

Roles of Extrahydrogen in the Preparation of Mesophase Pitch

Yang Duk Park, Yozo Korai and Isao Mochida
Research Institute of Industrial Science,
Kyushu University 86, Kasuga 816, Fukuoka, Japan

Carbonaceous mesophase pitches were prepared from two kinds of pitches by assuring homogeneous heating under vacuum and stirring. The different solubilities of mesophase pitches are compared in relation to their chemical structures and reactivities. Their molecular weight and contents of naphthenic and alkyl groups which inherited their starting pitches, appear to be the key factors controlling their solubility.

INTRODUCTION

Mesophase pitch, which has been recognized as essential precursor for carbon fibers of high performance (1,2), should satisfy the several requirement, such required properties have intimate relation to the chemical structure of its constituent molecules.

In this report, the mesophase pitches, which were prepared from two kinds of petroleum pitches were characterized in terms of their solubility and optical anisotropy. The properties are related to their structure which may inherit those of the starting pitches.

EXPERIMENTAL

Analyses of two pitches (P1 and P2) are summarized in Table 1. Pitches were heated under nitrogen flow in a pyrex tube to 430°C and then were further heated under evacuation (10 torr) for variable times. Stringing was continued through the treatment to keep the homogeneous heating. The remaining residue in the tube was cooled to room temperature at the rate of 3°C/min to develop anisotropy in an annealed form (3). The mesophase pitches were analysed in terms of solubility, optical anisotropy and chemical structure.

Table 1. Some analytical data of raw pitches

Raw pitch	H/C	fa ^{a)}	Rnus ^{b)}	σ ^{c)}	M.P. (°C)
P1	0.75	0.84	0.40	0.20	110
P2	0.73	0.86	0.80	0.28	115

a): carbon aromaticity

b): naphthenic ring number per unit structure

c): number of substitution groups per unit structure

RESULTS

Both mesophase pitches, which were prepared at 430°C for 1 h (P1-430-1VS and P2-430-1VS), consisted mainly of isotropic matrix with a large number of small anisotropic spheres (Fig. 1-a and 1-d). The anisotropic contents, solubilities and residue yields of the mesophase pitches are summarized in Fig. 2. The anisotropic contents were less than 10 vol% at the residue yields of 70 and 69 wt%, respectively. The major portions (86 and 75 wt%) were soluble in THF with 8 and 15 wt% insoluble in quinoline.

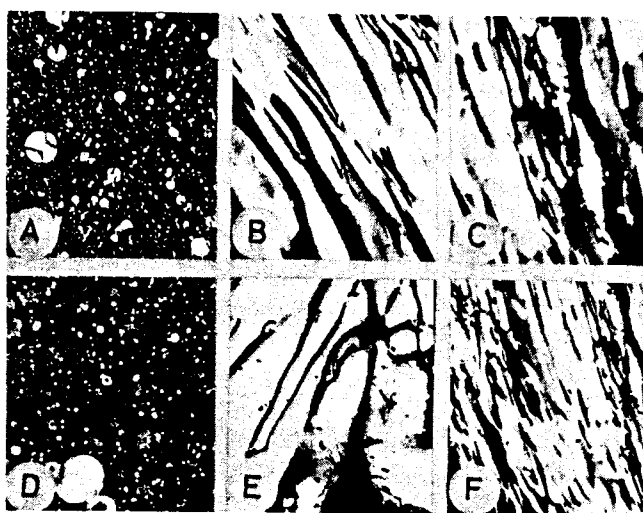


Fig.1 Optical micrographs of mesophase pitches.

(a):P1-430-1VS (b):P1-430-5VS (c):P1-430-7VS
(d):P2-430-1VS (e):P2-430-5VS (f):P2-430-7VS

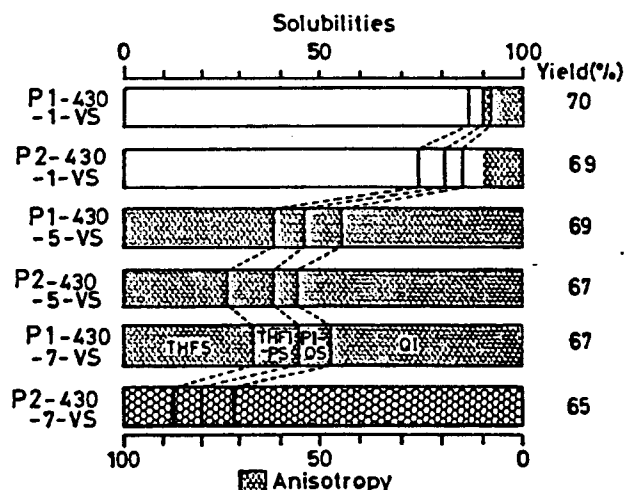


Fig.2 Solubilities and anisotropy contents of mesophase pitches.

A longer heat-treatment of 5 h (P1-430-5VS and P2-430-5VS) increased the anisotropic contents to 100 % and the QI to 45 and 55 wt%, with 40 and 28 wt% of THFS remaining respectively. A further longer treatment of 7 h (P1-430-7VS and P2-430-7VS) increased the amount of insoluble material. The amounts of insoluble material of P2-430-7VS, especially QI, increased more rapidly than those of P1-430-7VS.

When the mesophase pitches of 100 % anisotropy are compared, P1 provided higher solubility and lower melting temperature.

The PS fraction of P1-430-5VS was found to have value of larger H/C, a smaller fa, and higher average molecular weight than those of P2-430-5VS. The PS fractions of P1 gave much more hydrogen sulfide below 250°C during the heat-treatment.

Optical micrographs of cokes, produced from the original pitches with sulfur are compared in Fig.3, where the heat-treatment was carried out at 450°C for 5 h. P2-coke showed very fine anisotropic units in the major isotropic matrix. P1-coke showed 100 % anisotropy mixture of flow, coarse and fine mosaics. The PS fractions of mesophase pitches prepared from P1 also gave much more hydrogen sulfide below 250°C during the heat-treatment.

DISCUSSION

The properties of a mesophase pitch such as solubility, melting temperature and stability against the further their condensation were found to strongly depend on the starting pitch.

The properties reflect the chemical structure of a mesophase which inherit that of the starting pitch. A pitch which contains more naphthenic hydrogen (measured by desulfurization) leaves more hydrogens in the mesophase pitch. Such hydrogen in the constituent molecules allowed their higher solubility, lower the melting tem-

Table 2. Some analytical data of mesophase pitches

Abbriviation	C%	H%	N%	H/C	M.P.(°C)
P1-430-1VS	94.08	4.90	0.17	0.63	235
P2-430-1VS	92.52	5.09	0.11	0.66	245
P1-430-5VS	90.29	4.29	0.27	0.57	270
P2-430-5VS	90.01	4.81	1.46	0.57	310
P1-430-7VS	94.75	4.50	0.12	0.57	300
P2-430-7VS	93.06	4.20	0.10	0.54	330

Table 3. Some analytical data of PS fractions from mesophase pitches

Abbriviation	H/C	fa	σ	AMW ^{a)}
P1-430-1VS-PS	0.69	-	-	600
P2-430-1VS-PS	0.66	-	-	400
P1-430-5VS-PS	0.66	0.90	0.20	1050
P2-430-5VS-PS	0.63	0.92	0.25	710
P1-430-7VS-PS	0.66	0.90	0.20	710
P2-430-7VS-PS	0.63	0.92	0.26	650

a): average molecular weight

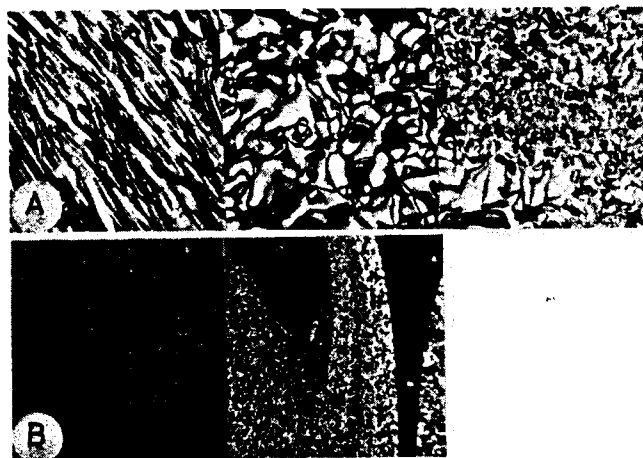


Fig. 3 Optical micrographs of cokes, produced from the original pitches with sulfur. (a): P1-pitch, (b): P2-pitch

perature and stability against the further their condensation in spite of large molecular weight through higher affinity to the solvents, lower intramolecular Van der Waals forces and the hydrogen transfer during the heat-treatment.

It is worth while to discuss reasons why P1 gave an anisotropic coke in the presence of excess sulfur. The dehydrogenated form of the pitch may have moderate condensation reactivity suitable for the anisotropic development.

In contrast, more alkyl groups in P2 may be highly activated by sulfur to give an isotropic carbon.

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