THE PRODUCTION OF COAL-DERIVED MESOPHASE PITCH

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INTRODUCTION

Because of its unique properties, carbonaceous mesophase is finding use in the production of carbon fibers, microbeads, and high-strength, low-weight composites. Usually mesophase is obtained by the liquid-phase carbonization of complex pitches derived from petroleum, coal tar, or model aromatic compounds. When these materials are heated to temperatures up to 500 °C, anisotropic units of mesophase can be detected optically as small spheres suspended in an isotropic matrix. By careful control of the pyrolysis conditions, pitches containing high concentrations of mesophase with low softening points are possible(1).

Compared with traditional sources of mesophase pitch, relatively little attention has been given to the characterization of mesophase obtained from the products of direct coal liquefaction. Herein we present preliminary work on the properties of coal-derived mesophase pitch compared to mesophase pitch developed from naphthalene and petroleum.

EXPERIMENTAL

A naphthalene pitch was obtained by the pyrolysis of naphthalene under pressure similar to a method described in the literature(2). The naphthalene pitch was partially converted into mesophase upon further heat treatment at atmospheric pressure in a 1-L reactor. The reactor was equipped with an anchor stirrer to provide agitation and a blanket of inert gas to prevent oxidation. An Ashland petroleum pitch (A240) was also partially converted into mesophase using the same reactor system. Two coal-derived "pitches" were made by the direct liquefaction of a hvA bituminous coal in tetralin at 400 °C for 1 hour and at 450 °C for 15 minutes. They were defined as coal pitch 1 (CP1) and coal pitch 2 (CP2), respectively. After removal of tetralin, the coal product was isolated from the unconverted coal and mineral matter using solvent extraction and either filtration or centrifugation, as described elsewhere(3). These coal pitches were then partially converted into mesophase, similar to the method used for the naphthalene and A240 pitch. Moreover, the mesophase-containing coal pitches were also subjected to an additional hydrogenation.

Each mesophase pitch was placed into a hand-fashioned glass ampule and sealed with a flame while under a vacuum to minimize exposure to oxygen. The ampules were placed in a high-temperature centrifuge and the mesophase separated from the surrounding isotropic phase(4). Following centrifugation, the mesophase content can be easily determined by simple weighing after careful physical removal from the isotropic phase. Conventional sample preparation and polishing techniques were employed for reflected, polarized light microscopy in order to estimate the content of mesophase in the pitches before centrifugation as well as to determine when nearly complete separation of the phases occurred.

The starting isotropic pitch, mesophase-containing pitch, and each separated phase were characterized for insolubility in pyridine (PI) and toluene (TI) by Soxhlet extraction, softening point by the Mettler method, and density by helium pycnometry. A Haake Rotovisco RV3 was used to determine absolute viscosity.

RESULTS AND DISCUSSION

In Table 1 are shown some of the data for the starting isotropic materials and their heat treated counterparts. All the pitches were essentially completely soluble in pyridine prior to mesophase conversion. Toluene

insolubles were between 50 and 60 wt% except for A240, which was significantly lower. The naphthalene-based pitch and A240 have relatively low softening points compared to either CP1 or CP2, with CP1 having the highest softening point.

Following partial conversion to mesophase, PI increased dramatically for all the specimens. TI contents also increased and were approximately the same except for CP1, which was nearly 90 wt%. As expected, softening points and densities also increased.

In Table 2 are shown the properties of the isolated mesophase and isotropic phase after high-temperature centrifugation. Mesophase could not be separated from the heat treated coal pitches under the centrifugation conditions employed, however. Thus, the mesophase containing coal pitches were subjected to an additional hydrogenation after which the softening points decreased from 346 to 207 °C and 285 to 188 °C for CP1 and CP2, respectively.

The mesophase from CP1 and CP2 had similar PI but dramatically greater TI content compared with either the naphthalene-based or A240-based substances. Softening points and densities were also comparable.

Shown in Figure 1 are the plots of viscosity versus shear rate for the naphthalene, A240, and CP1 mesophase pitches at 25 °C above their softening points. All the pitches show yield-type behavior with the viscosity becoming constant at the higher shear rates.

CONCLUSIONS

Pitches made from coal liquefaction liquids can be converted into mesophase. However, an additional hydrogenation step must be used in order to lower the softening point of the isotropic phase such that the mesophase can be removed by centrifugation. In many respects, coal-derived mesophase exhibits properties similar to those obtained from petroleum or model compounds.

REFERENCES

1) Korai, Y. and Mochida, I., Carbon, 23, 97 (1985).

2) Greinke, R. A. and Lewis, I. C., Carbon, 22, 305 (1984).

3) Coal-Based Nuclear Graphites for the New Production Gas-Cooled Reactor, DOE DE-FG02-91NP00159, Final Report, May, 1994.

4) Singer, L. S., Lewis, I. C., and Greinke, R. A., Mol. Cryst. Liq. Cryst., 132, 65 (1986).

Table 1 Characteristics of Starting Isotropic and Heat Treated Pitches

	Prior to Heat Treatment			
	Naphthalene Pitch	A240	CP1	CP2
PI wt%	1	0	0	0
TI wt%	53	35	52	59
Softening Point °C	122	140	231	184
Density g/cm³	1.263	1.239	1.244	1.238

	After Heat Treatment			
	Naphthalene Pitch	A240	CP1	CP2
PI wt%	63	62	66	62
TI wt%	63	66	88	68
Softening Point °C	319	212	346	285
Density g/cm³	1.314	1.302	1.235	1.262

Table 2 Characteristics of Separated Phases

	Naphthalene MP	Naphthalene ISO	A240 MP	A240 ISO
PI wt%	75	45	60	44
TI wt%	73	52	68	49
Softening Point °C	349	221	328	178
Density g/cm³	1.342	1.300	1.331	1.281

	After Rehydrogenation			
	CP1 MP	CP1 ISO	CP2 MP	CP2 ISO
PI wt%	67	<1	67	<1
TI wt%	94	59	87	44
Softening Point °C	356	204	350	168
Density g/cm³	1.344	1.254	1.341	1.257

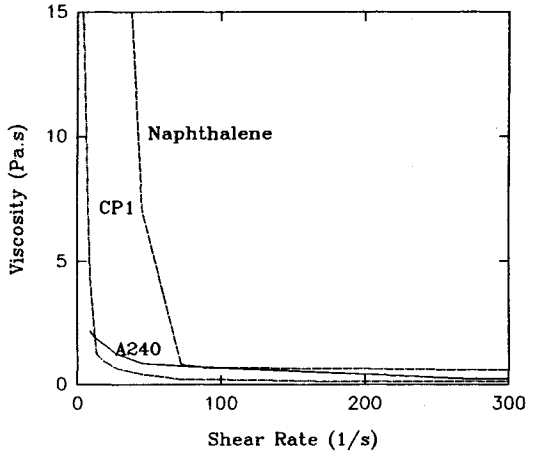

FIGURE 1: Viscosity Vs Shear Rate for A240, Naphthalene, and Coal-based mesophase pitches.