

The carbonization process giving a graphitizable needle coke consists of the condensation reaction and rearrangement of condensed molecules into layer structure. Then, fusibility and suitable reactivity which may lead to low viscosity of the carbonization matrix are required for the carbonizing materials to be the source of needle cokes¹⁾. Such requirements must reflect the total features of a pitch because a pitch is composed of many components, one of which may sometimes play a role of a solvent to keep the system fusible, and the other of which can initiate the condensation, accelerating the carbonization. Although it is difficult to define the components of a pitch precisely, benzene soluble (BS) or insoluble (BI) is a practical fractionation because fusible BS can often work as a solvent during the carbonization and dissolved BI accelerates the carbonization. Thus, the concept of compatibility was introduced to describe the cocarbonization properties of the mixtures of BS and BI. In the present paper, the concept of compatibility is reviewed from the viewpoints of its qualitative representation and its modification, referring the structural argument of the pitch.

Material: Two kinds of SRC (Solvent Refined Coal) pitch named No.1 and No.2 were used in the present study. The BS fractions of coal-tar pitch (Nittetsu Chemical Co.), ethylene-tar pitch (ET) (by-product at the thermal cracking of naphtha (Kōa Oil Co.)), and Kureha pitch (KP-BS) (by-product at the thermal cracking of crude oil. Kureha Chemical Industry) were also used. Carbonization was carried out in a pyrex tube (30 mm ϕ x 300 mm) under a nitrogen gas flow. The rate of temperature increase was 150°C/hr. The holding time at a fixed temperature was 2 hr. The mixed pitch consists of 60% BS and 40% SRC-BI in every case.

Cocarbonization of SRC-BI fractions with the BS fractions of other pitch sources clearly suggested the concept of compatibility. Although all BS fractions used in the present study gave needle cokes in their single carbonization, some of their mixtures with the SRC-BI gave needle cokes and other did mosaic ones, that is, KP-BS and No.1-BS gave needle cokes in cocarbonization with both SRC-BI fractions, but ET and No.2-BS did mosaic one with both SRC-BI. The CP-BS formed a needle coke with No.1-BI but did a mosaic one with No.2-BI.

The cocarbonization compatibility could be qualitatively described by observ-

ing a series of the cokes which were produced by varying the mixing ratio of BS and BI.

The cocarbonization properties were tried to be correlated with the molecular weight, H/C ratio and fa value²⁾ of BS, however no relation was observable. Nevertheless, the poor compatibility of ET which produced fine mosaic cokes with SRC-BI is presumable to come from its small molecular weight. Based on above assumption, modification of ET to be compatible with SRC-BI was carried out by the thermal and acid-catalyzed reactions. The reactions can be classified into three categories. The first one is the catalytic reaction with aluminum chloride which is a typical Lewis acid of non-transition metal ion, the second one is the catalytic one with ferric chloride which is a typical Lewis acid of transition metal ion, and the third one is the thermal reaction without catalyst. Microphotographs of carbons obtained from SRC-BI and ET or BS fraction of modified ET (M-ET-BS) are shown in Fig. 1. Although original ET gave fine mosaic cokes with SRC-BI regardless of No.1 and No.2. Modification with aluminum chloride (I: refer to Table 1) converted ET compatible with both SRC-BI to give needle cokes, however modification with ferric chloride (II: refer to Table 1) produced still fine mosaic cokes with both SRC-BI similarly as the original ET did. Thermal treatment (III: refer to Table 1) gave a needle coke with No.1-BI but failed with No.2-BI.

Some properties of original ET and M-ET-BS were summarized in Table 1. Although all reactions increased the molecular weight by 110-180, they brought about slight change in the values of H/C and fa. The most significant difference is observed in the values of Ho/H and Hy/H, which are calculated from NMR analysis. The pitch modified with aluminum chloride had the higher values to giving the excellent needle cokes with SRC-BI. In a previous paper³⁾, the values of Ho/H of the carbonization intermediates were reported high when aluminum chloride was used as the catalyst giving needle cokes, whereas they were low when alkali metals or transition metal chlorides were used to give isotropic or mosaic cokes. Such observation could be explained in terms of lowered melting point and suitable reactivity of the partially hydrogenated ring which were preferable for the carbonizing system to maintain the liquid phase.

The same explanation may be applicable for the better compatibility, and suggests a possibility that further hydrogenation may improve the compatibility of M-ET-II-BS. The results are shown in Fig.2, indicating that the above explanation is valid.

Thus, the concept of compatibility is quite useful to describe the carbonization properties of the pitches and provides directions for their modification.

References

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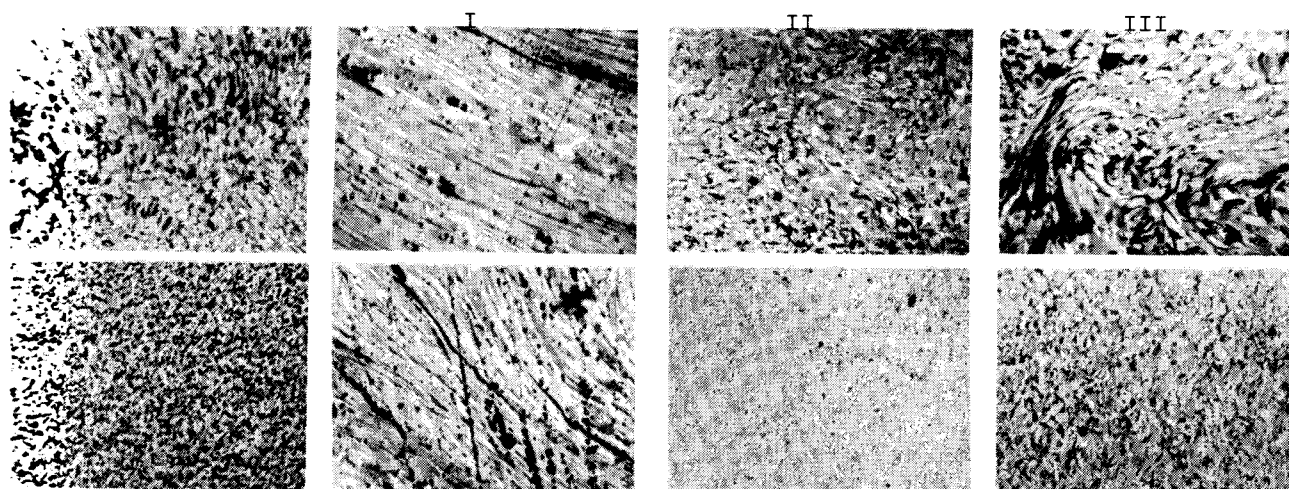


Fig.1 Microphotographs of cokes obtained from the mixture of ET or MET-BS and SRC-BI under crossed nicols (X 200). Carbonization; 600°C-2hr (1) No.1-BI (2) No.2-BI (Orig.) ET original, (I) MET-I-BS, (II) MET-II-BS, (III) MET-III-BS

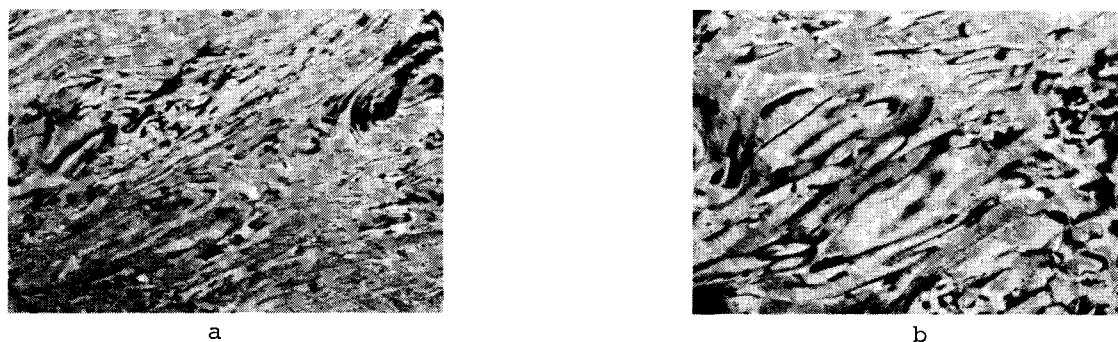


Fig.2 Microphotographs of cokes obtained from the mixture of hydrogenated MET-II-BS and SRC-BI under crossed nicols (X 200). Carbonization; 600°C-2hr
(a) cocarbonization with No.1-BI
(b) cocarbonization with No.2-BI

Table 1. Some properties of ET and MET-BS

	Modification Conditions	Y. ¹ (%)	BS ² (%)	H/C	Ha/H ³	H ¹ -NMR Ha/H ³	Ho/H ³	Hγ/H ³	fa	C ¹³ - fa	MW
Orig.	ET-Original		100	0.95	50.0	35.9	12.2	1.9	0.76	0.76	230
MET-I	1.0 mol AlCl ₃ 260°C-4 hr	97	71	0.90	33.7	35.8	24.2	6.3	0.70	0.63	410
MET-II	1.0 mol FeCl ₃ 400°C-0 hr	85	74	0.90	47.6	34.5	15.0	2.9	0.76	0.72	340
MET-III	None catalyst 400°C-0.5 hr	50	99	0.83	48.5	33.3	15.8	2.4	0.79	-	350

1) Y.(%) = $\frac{\text{MET after modification}}{\text{ET before modification}}$

2) BS(%) = $\frac{\text{BS in MET}}{\text{MET after modification}}$

3) %