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A structural study on the stabilization and enhancement of mesophase pitch fibre

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The components of coal tar-derived mesophase pitch fibre and its blend with polyvinyl chloride (PVC) pitch were studied for chemical changes after the stabilization. Microanalyses, solubility and solid ^{13}C NMR measurements were performed. The temperature was found to be very influential on the progress of the stabilization. At a temperature of 230° C, PVC pitch enchanced the oxygen uptake of both fusible pyridine soluble (PS) and non-fusible pyridine insoluble (PI) fractions in the pure mesophase pitch, so shortening the time required for complete stabilization and raising more rapidly the softening point of the PS fraction. More oxygen-containing functional groups, such as phenolic, ether, carboxylic and carbonyl groups, were formed in both fractions. It is noted that any increase in the aromatic ring size of the PI fraction is rather limited at this temperature. In contrast, stabilization of PVC pitch at a higher temperature of 300° C, accelerated the increase in PI without accelerating oxygen uptake of both fractions. Hence, the softening point of the remaining PS was unchanged or even lowered. An increase of aromatic ring size of the PI component by stabilization was marked at the higher temperature. Suggested stabilization schemes and the role of added PVC pitch in accelerating stabilization are discussed for each of these temperatures taking account of the above results.

1. Introduction

Pitch-based carbon fibre is recognized as a promising filler for advanced composite materials [1, 2]. However, it suffers from high cost of production in spite of the cheap price of starting feedstocks. Among the factors pushing up the cost is the slowest step of stabilization; this is one of the targets for extensive study [3].

The present authors have reported that the blending of polyvinyl chloride (PVC) pitch into the precursor for coal tar-derived mesophase pitch fibre enhanced the stabilization of whole fibre, shortening significantly the time required for stabilization [4–6]. Such an enhancement suggests the importance of the chemical structure of the mesophase pitch components on the stabilization reaction. The rate of diffusion of the oxidant to the centre of thick fibres also became important as the stabilization reaction was rather rapid at the surface of the fibre at relatively high temperatures [6]. Detailed knowledge of the chemistry of the stabilization process is needed in order to find ways of accelerating it as well as to improve fibre quality.

In the present study, in order to determine the reaction scheme of stabilization, structural changes in the pitch components induced by oxidative stabilization were investigated at lower and higher temperatures. The processes of the reaction at each temperature are expected to be very different because the extent of oxygen uptake sufficient for stabilization differs so much [6]. The reactivity enhanced by PVC pitch was also studied.

Mesophase pitch is known to consist of fusible pyridine soluble (PS) and non-fusible pyridine insoluble (PI) fractions [7]. Hence, their separate analyses will clarify more appropriately the chemistry of stabilization.

2. Experimental details

2.1. Materials

The mesophase pitch used in the present study was prepared by heat treatment of a coal tar which was hydro-treated by tetrahydroquinoline (THQ) [8]. PVC pitch miscible with mesophase pitch was obtained by heat treatment of a commercial grade PVC at 420° C for 2 h at a controlled heating rate of 10° C min^{-1} [4]. Some properties of the mesophase and PVC pitches are shown in Table I.

PVC pitch (10 wt %) was blended into mesophase pitch with vigorous stirring (600 r.p.m.) at 360° C for 10 min, at a heating rate of 5° C min^{-1}. The blended pitch obtained had enhanced stability [4].

Both the mesophase pitch (MP) and its blend with 10 wt % PVC pitch (PVC-10) were spun into fibres using a steel spinneret (of length (L) and nozzle diameter (D) where $L = D = 0.4$ mm) with the application of pressurized nitrogen of 0.12 MPa.

2.2. Stabilization of pitch fibres

Bundles of MP and PVC-10 fibres (*ca.* 0.2 g) were

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TABLE I Some properties of the mesophase and PVC pitches (f_a = carbon aromaticity; R_n = number of naphthenic rings in the unit structure; s.p. = softening point

Sample	Composition (wt %)				H/C	f_a	R_n	s.p. (° C)	Solubility (wt %)			
	H	C	N	O*					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

*Obtained by difference of other elements from IDO.

stabilized by heating under air at 230, 270 and 300° C for variable periods of time. The heating rate to reach these temperatures was controlled at 5° C min^{-1} in all cases. The stabilized fibres were characterized by elemental analyses.

2.3. Extraction of stabilized fibres

The stabilized fibres were extracted with pyridine using Soxhlet's apparatus to estimate the amount of infusible fraction within the fibres.

2.4. Structural analyses

2.4.1. Analyses of PS fractions

The PS fractions of the stabilized fibres were characterized by elemental analyses. The softening points of the PS fractions were measured by applying the Hot Stage (Leitz 1350) attached to a polarized-light microscope (Lietz Orthoplam Pol). The molecular weight distribution of the PS fractions was measured with gel permeation chromatography by using 5 wt % quinoline solutions. The hydrogen distribution and some structural parameters of the fractions were obtained according to Brown–Ladner analyses, based on ^{1}H NMR (Joel FT-100X) in deuterated pyridine.

2.4.2. Analyses of PI fractions

The PI fractions of stabilized fibres were characterized by elemental analyses and solid ^{13}C NMR (JNM-FX100, NM-SH100, CP/MAS Unit) to estimate the extent of dehydrogenation, oxygen uptake, the type of oxygen-containing functional groups and the average size of the aromatic rings in the fractions.

The solid ^{13}C NMR spectra of both fractions were obtained using a contact time of 1.0 to 1.5 msec and magic angle spinning rate of 3.5 kHz (magic angle: 54° 44′). The dipolar dephasing (DD) technique [9, 10] was also applied to distinguish signals ascribed to quaternary ^{13}C from those of other carbon species, in order to estimate the average size of the aromatic rings.

3. Results

3.1. Chemical changes in pitch fibre during stabilization

Fig. 1 illustrates the oxygen uptake by the MP and PVC-10 fibres during stabilization at 230, 270 and 300° C.

On reaching a temperature of 230° C, the fibre took up oxygen steadily, increasing from 2.0 wt % to 4.9 wt % after 6 h, and then increasing more slowly to 5.5 wt % after 9 h, by which time stabilization of the fibre was complete. Fusion of the mesophase pitch fibre after such treatment could not be observed in successive carbonization (heating rate 10° C min^{-1}). The addition of 10 wt % PVC pitch accelerated oxygen uptake to 5.8 wt % after 6 h, when the whole fibre was sufficiently stable.

A higher temperature of 270° C markedly accelerated the oxygen uptake of the mesophase pitch fibre, reaching 5.2 wt % after 80 min. Further uptake was very slow and another 40 min was required for complete stabilization. Addition of PVC pitch again shortened the time required for stabilization under these conditions to 80 min, when 5.5 wt % of oxygen was accumulated in the fibre. The rate of oxygen uptake was almost the same regardless of the addition of PVC pitch until the oxygen content reached around 5.0 wt %.

An even higher temperature of 300° C further accelerated oxygen uptake. The oxygen content reached 2.5 wt % during heating up to the treatment temperature and this increased to 4.2 wt % after 15 min when the fibre was stable. Addition of PVC pitch shortened the stabilization period to 12 min, with final oxygen content of 4.0 wt %. The rates of oxygen uptake with or without PVC pitch were very similar. It should be noted that the amount of oxygen required for sufficient stabilization differed according to the stabilization temperature or presence of PVC pitch.

Fig. 2 illustrates the change in solubility of the pitch

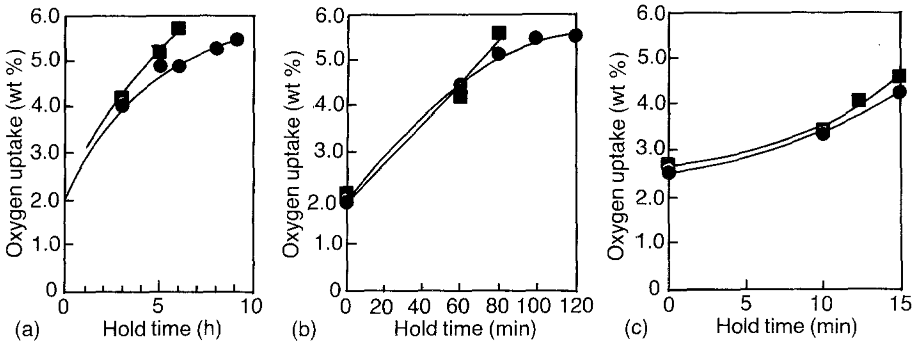

Figure 1 Oxygen uptake during stabilization. Heating rate was 5° C min^{-1} in air. (a) 230° C, (b) 270° C, (c) 300° C. (●) Mesophase pitch (MP), (■) blend containing 10 wt % PVC (PVC-10).

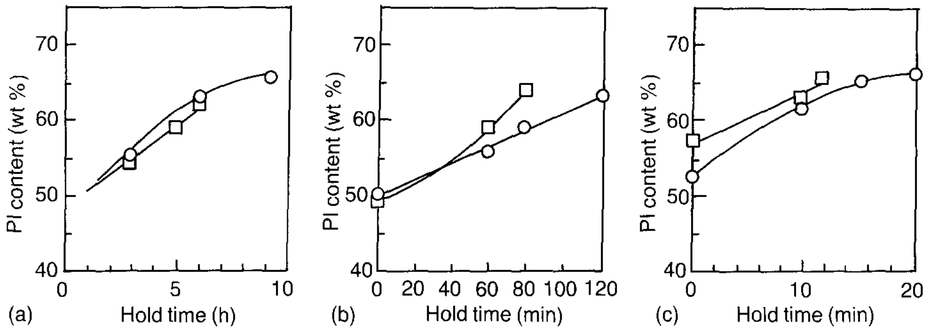

Figure 2 Pyridine insoluble content of oxidized fibres. Heating rate was 5° C min^{-1} in air. (a) 230° C, (b) 270° C, (c) 300° C. (○) MP, (□) PVC-10.

during stabilization. In all cases stabilization reduced the solubility of the pitch due to an increase in the PI content. Stabilization at 230° C increased PI content steadily to 63 wt % after 6 h, but required another 3 h for completion when the PI content reached 66 wt %. Addition of PVC pitch showed the same increase of PI content, although stabilization was achieved when the PI content reached 62 wt % after 6 h.

A higher temperature of 270° C accelerated the rate of increase of PI, providing 65 wt % after 120 min when stabilization was complete. Addition of PVC pitch accelerated the increase of PI content at this temperature, 65 wt % of PI fraction in the stabilized fibre being achieved after 80 min.

An even higher temperature of 300° C further increased the rate of increase of PI, 66 wt % of PI being achieved after 15 min when stabilization was complete. Addition of PVC pitch further accelerated the PI increase. The PI content reached 58 wt % during the rise to the stabilization temperature and 66 wt % after 12 min when stabilization was complete. Thus, stabilization was complete when the PI content reached 62% to 66 wt % regardless of the stabilization temperature, although the times required were very different and depended upon the temperature and the presence of PVC pitch.

3.2. Structural and property changes of PS in the fibres on stabilization

Changes in the oxygen uptake of PS fraction in mesophase fibres during stabilization of 230, 270 and 300° C are summarized in Fig. 3. The oxygen content of PS in the mesophase pitch increased linearly with 3 to 5 wt % at 230° C after 9 h, when stabilization was complete, as illustrated in Fig. 3a. The blending of PVC pitch accelerated the oxygen uptake of this fraction, providing 5.6 wt % oxygen after 6 h when stabilization was complete.

In contrast, the oxygen content of this fraction remained low, in the range from 3 to 4 wt %, during stabilization at 270 and 300° C (Figs 3b and c). Stabilization was complete at 4 wt % at both temperatures, although the time required for stabilization varied according to the temperature. The addition of PVC pitch had little effect on the oxygen uptake of the fraction at these temperatures, although stabilization was accelerated as described above.

Fig. 4 illustrates the gel permeation chromatography profiles of the PS fractions in both the original and stabilized mesophase pitch fibres. The molecular weight of the original PS fraction ranged from a few hundreds to 2500. Although stabilization at 230° C removed half of the heavier portion of molecular weight above 1000 (which should be converted to be pyridine insoluble), the major portion ranging up to 2000 stayed in the PS fraction. More of the heavier fraction remained in PS on the addition of PVC pitch, suggesting that coupling of PVC pitch components keeps the mesophase molecule soluble in pyridine in spite of oxygenation.

Stabilization at 300° C also converted the heavier portion to be insoluble in pyridine. At the same time, the molecular weight of the remaining PS also shifted to be heavier, suggesting a significant extent of oxidative coupling.

Table II and III summarize ^{1}H NMR data of the PS fraction before and after stabilization. It is noted that the addition of PVC pitch increased markedly the contents of both H_α and H_β hydrogen, leading to a larger degree of aliphatic substitution at the aromatic nuclei (σ_{al}), a larger number of aliphatic and naphthenic carbons per structural unit (C_{al}) and a larger number of naphthenic or heterocyclic rings per structural unit (R_n).

Stabilization at 230° C decreased the amount of hydrogen markedly, while the relative contents of H_β and H_γ increased initially, although both hydrogens also decreased in the later stage of stabilization. Aromatic hydrogen dominated when stabilization was achieved, reflecting perhaps the high reactivity of

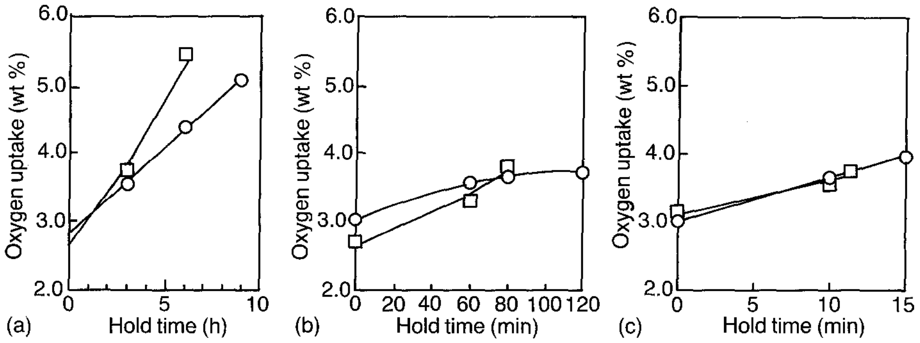

Figure 3 Oxygen uptake of PS fractions during oxidation. Heating rate 5° C min^{-1} in air. (a) 230° C, (b) 270° C, (c) 300° C. (○) MP, (□) PVC-10.

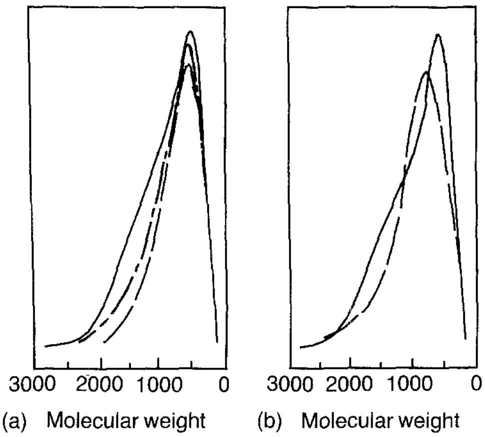

Figure 4 Gel permeation chromatography profiles of the PS fractions in oxidized fibres. (a) Treated at 230° C (—— MP, – – MP at 230° C for 9 h, —·— PVC-10 at 230° C for 6 h), (b) treated at 300° C (—— MP, – – MP at 300° C for 15 min).

β-hydrogens. Addition of PVC pitch exhibited a similar reduction of hydrogens, however stabilization was achieved at a higher level of remaining aliphatic hydrogens.

Stabilization at 300° C significantly increased the aliphatic hydrogens in the PS fraction in the initial stages. Stabilization at this temperature converted the heavy PS portion into PI, leaving the lighter portion of PS rich in aliphatic hydrogens and only slightly dehydrogenated. Addition of PVC pitch allowed more aliphatic hydrogens to remain in the fraction, although their decreases were rather rapid. The fibre stabilized at this temperature contained PS with more aliphatic hydrogens than that at 230° C.

3.3. Changes in the softening points of PS fractions

Changes in the softening points of the PS fractions in the mesophase pitch fibres during stabilization are illustrated in Fig. 5. Stabilization at 230° C raised the softening point of the remaining PS fraction up to 235 to 240° C until complete stabilization. PVC pitch accelerated this rise in the softening point.

In marked contrast, stabilization at 270 and 300° C maintained or even lowered the softening point of the same fraction during its initial stages, and then raised it to some extent. The lowering was more marked at 270° C. PVC pitch essentially did not influence the change in the softening point at these stabilization temperatures.

3.4. Changes in PI fraction during stabilization

Fig. 6 illustrates the oxygen uptake of the PI fraction during stabilization. Stabilization at 230° C increased the oxygen content of PI proportionally with time until complete, when the content was 6.5 wt %. PVC pitch accelerated the oxygen uptake of this fraction.

Stabilization at higher temperatures also increased the oxygen content, complete stabilization being achieved at contents of 6.7 and 5.6 wt %, respectively, at 270 and 300° C. The addition of PVC pitch did not accelerate the oxygen uptake of the fraction at these temperatures. It should be noted that further heating of MP was necessary for complete stabilization after the oxygen content had reached these levels. In contrast, the additional PVC pitch allowed complete stabilization soon after the oxygen content reached these levels. These features were very common to those observed with the fractions of unblended fibres.

Solid ^{13}C NMR spectra of the PI fractions in the initial and stabilized mesophase pitch fibres are illustrated in Figs 7 and 8, which respectively show the regions of aromatic and aliphatic carbons. Stabilization increased the oxygenated aromatic carbons, which are identified as phenolic or ether, carboxylic and carbonyl (or aldehyde) carbons (as shown in Fig. 7). More oxygens were taken up in the fibre stabilized at 230° C. The aliphatic carbons were also strongly reduced by stabilization, as indicated by the decreased intensities of the peaks in the regions for methoxy, methylene (CH_2 in alkyl chain and CH_2' bridged to aromatic rings) and methyl carbons. The chemical shifts of the peaks were also modified strongly by stabilization. However, their detailed identification may not be so fruitful because the structure of the mesophase components is very complex.

Table IV summarizes the relative intensities of carbon functional groups in the PI fractions of the mesophase pitches. Stabilization increased the oxygen-carrying functional groups; among these, phenolic or ether groups increased most, followed by the carboxyl, ester and carboxylic acid groups. The greater number of aromatic carbons were probably reduced to phenolic and/or ether groups. Methyl and methylene groups were reduced similarly, probably to produce carboxyl and carbonyl groups. The methoxy group was reduced slightly, probably to produce hydroxyl groups. It is very clear that stabilization at lower temperatures introduced more oxygen

TABLE II Brown–Ladner analyses of PS fractions stabilized at 230° C (f_a = carbon aromaticity; σ_{al} = degree of aliphatic substitution in aromatic nuclei; C_{al} = number of aliphatic and naphthenic carbon atoms per structural unit; R_n = number of naphthenic or heterocyclic rings per structural unit)

Sample	Treatment time (h)	Hydrogen concentration (%)				f_a	σ_{al}	C_{al}	R_n
		H_{ar}	H_α	H_β	H_γ				
MP	untreated	89.7	7.2	2.1	1.0	0.97	0.036	1.546	0.55
	3	87.5	4.7	3.9	3.9	0.97	0.023	2.125	1.61
	6	89.2	7.8	2.3	0.7	0.97	0.036	1.170	1.00
	9	97.0	2.0	0.9	0	0.99	0.009	0.228	0.34
PVC-10	untreated	82.1	10.4	6.6	0.9	0.95	0.056	2.849	0.75
	3	80.2	8.5	7.3	4.0	0.95	0.044	2.218	0.72
	6	90.3	6.9	2.8	0	0.97	0.032	0.754	0.52

TABLE III Brown–Ladner analyses of PS fractions stabilized at 300°C (f_a = carbon aromaticity; σ_{al} = degree of aliphatic substitution in aromatic nuclei; C_{al} = number of aliphatic and naphthenic carbon atoms per structural unit; R_n = number of naphthenic or heterocyclic rings per structural unit)

Sample	Treatment time (min)	Hydrogen concentration (%)				f_a	σ_{al}	C_{al}	R_n
		H_{ar}	H_α	H_β	H_γ				
MP	untreated	89.7	7.2	2.1	1.0	0.97	0.036	1.546	0.55
	0	79.7	10.2	5.1	5.0	0.95	0.054	4.635	2.33
	10	75.6	9.8	7.5	7.2	0.94	0.053	4.840	2.02
	15	82.8	6.9	5.2	5.1	0.96	0.035	3.755	2.62
PVC-10	untreated	82.1	10.4	6.6	0.9	0.95	0.056	2.849	0.75
	0	83.7	5.8	7.0	3.5	0.96	0.030	2.361	0.85
	10	82.2	7.8	7.8	2.2	0.95	0.040	2.083	0.65
	12	91.6	3.7	2.8	1.9	0.98	0.018	0.926	0.59

and decreased the relative amounts of unoxidized aliphatic as well as aromatic carbons.

Solid NMR allows the estimation of the average size of the aromatic ring by distinguishing quaternary aromatic carbons from those carrying hydrogen and aliphatic carbons. The estimated numbers of aromatic rings in a molecular unit are summarized in Table V.

Stabilization increased the carbon number of the initial mesophase pitch component from 6 to 7 to 8 to 9 for pitch stabilized at 230°C and 12 to 13 for that stabilized at 300°C. Thus, stabilization at a higher temperature promoted the dehydrogenation–condensation of aromatic rings instead of oxygenation, which was the major consequence of stabilization at a lower temperature.

4. Discussion

Mesophase pitch is considered to consist of fusible pyridine soluble (PS) and non-fusible pyridine insoluble (PI) fractions which exhibit liquid crystal properties at elevated temperatures as a result of PI dissolving fused PS [7, 11]. Thus, mesophase pitch fibre is, in principle, stabilized as a non-fusible fibre in one of four ways.

(1) Conversion of fusible PS to a non-fusible form or causing it to be adsorbed on the non-fusible PI surface.

(2) Reduction of solvent ability of fusible PS compared to PI at elevated temperatures.

(3) Removal of PS from the fibre [12].

(4) Reduced solubility of non-fusible PI in fusible PS.

Such modification of mesophase pitch components can be carried out by the oxidative reactions outlined in the present study. Route 3 may be ruled out in oxidative stabilization, although it is the major one in extractive stabilization [13]. Dehydrogenation, dehydrogenation coupling and oxygen coupling are among the oxidation reactions that can convert non-fusible, insoluble and insolvent components. The dominant reaction will depend very much on reactivity of the mesophase pitch as well as the oxidation conditions.

The present study indicated that stabilization was complete when the PI content reached *ca.* 65 wt % regardless of the oxidation conditions and the presence of PVC pitch, suggesting that all three routes may contribute to stabilization, although the extent of their contributions varies depending on the conditions. Thus, the reaction scheme of oxidative stabilization can be described by the following equation.

$$\begin{tikzcd}
\mathrm{PS} \arrow[rr, "(a)"] \arrow[dd, "(b)"'] & & \mathrm{PS'} \arrow[dd, "(e)"'] \arrow[dr, "(f)"] & \\
& & & \mathrm{PI'_{is}} \\
\mathrm{PI} \arrow[rr, "(c)"] \arrow[urrr, "(d)"] & & \mathrm{PI_{is}} \arrow[ur, "(g)"'] &
\end{tikzcd} \qquad (1)$$

The PS and PI fractions in the initial mesophase pitch are changed to PS′, PI_{is} and PI'_{is} fractions in oxidized pitch. PS′ and PI'_{is} carry more oxygen than PS or PI_{is}, respectively. (Suffix is means insoluble in fused PS.)

Stabilization can convert PS into PS′, which is still pyridine soluble but carries more oxygen functionalities. The PI is similar to that in the starting pitch, and gives PI_{is} which is insoluble in fused PS. PS′ will be further converted into PI_{is} or PI'_{ns}. PI in the starting pitch is also converted into PI_{is} and PI'_{is} to complete stabilization.

The stabilization temperature is found to influence very strongly the reaction scheme. Stabilization at a lower temperature of 230° C introduces more oxygens into the mesophase pitch until complete stabilization, producing PS′ and PI'_{is} preferentially as indicated by the chemical and NMR analyses. This suggests that paths (a), (d) and (f) in Equation 1 are dominant at

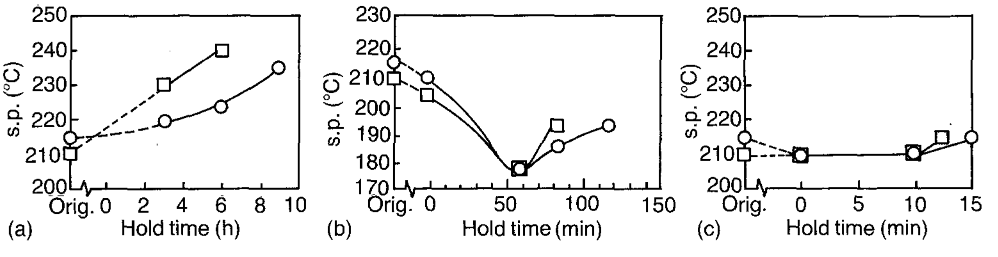

Figure 5 Softening points of PS fractions in stabilized fibres. (a) 230°C, (b) 270°C, (c) 300°C. (○) MP, (□) PVC-10.

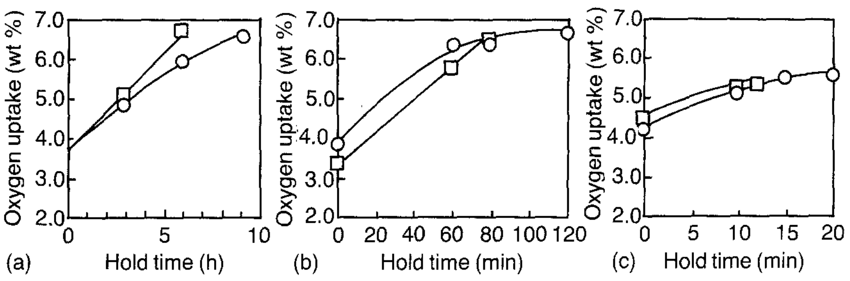

Figure 6 Oxygen uptake of the PI fractions in stabilized fibres. (a) 230° C, (b) 270° C, (c) 300° C. (○) MP, (□) PVC-10.

this temperature. Oxidized PS fractions (PS′) had a higher softening point than the original because of extensive oxidation. The reaction (g) may also take place, especially during longer stabilization processes. In contrast, the heavier component in the PS fraction is first oxidized to be pyridine insoluble at higher stabilization temperatures, leaving a lighter component containing more hydrogens than initially. Hence, the softening point of remaining PS is expected to be almost unchanged or even lowered as observed during stabilization at higher temperatures of 300 and 270° C, respectively. This suggests the main stabilization routes of (b) and (c) (Equation 1). The reaction (e) (dehydration) may also take place at higher temperature as observed in air-blowing [14–16]. Thus, the contrasting features of stabilization are clearly temperature dependent, even if the conversion of PS into PI is common.

The major reactions in stabilization are thus concluded to be as follows. Oxygenation to form Ar–O, ArCOO- and ArCOOH from $ArCH_2X$, is the major reaction with a slight increase in aromatic condensation at 230° C, while the latter reaction becomes major at 300° C.

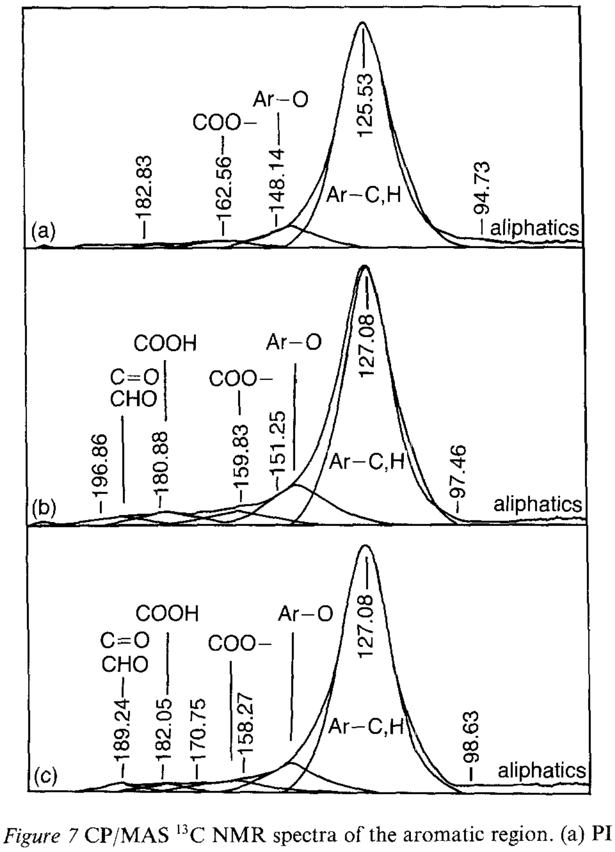

Figure 7 CP/MAS ^{13}C NMR spectra of the aromatic region. (a) PI fraction of MP, (b) after heating at 230° C for 9 h, (c) after heating at 300° C for 15 min.

It should be noted that stabilization time should also influence the structure of the stabilized pitch. A long stabilization time may lead to the introduction of more oxygens beyond that sufficent for stabilization (reaction (g) in Equation 1).

Another point for discussion in the present study is the role of PVC pitch, which accelerates stabilization at both lower and higher temperatures. It is very interesting that the PVC pitch influenced stabilization differently at 230 and 300° C. It accelerated oxygen uptake at the lower temperature while the formation of PI was accelerated at the higher temperature. The contrasting features of stabilization enhanced by PVC pitch at different temperatures may be thus reasoned.

PVC pitch, which is polymeric, aliphatic and naphthenic, in spite of its miscibility with mesophase pitch, is expected to be more reactive with molecular oxygen. It is oxidized easily to initiate chain oxidation reactions, producing activated oxygen species which can

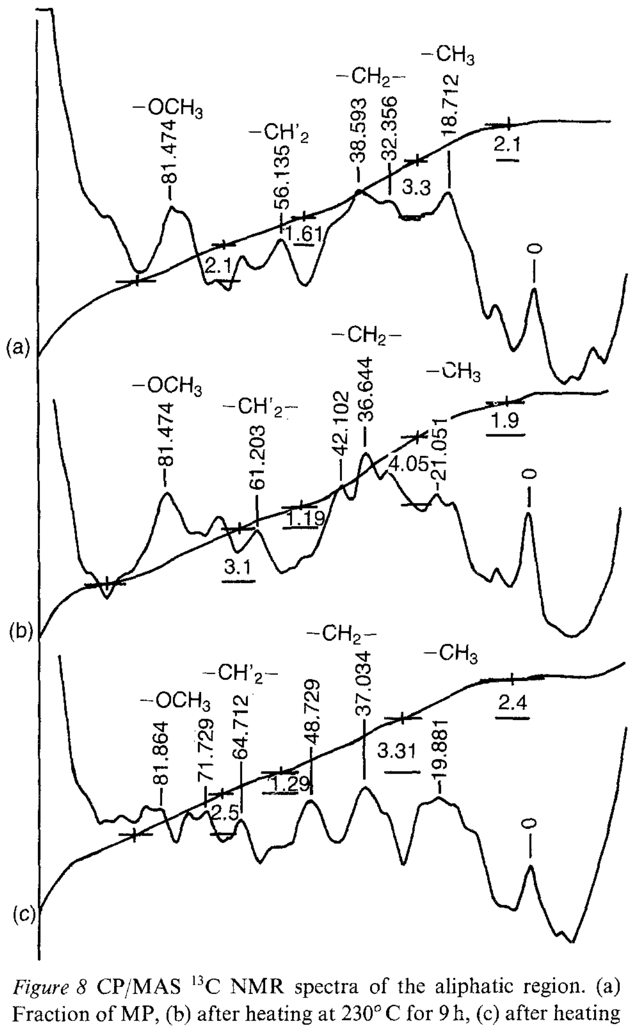

Figure 8 CP/MAS ^{13}C NMR spectra of the aliphatic region. (a) Fraction of MP, (b) after heating at 230° C for 9 h, (c) after heating at 300° C for 15 min.

TABLE IV The relative concentrations of functional groups in the PI fractions of stabilized pitch calculated by ^{13}C NMR

PI fraction	$-CH_3$	$-CH_2$	$-CH_2'$	$-OCH_3$	Ar–C, H	Ar–O	COO–	COOH	C=O, CHO
1	3.0	4.7	2.3	3.0	79.5	6.0	1.5	–	–
2	1.5	3.1	0.9	2.4	70.4	12.1	4.6	3.4	1.8
3	2.2	3.1	1.2	2.3	76.8	8.3	3.7	1.4	1.0

PI fraction 1 is that in MP, PI fraction 2 is in MP treated at 230° C for 9 h, PI fraction 3 is in MP treated at 300° C for 15 min.

oxidize the mesophase pitch components. Such is the expected role of PVC pitch at lower temperatures, where the activation of oxygen is rather limited.

Polymeric components of PVC pitch oxidatively activated can react with the surrounding molecules in the mesophase pitch to form larger molecules, lowering their solubility and fusibility, and accelerating PI formation. Such coupling is expected at a higher temperature because both molecules are activated. Hence, oxygen uptake was apparently not accelerated by PVC pitch.

The present study resolves some of the chemistry in the stabilization of coal tar-based mesphase pitch fibre, one of the most important steps in carbon fibre production with regard to cost and quality. The chemistry of fibre geometry and its influence on the quality of the resultant carbon fibre still remains to be studied in detail.

TABLE V Average number in the aromatic rings of the PI fraction

Treatment temperature (° C)	Treatment time	Aromatic ring number
untreated		6–7
230	9 h	8–9
300	15 min	12–13

References

1. S. OTANI, K. OKUDA and H. S. MATSUDA, "Carbon Fiber" (Kindai Henshusha, Tokyo, 1983) p. 231.
2. K. KAWATA, S. UMEKAWA and K. KOBAYASHI, in Composites '86: Recent Advances in Japan and the United States (Japan Society for Composite Materials, 1986) p. 1.
3. S. OTANI and A. OYA, "Carbon Fiber Nyumon", (Kindai Henshusha, Tokyo, 1983) p. 71.
4. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. MATSUMOTO, *Chem. Lett.* **11** (1987) 279.
5. *Idem, J. Mater. Sci.*, in press.
6. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. HINO, *ibid.*, in press.
7. I. MOCHIDA and Y. KORAI, *J. Fuel Soc. Jpn* **64** (1985) 802.
8. Y. YAMADA, H. HONDA and T. INOUE, Japan Patent 58 18421, (1983).
9. P. TEKELY, J. BRONDEAU, J. P. MARCHAL and J. J. DELPUECH, *Fuel* **65** (1986) 997.
10. K. W. ZILM and G. G. WEBB, *ibid.* **65** (1986) 721.
11. Y. KORAI and I. MOCHIDA, *Carbon* **23** (1985) 97.
12. Y. D. PARK and I. MOCHIDA, in Proceedings of the 13th Annual Meeting of the Japan Carbon Society, Tsukuba, Extended Abstracts (Japan Carbon Society, 1986) p. 12.
13. *Idem, Carbon*, submitted.
14. I. MOCHIDA, Y. KORAI, Y. MATSUMURA and T. MAEDA, *Sekiyu Gakkaishi* **28** (1985) 1.
15. I. MOCHIDA, T. INABA, Y. KORAI, H. FUJITSU and K. TAKESHITA, *Carbon* **21** (1983) 543.
16. I. MOCHIDA, K. TAMARU, Y. KORAI, H. FUJITSU and K. TAKESHITA, *Carbon* **20** (1982) 231.

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and accepted 27 February 1989