

Preparation of Anisotropic Pitch by Carbonization Under Vacuum

Yang Duk Park, Yozo Korai and Isao Mochida

Research Institute of Industrial Science,
Kyushu University 83, Kasuga 816, Fukuoka, Japan

Anisotropic mesophase pitch of high solubility and low melting temperature was prepared from a petroleum pitch by carbonizing under vacuum conditions at 430 °C for 5 h. The solubility and melting temperature were 55 wt% in quinoline and 270 °C, respectively at complete development anisotropic mesophase pitch. This solubility is much higher than that of mesophase pitch from the same feedstock using refluxing and gas blowing conditions. Yields of the mesophase pitch of complete anisotropic development were 60 wt% under vacuum. Structure of these mesophase pitches were analyzed.

Introduction

Mesophase pitch, recognized as an essential precursor for high performance carbon fiber(1), needs to be spinnable at low temperature, highly oriented, reactive for oxidation to promote thermosetting, and of high coking value.

Mesophase pitch has been prepared via several stages of pitch modification and mesophase induction. Thus, efficiency of removal of light components is important for the preparation of mesophase pitch of high solubility and fusibility.

In the present study, mesophase pitch from a petroleum pitch of relatively high hydrogen content was prepared under vacuum at a relative high temperature at short experimental times to achieve efficient removal of light components. The comparative study of properties and structure of mesophase pitch prepared under refluxing, gas blowing and vacuum conditions, discusses the origins of high solubility, low melting temperature and formation of mesophase pitch.

Experimental

The petroleum pitch used and analyses are in Table 1. Sample pitch was heat-treated in a pyrex glass tube at 430 °C under refluxing, gas blowing or vacuum conditions. The pitch was stirred vigorously during heat-treatment in all system at 600 rpm with a stirring screw made of stainless steel. After the prescribed soak time, the mesophase pitch thus produced was cooled to room temperature.

Table 1. Analyses of Parent Pitch

Source	H/C	fa ^{a)}	Rnus ^{b)}	Rnus/Rtus(%) ^{c)}
Petroleum	0.75	0.839	0.40	6.8

a) carbon aromaticity

b) naphthenic ring number per unit structure

c) naphthenic ring number/total ring number per unit structure

Results

Pitches RS and BS consisted mainly of isotropic carbon with a small amount of anisotropic carbon and anisotropic spheres were scattered within in the isotropic matrix (Fig. 1-a and 1-b). In contrast, the VS pitch was totally anisotropic in Fig. 1-c. The anisotropic contents and solubilities of the mesophase pitches are summarized in Fig. 2. A major portion (86 wt%) was soluble in THF with 9 wt% insoluble in quinoline (P-430-5RS). Blowing heat-treatment (P-430-5BS) increased the anisotropic content to 28 vol% and the QI to 26 wt%. Heat-treatment under vacuum (P-430-5VS) was effective in enhancing the development of anisotropic carbon (100 %) with a moderate increase in QI (45 wt%). This anisotropic mesophase pitch contained 40 wt% THFS, 11 wt% THFI-PS and 4 wt% PI-QS, soluble fractions.

Longer treatment under RS and BS conditions increased the anisotropic content, 30 and 12 h being required, respectively to develop 100 % anisotropy. At the same time, QI contents increased to

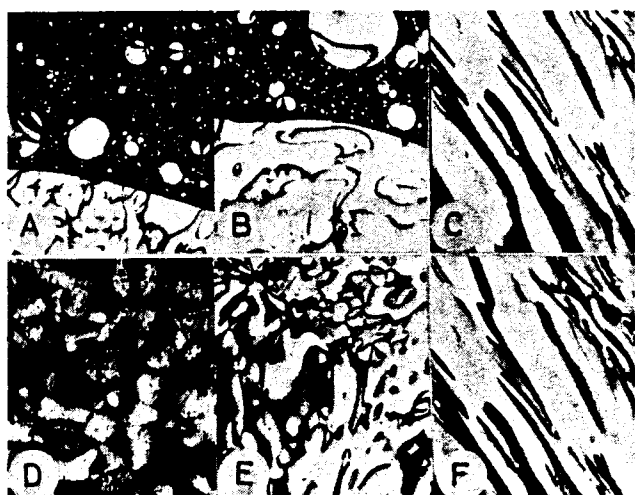


Fig. 1 Optical micrographs of mesophase pitches.

(a):P-430-5RS (b):P-430-5BS (c):P-430-5VS
(d):P-430-30RS (e):P-430-12BS (f):P-430-5VS

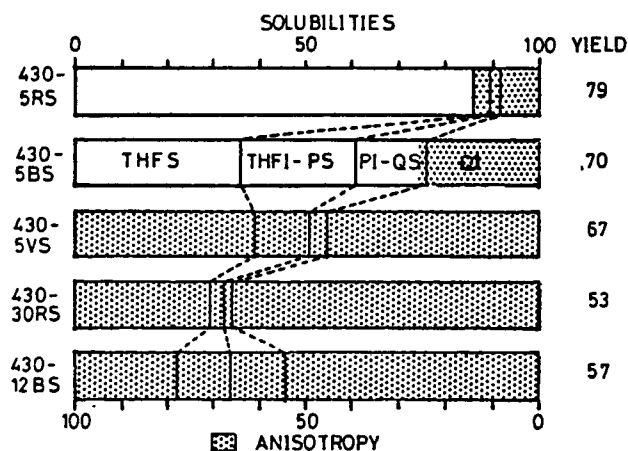


Fig. 2 Solubilities and anisotropy contents of mesophase pitches.

65 and 55 wt%, with 30 and 23 wt% of THFS remaining respectively. When the mesophase pitches of 100 % anisotropy are compared, the yield of P-430-5VS was 67 wt% being higher by 10~14 % than the other (Table 2). The lowest melting points of all mesophase pitch was 270 °C. Thus, the mesophase pitch prepared under vacuum has the highest solubility, lowest melting point, and highest yield at 100 % anisotropy development.

The THFI-PS fraction of P-430-5VS had

Table 2. Analyses of mesophase pitches

Mesophase pitch	H/C	M.P. (°C)	Yield (wt%)
P-430-5RS	0.67	125	79
P-430-5BS	0.61	170	70
P-430-5VS	0.57	270	67
P-430-30RS	0.55	395	57
P-430-12BS	0.55	290	53

Table 3. Analyses of the THFI-PS fraction from mesophase pitches

Mesophase pitch	H/C	fa	Rnus	σ	a) AMW ^{b)}
P-430-5RS	0.61	0.90	1.36	0.24	1800
P-430-5BS	0.64	0.90	0.59	0.20	1600
P-430-5VS	0.56	0.93	2.47	0.16	1000
P-430-30RS	0.65	0.93	0.04	0.17	800
P-430-12BS	0.63	0.95	0.02	0.16	600

a): number of substitution groups per unit structure

b): average molecular weight

larger fa and smaller H/C values and a lower average molecular weight than the other mesophase pitches. The extended treatment (RS, BS) increased H/C and fa and decreased the molecular weight and σ value, indicating that the components became smaller in molecular weight although the aromatization (dehydrogenation) and dealkylation had taken place (Table 3).

The QI of P-430-5VS showed similar H/C and slightly larger fa value than those of P-430-5RS and P-430-5BS. However, the former values were considerably lower and greater respectively than those of P-430-30RS and P-430-12BS which exhibited 100 % anisotropy.

Discussion

The mesophase pitch prepared under vacuum and vigorous stirring exhibited higher solubility and lower melting point at 100 % anisotropic development than pitches prepared under refluxing and gas blowing conditions. Mesophase pitch prepared under vacuum has more homogeneous distribution of molecular size at 100 % anisotropy than pitches prepared under RS and BS conditions; the soluble fraction of the former pitch has a larger average molecular weight than the latter.

The structure of the mesophase pitch prepared under vacuum is created during its preparation. Vacuum pyrolysis with vigorous stirring assures the efficient removal of the lightest components, allowing anisotropic development with a relatively short soak time at a relatively high temperature. The shorter time suppresses excess condensation and cracking which lead to the formation of more QI and lighter fractions, so maintaining a more homogeneous distribution of components and improving the pitch yield. Dehydrogenation is kept to a minimum to maintain naphthenic groups.

In contrast, the relatively poor efficiency of removal under the refluxing condition necessitates a longer soaking time for complete anisotropic development and this causes excessive condensation and cracking during the extended heat-treatment.

References

1. S. Otani, Carbon 3 (1965) 31