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The relationship between structure and viscosity of petroleum pitch in the process of mesophase formation

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A change in the viscosity of a petroleum pitch with heat-treatment time was measured at constant heat-treatment temperature with a capillary viscometer. At heat-treatment temperatures of 673, 723 and 753 K, the viscosity is initially increased with heat-treatment time due to an increase in the average molecular weight of the sample and then decreased by the formation of optically anisotropic spherules, which is also caused by the increase in the average molecular weight. After this decrease the viscosity is increased again by the growth of the spherules. The viscosity of the grown spherules may become higher than that of isotropic phases. With higher heat-treatment temperatures, the viscosity curve showing the above behaviour shifts to the side of the shorter heat-treatment time. The average molecular weight of the sample necessary for the formation of the spherules is higher at higher heat-treatment temperatures. The decrease in the viscosity due to the formation of the spherules took place once the extent of the stacking layers of aromatic hydrocarbons, evaluated from X-ray diffraction, was in the range of 1.41 to 1.47 nm along the stacking direction, independent of the heat-treatment temperature.

1. Introduction

Much attention has been given to mesophase pitch in the preparation of a low cost carbon fibre [1, 2]. The viscosity of mesophase pitch is one of the most important factors in the spinning of highly oriented carbon fibres [3]. Barr *et al.* [4] measured the temperature dependence of the apparent viscosity at a programmed heating rate of 40 K min^{-1} for a starting isotropic pitch and two different mesophase pitches. Below about 670 K, the viscosity variations are reversible, the viscosity first decreases rapidly with increasing temperature, and then becomes approximately constant. Such discontinuities in the viscosity are presumably due to the two-phase and liquid-crystal character of the system. At temperatures higher than about 670 K, polymerization to coke occurs quite rapidly and the corresponding rapid increase in viscosity is irreversible.

Collett and Rand [5] measured the rheological characteristics of two coal-tar ptiches, during their transformation to a mesophase by means of rotational viscometry. The apparent viscosity, at all rates of shear, increased very rapidly at temperatures above 693 K when the mesophase content was in excess of 25%. A peak in the apparent viscosity–temperature curves appeared at all the rates of shear investigated. Initially an emulsion of the mesophase in an isotropic liquid exists but this transforms, at higher temperatures, to one of an isotropic liquid in a mesophase. The maximum in the apparent viscosity appears to correspond to the phase inversion point.

In this work, the viscosities of petroleum pitch in the process of mesophase formation are measured at constant temperatures with a capillary viscometer and the structural changes are explored using a polarizing microscope, X-ray diffractometer, thermogravimeter (TG) and differential scanning calorimeter (DSC), in addition to the measurement of the fraction of the pyridine-insoluble phases. The relationship between mesophase formation and viscosity is elucidated.

2. Experimental details

The sample used was an optically isotropic petroleum pitch, Ashland A-240 LS. A uniform-bore capillary viscometer equipped with a heating bath and thermostat was used to measure the change in the viscosity of the petroleum pitch at constant temperatures of 673, 723, 753 and 773 K in an atmosphere of nitrogen.

The pyridine-soluble phases of the sample heat-treated in an atmosphere of nitrogen were extracted by using a Soxhlet's extractor and the amount of pyridine-insoluble phase was measured. The lumpy samples prepared by the heat-treatment were embedded in a resin at room temperature and their surfaces were polished after the resin had hardened at room temperature. These samples were viewed with a polarizing microscope using reflected polarized light. The number ratios of carbon to hydrogen atoms for the lumpy samples were evaluated as a function of heat-treatment time by means of elementary analysis. Thermal degradation and the change in the heat capacity of the sample as a function of time were measured at the

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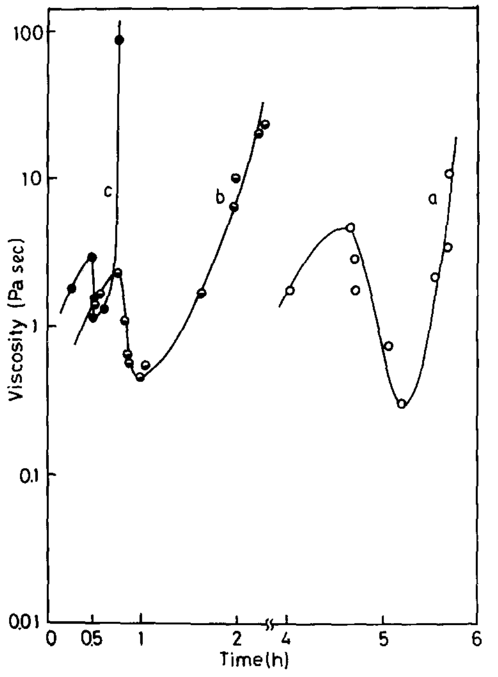

Figure 1 Viscosity as a function of heat-treatment time at (a) 673, (b) 723 and (c) 753 K.

same constant temperatures as the heat-treatment temperatures in an atmosphere of nitrogen with a Shimazu DT-30 thermal analyser (Shimazu Seisakusho Co., Ltd) and a Unix differential scanning calorimeter (Rigaku Denki, Co., Ltd), respectively. For the fine-powder samples heat-treated in an atmosphere of nitrogen, the spacing d_{002} between the stacked layers of aromatic hydrocarbons and the extent L_c of the stacking layers along the stacking direction were evaluated, using wide-angle X-ray diffraction curves obtained using an X-ray diffractometer. In the evaluation of L_c the instrumental broadening was corrected for using a quartz standard and Scherrer's equation.

3. Results

Fig. 1 shows the viscosity of the petroleum pitch as a function of heat-treatment time at 673, 723 and 753 K. The viscosity at 773 K could not be measured because of the vigorous evolution of gas during the heat-treatment. At each temperature the viscosity first increased with heat-treatment time and then decreased. However after the decrease the viscosity increased again. For higher temperatures, the viscosity curve exhibiting such behaviour shifted to the side of the shorter heat-treatment time.

Fig. 2 shows the polarization optical micrographs under crossed Nicol prisms in the samples which are heat-treated at 723 K for 0.5, 1, 2 and 5 h. The micrographs of the heat-treated samples were taken at room temperature, where the heat-treated samples had been rapidly quenched from the heat-treatment temperature of 723 K to room temperature. The anisotropic structure formed by the heat-treatment was fixed immediately by the quenching. The sample fused at 723 K was optically isotropic within the heat-treatment time of 0.5 h, spherules appeared initially after 0.5 h. and grew after that transforming into a continuous anisotropic phase after 2 h. A similar growing process for anisotropic phases could be observed at the heat-treatment temperatures of 673, 753 and 773 K. The higher the temperature, the shorter the time for the appearance and growth of the spherules. Comparison of the polarizing microscopic observation with the heat-treatment time dependence of viscosity, which is shown in Fig. 1, indicates that the viscosity increase during early stage of the heat-treatment began to decrease at the initial stage of the appearance of the spherules. The viscosity increased again in the course of the spherule growing process. The spherules changed finally into the continuous anisotropic phase.

Fig. 3 shows the relationship between the viscosity and the amount of pyridine-insoluble phase as a

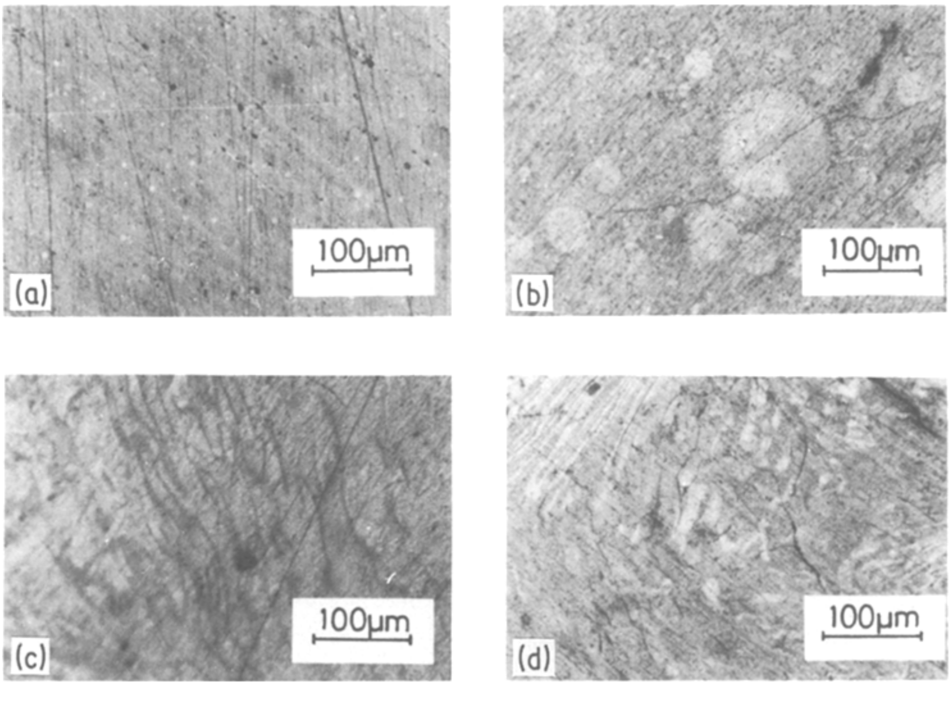

Figure 2 Change of polarizing microscopy with heat-treatment time at 723 K. (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 5 h.

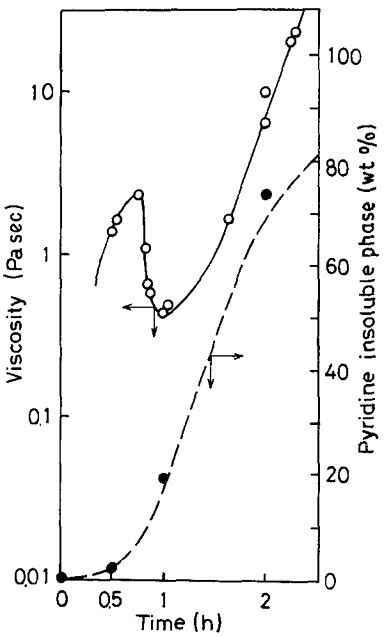

Figure 3 Relationship between viscosity and the pyridine-insoluble phase as a function of heat-treatment time at 723 K.

function of heat-treatment time at 723 K. The non-heat-treated sample can be almost completely dissolved in pyridine. The appearance of pyridine-insoluble phases was initiated by heat-treating for more than 0.5 h, whereas the spherules initially appeared after about 0.5 h, as shown in Fig. 2. After about 1 h the pyridine-insoluble phase largely increased with the growth of the optically anisotropic phases. The increase of the pyridine-insoluble phase with heat-treatment time was conspicuous within ~ 2 h. According to Barr *et al.* [4], the pyridine-soluble phase of a mesophase pitch is usually found to have an average molecular weight of ~ 600. The liquid crystalline phase remains largely insoluble because of its higher average molecular weight [4]. Table I shows the amounts of pyridine-insoluble phase at the maximum and minimum viscosities which were observed at the heat-treatment temperatures of 673, 723 and 753 K, as shown in Fig. 1. The amount of pyridine-insoluble phase at the maximum and minimum viscosities increased with increasing heat-treatment temperature.

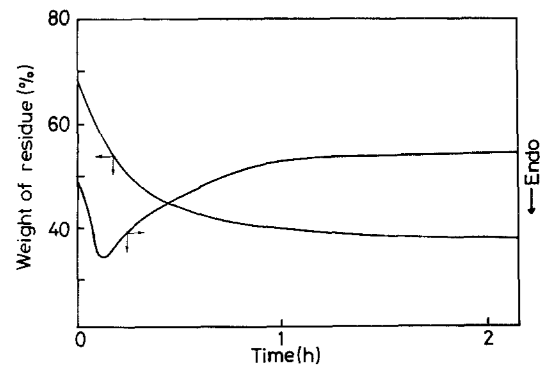

Figure 4 TG and DSC curves as a function of heat-treatment time at a constant temperature of 723 K.

Fig. 4 shows the TG and DSC curves as a function of heat-treatment time at the constant temperature of 723 K. Within the heat-treatment time of ~ 2 h the weight of the sample decreased significantly and the endothermic broad peak appeared. However both the TG and DSC curves showed less change after ~ 2 h. Fig. 5 shows the number ratio of carbon to hydrogen atoms which was evaluated as a function of heat-treatment time at 723 K. The total content of carbon and hydrogen in the non-heat-treated sample was 98 wt %. The evaporation of low-boiling point compounds and the condensation polymerization to large aromatic hydrocarbons proceeded rapidly within a heat-treatment time of ~ 2 h, considering the increase in the number ratio of carbon to hydrogen atoms with time. This mechanism for the evaporation and condensation polymerization is supported by the results of the TG and DSC shown in Fig. 4. The increase in the pyridine-insoluble phase shown in Fig. 3 indicates an increase in the average molecular weight in the sample. This increase in the average molecular weight is caused by both the evaporation of low-boiling point compounds and the condensation polymerization to large aromatic hydrocarbons.

TABLE I Quantity of the pyridine-insoluble phase at the maximum and minimum viscosities shown in Fig. 1, at heat-treatment temperatures of 673, 723 and 753 K

Viscosity	673 K	723 K	753 K
Maximum	3 wt %	7 wt %	63 wt %
Minimum	4	19	65

Fig. 6 shows the spacing d_{002} between the stacking layers of the aromatic hydrocarbons and extent L_c of the stacking layers along the stacking direction, as a function of heat-treatment time at 723 K. It becomes apparent from Fig. 6 that the number of hydrocarbons in the stacking layers is increased and the hydrocarbons are more compactly packed, as indicated by the increase in L_c and the decrease in d_{002} with heat-treatment time. However it seems that the extent L_c reaches a limiting value, as seen in Fig. 6 as the slope levels off gradually after ~ 2 h. The development of a three-dimensional graphite-like structure would not be realized by the heat-treatment carried out at temperatures of 673 to 753 K, because in the X-ray diffraction intensity curves the profile of the (0 0 2) reflection was broad and the other reflections from the anisotropic phases could not be observed. This means that the anisotropic phases are solidified in a nematic liquid crystalline order and the lateral and longitudinal extent of the stacking layers is much smaller than that in graphite.

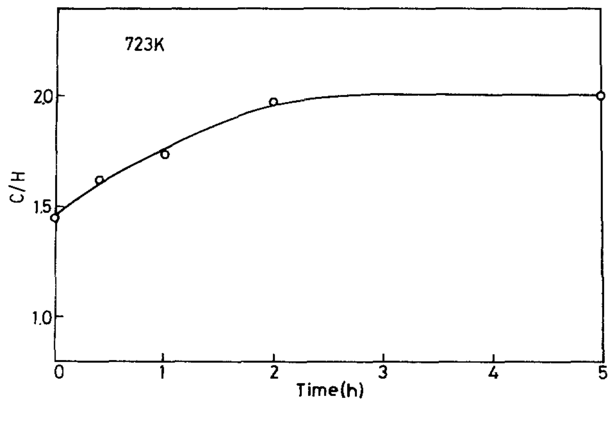

Figure 5 Number ratio of carbon to hydrogen atoms as a function of heat-treatment time at 723 K.

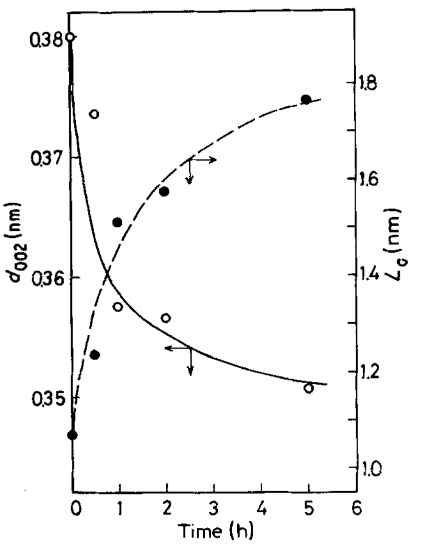

Figure 6 Spacing d_{002} between the stacking layers of the aromatic hydrocarbons and the extent L_c of the stacking layers along the stacking direction, as a function of heat-treatment time at 723 K.

Table II shows the extents L_c of the stacking layers at the maximum and minimum viscosities shown in Fig. 1. The values of L_c at the maximum and minimum viscosities did not change significantly with increasing heat-treatment temperature. It becomes apparent that above a critical value of L_c, 1.41 to 1.47 nm, the viscosity decreases and the optically anisotropic phases form as the spherules are initially observed.

4. Discussion

In the non-heat-treated sample composed of overall isotropic phases, the X-ray diffraction peak of (0 0 2) was measured, in addition to the broad peak originating from the amorphous phases. This indicates that in the optically isotropic phases the stacking layers composed of several planar aromatic hydrocarbons are formed in addition to the amorphous phases. In fact the extent L_c of the stacking layers along the stacking direction was ~ 1.1 nm, as shown in Fig. 6. However, even if the stacking layers are aggregated to form spherules, the size of the spherules is too small to observe as an anisotropic phase with a polarizing microscope. As shown in Figs 3 and 4, the average molecular weight of the aromatic hydrocarbons in the sample is increased with heat-treatment time by the evaporation of low-boiling point compounds and the condensation polymerization to result in an increase in the viscosity of the isotropic state. Such an increase in viscosity during the early stage of heat-treatment may arise as a result of the stronger intermolecular interaction between growing molecules which are distributed randomly in the isotropic phases.

In the two-dimensional extension process of the aromatic hydrocarbons caused by condensation polymerization, the hydrocarbons begin to aggregate to form stacking layers the extent of which is larger than that in the optically isotropic phases, as shown in Fig. 6, and thus optically anisotropic spherules composed of the stacking layers are formed. The size of the spherules increases with heat-treatment time at the expense of the isotropic phase after the formation of the spherules. With the formation of the spherules the viscosity decreased, as shown in Figs 1 and 2, since the fraction of the isotropic phase is decreased by the growth of the spherules and the hydrocarbons in the spherules are oriented more easily to the flow direction. From Arrhenius plots of the heat-treatment time at the maximum viscosity shown in Fig. 1, the activation energy of the formation of the spherules can be evaluated as ~ 120 kJ mol^{-1}. From the fact that the amount of pyridine-insoluble phase at the maximum viscosities increased with increasing heat-treatment temperature, as shown in Table I, it becomes apparent that at higher heat-treatment temperatures the high molecular weight aromatic hydrocarbons are necessary to form optically anisotropic phases. As shown in Table II, the fact that the extents L_c of the stacking layers at the maximum viscosities were 1.41 to 1.47 nm along the stacking direction, independent of heat-treatment temperature, would be due to the following reason: the value of L_c depends on both the thermal molecular motion of the hydrocarbons and their molecular weights. That is to say, the larger thermal molecular motion taking place at higher heat-treatment temperature may prevent the stacking of the high molecular weight hydrocarbons which normally form the stacking layers more readily than the lower molecular weight hydrocarbons, and thus spherules composed of the stacking layers with almost the same extent L_c may be formed.

During the growth of the spherules the two-dimensional extension of the aromatic hydrocarbons which make up the growing spherules is more progressed corresponding to the increase in the average molecular weight and therefore the interactions between the hydrocarbons in the grown spherules are increased. Thus the viscosity of the grown spherules becomes much higher than that of the isotropic phase and subsequently the viscosity of the sample is increased again with heat-treatment time after the viscosity becomes minimum, as shown in Fig. 1.

TABLE II Extents, L_c, of the stacking layers along the stacking direction at the maximum and minimum viscosities shown in Fig. 1. Heat-treatment temperatures are 673, 723 and 753 K

Viscosity	673 K	723 K	753 K
Maximum	1.47 nm	1.41 nm	1.45 nm
Minimum	1.48	1.48	1.48

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