d). EPMA profiles are the intensity of characteristic X-ray liberated from oxygen atoms in a unit length (1 μm) along the diameter of the fibre. Such an intensity was normalized by the oxygen content of the stabilized fibre to describe the oxygen content in the respective length as shown in Figs 2e and 2f. The oxygen distribution was clearly subjective to the stabilization conditions. Before the stabilization, oxygen content in MP was around 1.0 wt % at each depth of the fibre.

Fig. 3 illustrates the oxygen distribution in the radial direction of the stabilized fibres (30 μm in diameter). The oxygen distribution along with the diameter of the fibre was almost flat at the level of 4.5 to 3.3 wt % after the stabilization at 230° C for 2 h. The longer stabilization at this temperature increased the oxygen content more rapidly at the skin and slowly at the centre, introducing the gradient in the oxygen distribution. The levels of oxygen content at the skin and centre were 6.6 and 3.6 wt %, respectively, after 4 h. Although the oxygen content further increased with the longer stabilization time, no increase of gradient was observed.

Oxygen up-take in the stabilization at 270° C was much more rapid, and the gradient of the oxygen distribution along the diameter was much more steep as shown in Fig. 3b. Stabilization for 60 min provided an oxygen content of 7.5 wt % at the skin surface of the MP fibre. The oxygen content decreased very sharply to the level of 4.8 wt % at 5 μm depth from the skin surface and gradually to 2.7 wt % at the centre of fibre. Another 60 or 120 min of stabilization further increased the oxygen content, however the gradient of oxygen distribution in the skin area of 5 μm depth remained steep.

Oxygen distribution in the cross-section of the stabilized MP fibres at 300° C is also illustrated in Fig. 3c. Oxygen up-take at the skin surface was very rapid so as to reach a level of 5.5 wt % during the temperature rise and a level of 8.0 wt % within 15 min. In contrast, the oxygen content at the centre increased very slowly: no increase during the temperature rise and 2.4 wt % after 15 min. Hence, steep gradient of oxygen distribution was observed. The inflection point of distribution was located at 8 μm depth from the surface. Longer stabilization times increased the oxygen content at both skin and surface, however, the gradient of oxygen distribution appeared to increase.

Blending of PVC pitch increased the rate of oxygen up-take significantly at the surface of the skin in the stabilization at 270° C, the oxygen content being as high as 9.0 wt % for the first 60 min as shown in Fig. 3b. This content was much higher than that of the parent MP fibre heat-treated at the same conditions. However, the content at the centre of PVC-10 fibre was certainly lower than that of MP fibre. Thus, the gradient of oxygen distribution in PVC-10 fibre was very steep. Longer stabilization increased the oxygen content at the skin surface very rapidly to 12.0 wt % after 180 min while the content at the centre was as low as 3.9 wt %. It may be of value to point out that the oxygen content of PVC-10 fibre was always higher at the skin area within 5 μm from the surface than that of MP fibre when compared at the same stabilization time.

4. Discussion

4.1. Relations between the stabilization extent, oxygen content and stabilization reactions

The stabilization of mesophase pitch fibre is achieved

TABLE II Oxygen up-take necessary for stabilization

r^2 (μm)	Sample	MP	MP	MP	PVC-10
	S.T.^{1}	230° C	270° C	300° C	270° C
5		–	4.8	4.4	–
10		–	4.8	4.5	2.7
15		6.6	5.3	4.2	3.8 (wt %)

^{1}Stabilization temperature.
^{2}Skin-thickness.

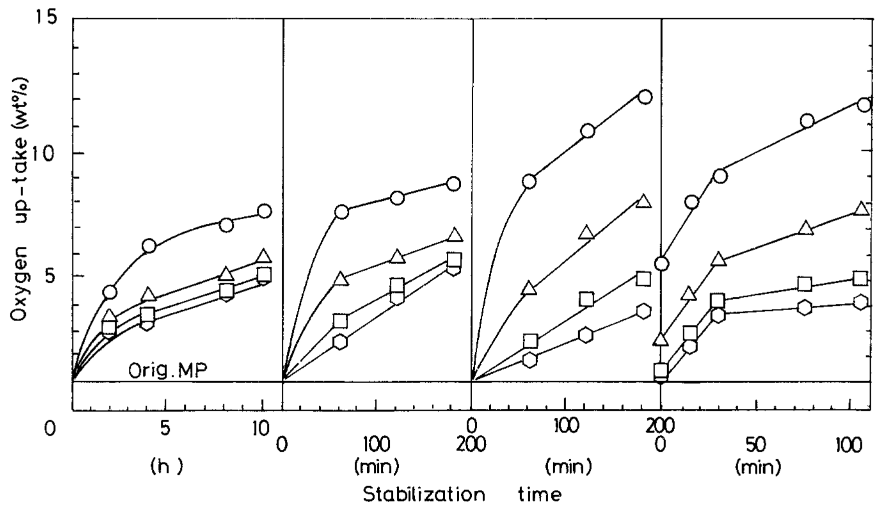

Figure 4 Oxygen up-take with stabilization time at each location in the fibre. ○ 0 μm (surface), △ 5 μm, □ 10 μm, ⬡ 15 μm (centre). (a) MP, 230° C, (b) MP, 270° C, (c) PVC-10 270° C and (d) MP, 300° C.

by oxygenative condensation, oxygenation and oxidative dehydrogenation and thermal condensation of the pitch constituent molecules of highly aromatic natures [16–22] by removing their fusibility, solubility and/or dissolving ability to maintain the fibrous shape and molecular orientation during successive carbonization [14]. Thus, the oxygen distribution in the stabilized fibre is expected to be related to the extent of stabilization. The oxygen distribution in the thick fibre revealed by EPMA in the present study certainly reflects the structural appearance of the carbonized fibre. Stabilization at 230° C provided rather flat distribution of oxygen and uniform appearance of microscopic structure. In contrast, stabilization at the higher temperatures of 270 and 300° C did give a rather steep gradient of oxygen distribution along the diameter of the filament and the skin–core structure, where the skin was fully stabilized but the centre was still fusible when the stabilization time was not long enough.

On the basis of such observation, the oxygen content necessary for the stabilization is estimated. Since the skin surface tends to be oxidized more extensively than required, the oxygen content necessary for stabilization may be better discussed at the central area of the fibre. The values estimated by comparison of Figs 1 and 3 are summarized in Table II. At the stabilization of 230° C, the oxygen up-take of 6.6 wt % (the stabilization time was 20 h) was necessary for the MP pitch fibre to maintain the molecular orientation firmly. When the stabilization was performed at 270° C, the oxygen up-takes of 4.8, 4.8 and 5.3 wt % were necessary at the skin-thickness of 5, 10 and 15 μm, respectively, to stabilize the MP pitch fibre. The oxygen up-takes of 4.4, 4.5 and 4.2 wt %, which were certainly less than those at 230 and 270° C, were necessary at the skin–thickness of 5, 10 and 15 μm, respectively, to maintain the molecular orientation of the MP pitch fibre.

Oxygen up-takes necessary for sufficient stabilization of the PVC-10 fibre at 270° C were 2.7 wt % at the skin thickness of 10 μm and 3.8 wt % at that of 15 μm, suggesting a smaller oxygen content required to the pitch components of the blend than to those of parent MP pitch fibre at the same stabilization temperature.

Thus, the oxygen content required for stabilization is variable according to the stabilization temperature and the mesophase components [14]. The stabilization reactions involved in the process may also be different. Stabilization at a lower temperature (230° C) may favour the oxygenation of the pitch components which removes the dissolving ability of the soluble components in the pitch fibre [14]. In contrast, stabilization at a higher temperature (300° C) was achieved with smaller oxygen up-take, suggesting that the dehydrogenation as well as oxygenation may convert the fusible component into an infusible one [14].

The presence of PVC pitch reduced the oxygen content required for the stabilization. Its highly polymeric structure may allow the stabilization through the least numbers of its binding with the surrounding molecules.

4.2. Stabilization kinetics

It is also of value to discuss the stabilization kinetics. The reaction should consist of at least of two steps as Diefendorf [7] and White [8] pointed out: the oxygen diffusion, determining its partial pressure at the reaction sites in the fibre filament and the oxidative reactivity of aromatic pitch components with the oxygen molecules, being strongly dependent upon their structure. The partial pressure of the oxygen differs according to the location in the fibre filament since there may be diffusion barriers and oxygen consumption before the oxygen reaches the reaction site according to the stabilization conditions.

Fig. 4 illustrates the increasing oxygen content with stabilization time at some locations in the fibre filament. At 230° C, oxygen up-take was comparatively rapid for the initial 2 h and then became rather slow. Although the oxygen contents achieved at the respective locations were slightly different, outer and inner areas carrying more or less contents, respectively, the slopes of the increase are much the same. The gradient of oxygen partial pressure within the filament is small or almost constant during the stabilization at this temperature.

At 270° C, the oxygen up-take was much more rapid and the oxygen contents at the outer and inner areas were very different until 60 min. Beyond this time, the difference became smaller and smaller because the oxygen up-take at the inner area became more rapid. The reaction at the outer surface appears to be almost complete at 60 min, sending more oxygen to the inner area of the fibre.

The considerable oxygen up-take occurred only at the outer area of the fibre during the temperature rise to 300° C above 270° C. For the first 30 min after reaching 300° C, the rates of increase of oxygen contents are much the same regardless of the location, although the contents achieved by this time were very different at the locations in this stabilization range. However, the rates in the inner areas became very slow after 30 min, whereas those in the outer area kept fairly large. Some barriers for oxygen diffusion may be built-in the stabilized zone in the outer area of the fibre at this stabilization extent.

The blending of PVC-pitch modified the profiles of oxygen up-take at 270° C somewhat similar to those observed at 300° C with MP alone, by increasing the reactivity for the oxygen up-take at the surface, while the rates in the inner area of PVC-10 were slightly slowed down along with the stabilization time. Some barriers may be also built-in.

Thus, the reaction temperature and reactivity of the pitch components influence not only the rate of oxygen up-take but also the difference of the rates due to the location in the fibre. The type of reaction, oxygen consumption relative to the oxygen diffusion in the outer area of the fibre during the stabilization, the diffusion rate in the oxidized zone and the shrinkage or densification due to the stabilization may differ, depending upon the stabilization conditions and reactivity of pitch components to modify the diffusion and oxygen partial pressure at the centre of the fibre during the stabilization. It is of value to note that the gradient of oxygen distribution in the thick fibre was very steep in the area 5 μm deeper from the outer surface. When oxygen is supplied from both surfaces of the fibre, the rate of stabilization may be much enhanced at the centre of the thinner fibre. The above results may indicate that 10 μm fibre diameter is a critical value to expect such stabilization at the centre of the fibre. Oxygen distribution in the thin fibre is wanted, however it is also difficult to measure.

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