Compatibility of Fractions for the Development of the Liquid Crystal State from Mesophase Pitch

Isao Mochida, Yoshihisa Sone and Yozo Korai

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

Mesophase pitches prepared under variable conditions were fractionated using benzene, THF and pyridine. The anisotropy and shape of solidified fraction mixture at variable ratios were examined after the annealing to reveal the interaction among fractions. The anisotropic content increased sharply when BI fraction was beyond the 50 wt%. The interlayer stacking of small molecule of the BS fraction among large planer molecules of BI fraction may allow the anisotropic development. The lighter fraction provides the fusibility of whole mesophase pitch by dissolving the heavier fraction.

INTRODUCTION

Carbonaceous mesophase pitch is recognized as a precursor for carbon fibers of high performance [1,2]. Patents have been issued for its preparation [3,4]. However, the origins and physicochemical understanding of mesophase pitch as a liquid crystal is not fully elucidated. Chemical structures created in the modified pitches under different conditions influenced significantly properties of resultant mesophase pitches [5].

In the present study, the authors have examined fractions of mesophase pitches prepared from modified ETP and naphthalene derived pitch in terms of interactions between fractions to describe the behaviours of the entire pitch as liquid crystal.

EXPERIMENTAL

Properties of mesophase pitches from ETP (provided by Koa Oil Co., LTD) are summarized in Table 1 together with conditions for acidic modification of ETP and anisotropic development from modified pitches. ETP and naphthalene was heat-treated with $AlCl_3$ (5-10 wt%) in a Pyrex tube (50 mm in dia.) under flowing nitrogen with vigorous stirring. The modified ETP (M-ETP) and naphthalene (NA) pitch was washed repeatedly with dilute HCl and then with water to remove the catalyst. Thus produced pitches were further heat-treated to prepare mesophase pitch. Solubility of the mesophase pitch was examined using benzene(B), THF, and pyridine(P). The mesophase pitch was fractionated into soluble(S) and insoluble(I) fractions.

Mesophase pitches, their fractions, and their combined fractions were heated at lower temperature by 20°C than the mesophase pitch preparation temperature for 10 min (heating rate: 5°C/min), and then cooled to room temperature at the rate of 3°C/min under flowing nitrogen.

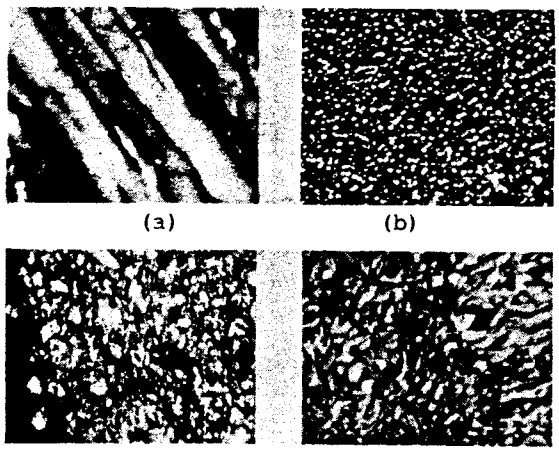
Table 1 Preparative conditions of mesophase pitch[a)]

	Acidic modification		Yield	Anisotropic content	Solubility (wt%)		
	$AlCl_3$ (wt%)	HTT (°C-h)	(wt%)	(vol%)	THFS	PS	QS
ETP	-	-	11	10	38	51	71
M1-ETP	5	250-12	22	70	50	64	69
M2-ETP	5	320- 2	30	90	14	31	34
M3-ETP	10	250- 7	33	100	29	42	52
NA	10	210- 8	50	0	100	100	100

a) prepared at 380° C for 15 h

RESULTS

The microphotographs of the THFS and PI fractions separated from M3-ETP/380-15 are shown in Fig. 1: that of the parent mesophase pitch is also included for comparison. Each fraction showed different features of anisotropy. The optical microphotographs of the mixture of THFS and PI



(a) (b)

(c) (d)

Fig. 1 Optical microphotographs of M3-ETP/380-15 and its fractions after annealing. (a)M3-ETP/380-15, (b)THFS, (c)PI, (d)THFS+PI(mixing ratio: 1/2)

(both fractions from M3-ETP/380-15) after the annealing are also shown in Fig. 1, where the mixing ratio was 1:2 by weight. The shape of optical anisotropy developed after the annealing was elongated mosaic, being quite different in those of each fraction alone. The very much increased size of anisotropy from the mixture indicated that the PI fraction was deformed in the mixture during the annealing.

The anisotropic contents in the respective fractions are compared in Fig. 2. The THFS-fraction alone showed a limited anisotropic content (15 vol%). However, the mixture exhibited anisotropy as high as 95 vol% (mixture volume base), indicating that 75 vol% of the THFS-fraction became anisotropic in the presence of PI.

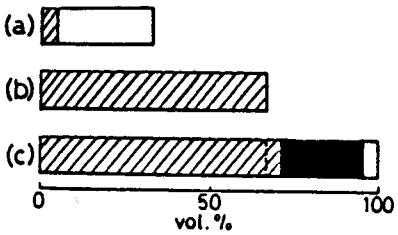


Fig. 2 Anisotropic contents in the THFS, PI, and their combined mixture prepared from M3-ETP/380-15.
Anisotropy, Interlayer stacking
(a) THFS, (b) PI, (c) THFS+PI (mixing ratio: 1/2)

Naphthalene pitch was isotropic even after the heat-treatment at 380°C for 15 h. This heat-treated pitch was separated into BS and BI fractions. The optical textures of BS and BI after the annealing were shown in Fig. 3. Both BS and BI fused during the annealing. The optical texture of the former was isotropic, while that of the latter was mozaic-anisotropic. These BS and BI fractions were mixed at variable mixing ratio and then annealed. The optical texture of the annealed mixtures were also shown in Fig. 3. The anisotropic content increased with the increase of BI content. The optical texture of these mixtures during the heat-treatment was examined using the hot-stage. The results were shown in Fig. 4. BI fused during the heat-treatment, exibited 100 vol% anisotropic. This fraction became isotropic by the increase of temperature.

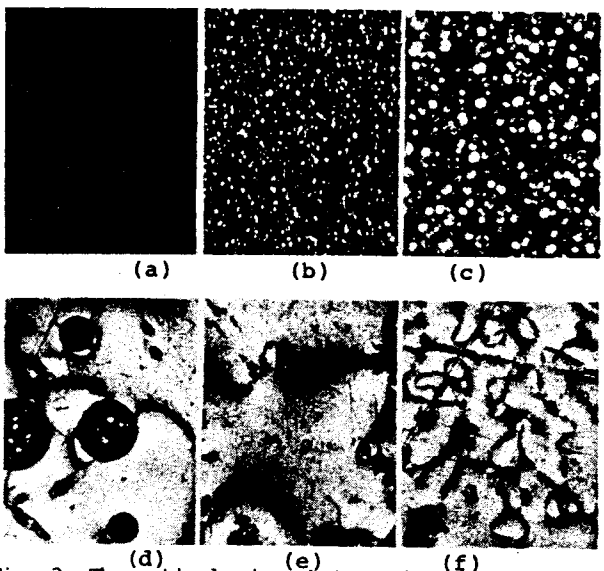


Fig. 3 The optical microphotographs of NA derived mesophase pitch at the variable BS/BI ratio.
(a) BS, (b) BS/BI=3/1, (c) BS/BI=1/1
(d) BS/BI=2/3, (e) BS/BI=1/3, (f) BI

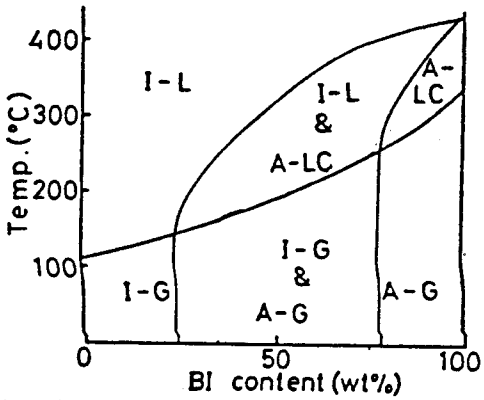


Fig. 4 The thermal behaviours of NA derived pitch

DISCUSSION

The mixture of two fractions from ETP derived mesophase pitch behaves as a liquid crystal during annealing even if, singly, they do not behave as typical liquid crystals. The BS-fraction can be either almost an isotropic liquid or glass-like, depending on temperature, whereas the PI remains as an anisotropic glass without fusing at all. The infusible fraction of anisotropy (PI in the present case) may become soluble in the fusible isotropic fraction at annealing temperatures and is then deformed. On the other hand, the fusible fraction exhibited anisotropy in the presence of the infusible fraction of anisotropy, probably because of its intermediate position in the layered stacking of PI molecules such a kind of mesophase liquid crystal can be defined co-operative one.

The susceptibility of the infusible fraction and the dissolving ability of the fusible fraction will ultimately determine the fusibility of the mixture and this will significantly influence the size of anisotropic optical texture developed after the annealing process. Amounts and nature of the isotropic fusible fraction in the stacked structure of the infusible fraction may influence strongly the extent of development of anisotropy and the fusibility of the mixture. Thus, the compatibility of the two fractions may be a useful concept to understand the above mentioned behaviour of mesophase pitch as reported in the co-carbonization process of pitches and QIs with additives.

Other combination of BS and BI fractions derived from NA pitch provides another kind of liquid crystal, which may be defined a dilute one, since BI alone exhibits liquid crystal state. In this case, the structure of BS should be carefully designed in order to improve the fusibility while maintaining the ordered stacking.

REFERENCES

1. S. OTANI, Carbon 3, 31 (1965)
2. L. S. SINGER, Fuel 60, 839 (1981)
3. R. J. DIEFENDORF and D. M. RIGGS, British Patent Application GB 2005024A (1978)
4. S. CHWASTIAK, British Patent Application GB 2005298A (1979)
5. I. MOCHIDA, Y. SONE and Y. KORAI, Carbon, in press