

CHARACTERIZATION OF COAL TAR PITCHES IN AIR-BLOWING REACTION BY ULTRASONIC METHOD

Akira Tanaka

Department of Materials Science

The University of Shiga Prefecture, Hikone 522, Japan

Chiharu Yamaguchi, Juji Mondori, and Hisaji Matsui

Fundamental Research Laboratory

Osaka Gas Co., Ltd., Osaka 554, Japan

Introduction

Coal tar pitch is one of important intermediates (or pre-cursors) for carbon materials. To get desirable carbon materials, one may modify the molecular structure and molecular aggregation state of pitch by various methods; Air blowing reaction is an effective method to elevate the softening point of pitches and to give pitches in isotropic molecular aggregation state. In the air blowing reaction, heat (or temperature), air (or oxygen), and distillation (or low pressure) are important factors to determine chemical and physical properties of pitch.

In previous studies [1], the authors (AT, CY) et. al. have showed that the ultrasonic method is useful to monitor the change in molecular structure and molecular aggregation state of pitch. In the present paper, we aimed to examine the change in molecular structure and molecular aggregation state of pitch with air blowing reaction using ultrasonic method.

Experimental

Preparation condition of pitches used in this study and their softening point (SP) are summarized in Table I. CT0 is QI-free pitch which was obtained by removing the pri-

Table I Preparation Condition of Pitch Samples and SP

Sample Code	Press (MPa)	Time (min)	Temp (°C)	SP (°C)
CT0	—	—	—	79
Air-blown				
CT5	1.6	280	330	282
CT6	1.6	90	330	153
N ₂ -blown				
CT7	1.6	280	330	85
CT8	0.02	280	330	224
CT9	1.6	280	430	95

mary quinoline-insoluble components in the tar by filtration followed by vacuum distillation.

The propagation intensity (A) was measured as a function of temperature on heating and cooling for all the pitch samples. In general, the propagation intensity (A) is expressed as in the following equation:

$$A = A_0 \exp(-\alpha L)$$

where L is the traveling distance of an ultrasonic wave in the sample, A_0 the propagation intensity when $L=0$, and α the attenuation coefficient. Accordingly, the value of $-\ln A$ is proportional to the attenuation coefficient (α) when the propagation distance (L) is constant.

To characterize all the pitch samples, in addition, we carried out solvent extraction analysis, ESR and NMR measurements, and polarizing optical microscope observation.

Results and Discussion

Figure 1 shows the effect of reaction (heating) temperature on the temperature dispersion curve of $-\ln A$. Both the pitches, CT7 and CT9 were prepared under the condition at pressure of 1.6Mpa and reaction time of 280 min. However, the pitches were prepared at different reaction temperatures; CT7 at 330°C and CT9 at 430°C. In the figure, thick lines denote the values of $-\ln A$. Thin lines denote the Lorentz type of curves obtained by peak separation. As is clear from the figure, the dispersion curve hardly changed with reaction temperature. Also, the curves for CT7 and CT9 were very similar to that for no heat-treatment pitch, CT0, indicating that the reaction temperature does not affect to the dispersion curve. By the way, the appearance of the mesophase was found by the polarizing optical microscope. This may indicates that the heating causes the development of aromatic structure.

Figure 2 shows the variation of $-\ln A$ with temperature for pitches prepared under air-blowing for different reaction times. The other preparation condition of the pitches

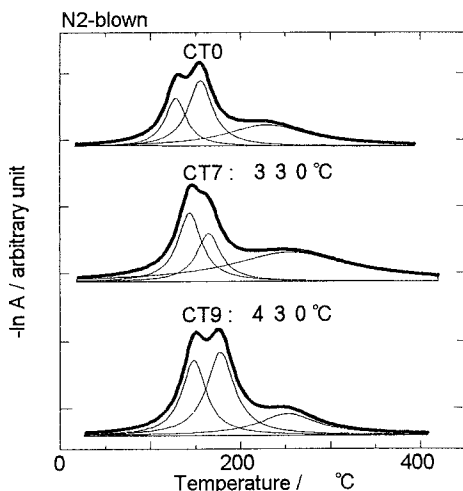


Figure 1 The variation of $-\ln A$ with temperature for pitches at different temperatures under nitrogen gas blowing. (Pressure: 1.6MPa / Reaction time: 280min)

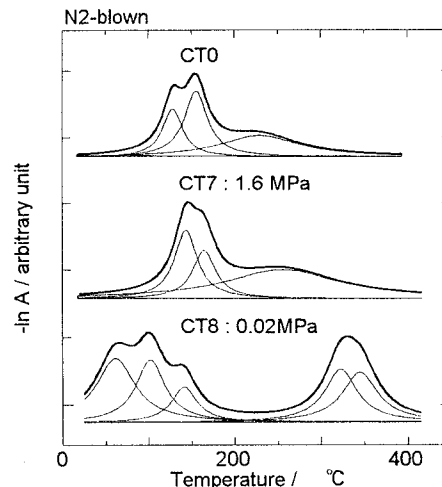


Figure 3 The variation of $-\ln A$ with temperature for pitches prepared under nitrogen gas blowing at different pressures. (Temperature: 330°C / Reaction time: 280min)

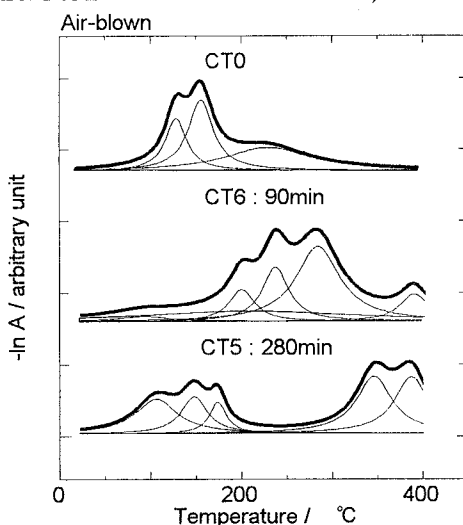


Figure 2 The variation of $-\ln A$ with temperature for pitches prepared under air-blowing for different reaction times. (Pressure: 330°C / Pressure: 1.6MPa)

was same as follows; heating temperature was 330°C and pressure was 1.6MPa. As is seen in the figure, the curve largely changed with reaction time; at 90min, new peaks appeared around 200°, 280°, and 380°C. At 280min, the peaks shifted discretely to higher temperatures over 300°C, and also three peaks appeared in the lower temperature region below the softening point; 105°, 150°, and 175°C. These peak temperatures seems to be rather characteristic to the molecular structures, respectively. From the NMR and ESR analysis, it was found that biphenyl bonds increased by the reaction with oxygen. This result may indicate that the polymerization proceeds with air (oxygen) blowing.

Figure 3 shows the effect of distillation on the temperature dispersion curve; the reaction was done under nitrogen gas blowing at 330°C for 280min. Also in this

case (CT8), new several peaks appeared in the temperature region above and below the softening point: 330° and 350°, and 60°, 100°, and 140°C. The peaks also seems to be characteristic to some phase transition (or structure change); the peak temperatures are lower than those appeared in the case of oxygen blowing, respectively, indicating that the peaks are due to the different molecular motions. The NMR and ESR analysis indicated that bridged bond (methylene bond, i.e., $-\text{CH}_2-$) increased with distillation. However, no polymerization reaction may occur in the nitrogen blowing under vacuum. To consider these results together, the peaks below the softening point may be ascribed to the motion due to rotation of sub-units of pitch molecules bonded by $-\text{CH}_2-$ bond. The higher temperature peaks above the softening point may be ascribed to the segmental motion of pitch molecules as a whole. Both the motions above and below the softening point may shift to higher temperatures. This may be caused by elimination of low molecular weight materials, which acts as a plasticizer.

Furthermore, we examined the ultrasonic properties and others for the distillates and residues which were sampled out on several stages of distillation. As distillation proceeded, the softening point of residue pitches became higher and the temperature dispersion peaks of $-\ln A$ shifted to higher temperatures. While for all the distillates, no clear peak appeared. This indicates that the dispersion peaks for pitches are not ascribed to the decomposed materials and/or lower molecular weight materials.

References

1. A.Tanaka, H.Matsumoto, C.Yamaguchi, K.Tokumitsu, Carbon, 32, 1137 (1994).