JOURNAL OF MATERIALS SCIENCE 28 (1993) 3741–3748

Enhanced mesophase formation of petroleum pitch by polyaromatic hydrocarbon addition

YUN-SOO LIM, BURT I. LEE*
Department of Ceramic Engineering, Clemson University, Clemson, SC 29634, USA

Enhanced mesophase yield was achieved for A-240 pitch by addition of aromatic hydrocarbon compounds (anthracene and acenaphthylene) as nucleating agents. A-240 pitch was acid/solvent extracted prior to adding the aromatic hydrocarbons. The mesophase yields increased by significant amounts at 1 wt% addition of the nucleating agents, but decreased at 3 wt% addition. A source of Brönsted acids was required to initiate the catalytic reaction enhancing the mesophase formation.

1. Introduction

The principal constituent molecules of the precursor pitch for carbon fibres are a disc-like aromatic pitch compound. The compound phase is composed of isochromatic areas that increase in size and magnitude at the expense of the original isotropic liquid phase, as carbonization proceeds. Such a structural characteristic causes several problems in the production of pitch-based carbon fibres. One problem causing concern is the strength of the as-spun pitch fibres as well as the carbonized fibres. The low reactivity of pitch fibres for oxidative stabilization is another problem. Such problems may be solved by the polymerization of the constituent molecules of precursor pitch and/or the addition of reactive functional compounds having, for example, naphthenic and alkyl groups [1, 2].

A number of researchers have recognized the importance of reactivity and coking rates while studying the carbonization for mesophase development by reactive aromatic hydrocarbon compounds [3–8]. Mochida *et al.* [9] noted that the carbonization reaction proceeds through radical initiation, propagation, recombination (condensation), and termination. Synthesis of pitch from pure aromatic hydrocarbons with the aid of catalysts which can provide more suitable structure has been examined using acids. Strong Lewis acids, e.g. $AlCl_3$, $FeCl_3$, $ZnCl_2$ and BF_3, have been used as the catalysts [10]. The acids were expected to perform selectively Friedel–Crafts reactions of aromatic rings. Brönsted acids, e.g. HNO_3, HCl, H_2SO_4 and HF, have also been used as catalysts in the Friedel–Crafts reaction for alcohols.

In this study, solvent-extracted/purified petroleum pitches were mixed with anthracene ($C_{14}H_{10}$) or acenaphthylene ($C_{12}H_8$) ranging from 1–3 wt % as a nucleation catalyst to enhance the mesophase formation. In other words, the purpose of adding a pure aromatic hydrocarbon is to promote the degree and kinetics of liquid crystallinity at lower temperatures. The characteristics of the nucleating agents used for mesophase formation in this study are given in Table I.

2. Experimental procedure

A quantity (20 g) of A-240 pitch (a petroleum pitch having a softening point of 240F (~115 °C), Ashland Co.) was magnetically stirred with organic solvents or acidified organic solvents for 5 h at room temperature, and the residue was filtered using a vacuum pump, and dried in a vacuum oven for 3 h at 60 °C. The solvent and acid composition and amounts of residue are shown in Table II. The acidified solvents were used to extract any inorganic impurities in the pitch; the results have been reported previously [11]. The results are potentially significant because the metallic impurities adversely affect the properties of the carbonaceous products. The dried pitch residue was mixed with 1 wt % anthracene or acenaphthylene as a nucleating agent for mesophase formation. The blended pitches were initially dissolved in benzene and dried in a nitrogen atmosphere at room temperature, then dispersed again in ethanol. The pitch slurry was heated to 350 °C for 1 or 2 h in a nitrogen atmosphere. Diffuse reflectance–Fourier transform–infrared spectroscopy (FT–IR) was used to analyse the nature and type of functional groups formed in the mesophase during the heat treatment.

Mesophase pitch specimens for microscopic examination were prepared by encapsulating the heat-treated pieces of pitch in a ring mould with a liquid epoxide resin and a hardener, which were cured at room temperature. The optical textures of the mesophase pitches after polishing were observed under a reflection polarized microscope to distinguish between isotropic and anisotropic regions and to compare the differences between the mesophase pitches.

---

*Author to whom all correspondence should be addressed.

0022–2461

Microscopic observations and photography were carried out with a Zeiss model ICM-405. All photomicrographs were taken at × 160. In general, several areas of the polished section were photographed with Polaroid Type 53 ISO 800 film.

The softening point was measured in air using Fisher–Jones melting point apparatus by the polymer melt or stick-temperature test using fine-powder mesophase pitches. The flow diagram for the experiment is shown in Fig. 1.

3. Results and discussion

3.1. Infrared spectroscopy

Fig. 2 shows the 1 wt % anthracene-added pitches after heat treatment at 350 °C. No qualitative differences between the different pitches are seen in Fig. 2. On comparing this figure with the FT–IR spectra of mesophase THE10 (350 °C/2h) pitch in Fig. 3b, no effect of anthracene in the mesophase pitches could be qualitatively distinguished except for the peak for atmospheric CO_2 at 2350 cm^{-1}. This indicates that

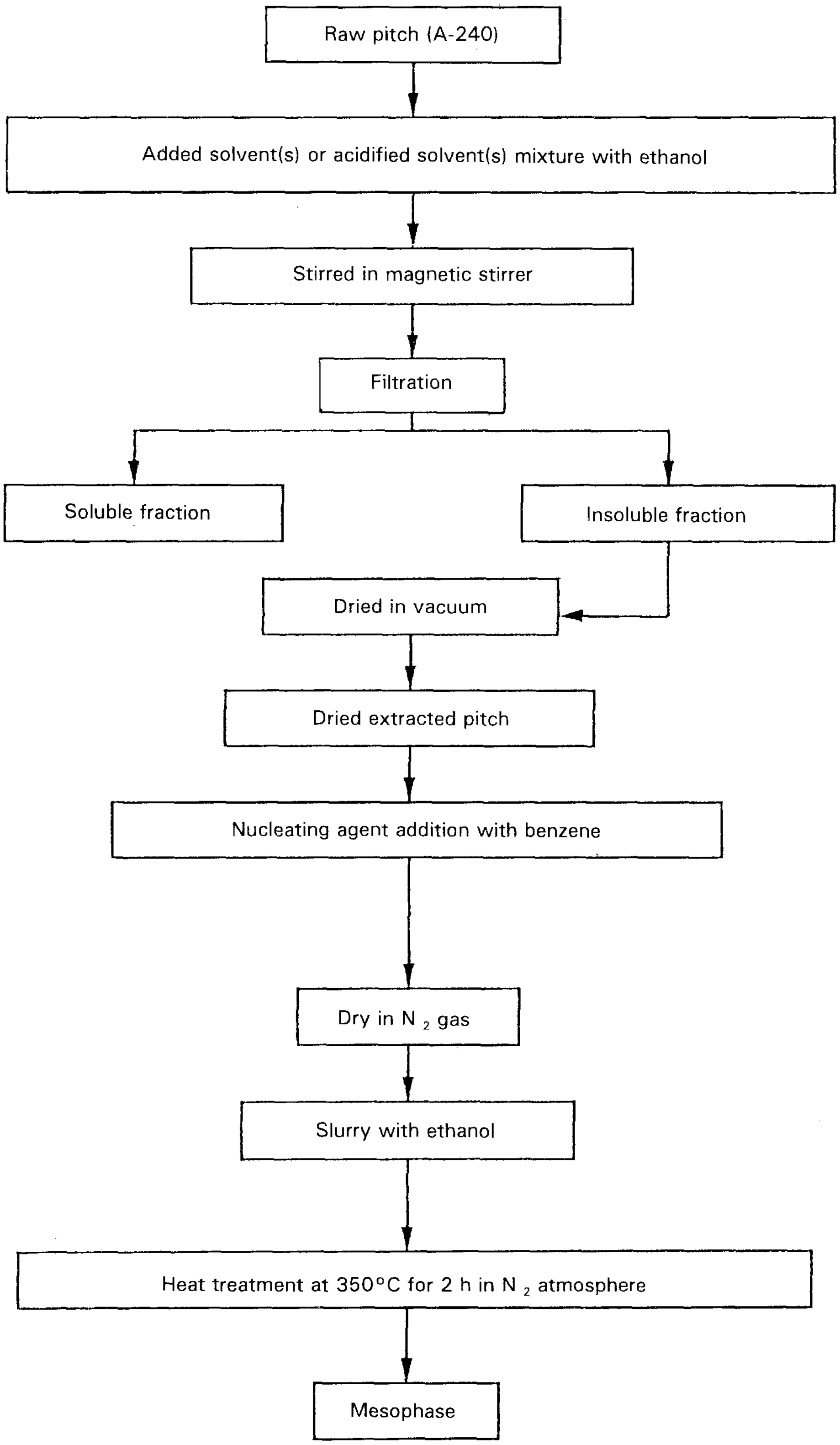


Figure 1 Flow diagram for the formation of nucleated mesophase.

TABLE I Characteristic properties of nucleating agents used

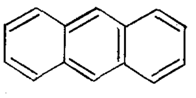
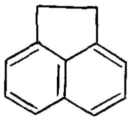
	Anthracene	Acenaphthylene
Mol. weight	178.24	152.21
Melting point (°C)	216	92
Boiling point (°C)	340	265
Density (g cm^{-3})	1.283	0.8988
Formula	$C_{14}H_{10}$	$C_{12}H_8$
Structure		

TABLE II Weight per cent of insoluble residue of A-240 pitch in various extraction systems (ml/20 g A-240 pitch)

Sample	Extraction system	Insoluble (%)
THE10	20 ml hexane + 180 ml toluene	21.8
THE30	60 ml hexane + 140 ml toluene	29.8
THE10A	20 ml hexane + 180 ml toluene + A[a]	28.9
THE30A	60 ml hexane + 140 ml toluene + A	31.2
THE10F	20 ml hexane + 180 ml toluene + F[b]	23.8
THE30F	60 ml hexane + 140 ml toluene + F	29.9

[a] A = 1 M HCl (15 ml) + 1 M HNO_3 (5 ml) + EtOH (20 ml).
[b] F = 6% HF (20 ml) + EtOH (20 ml).

TABLE III Aromaticity of pitches with various nucleating agents added after heat treating at 350 °C for 2 h

	Mesophase	1NU	1ACNU	3NU	3ACNU
A240	1.00	1.10		1.00	1.04
THE10	1.04	1.11	1.08	1.09	
THE30	1.03	1.04	1.07	1.07	1.06
THE10A	1.05	1.06	1.07	1.05	1.08
THE30A	1.05		1.06	1.07	1.09
THE10F	1.06	1.10		1.06	1.05
THE30F	1.03	1.09	1.06	1.06	1.08

Note: 1NU, 1 wt % anthracene-added pitch; 1ACNU, 1 wt % acenaphthylene-added pitch; 3NU, 3 wt % anthracene-added pitch; 3ACNU, 3 wt % acenaphthylene added pitch.

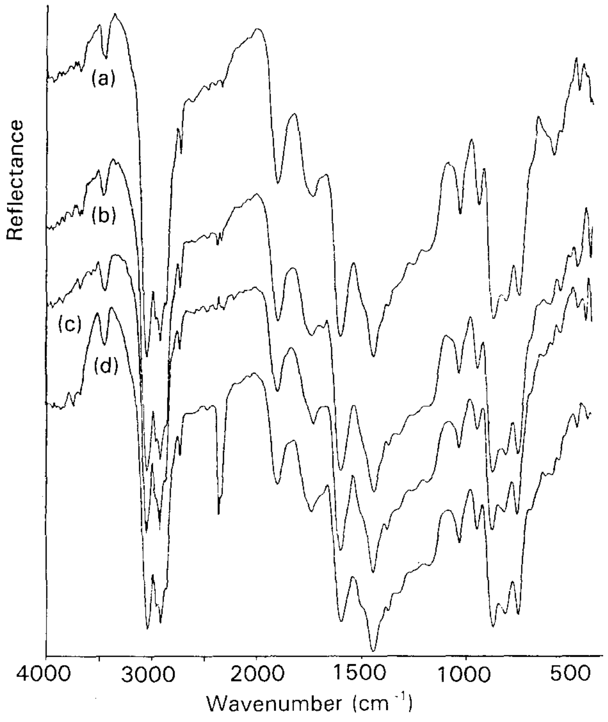


Figure 2 FT-IR spectra of 1 wt % anthracene-added mesophase pitches after heat treatment at 350 °C for 2 h: (a) A-240; (b) THE10; (c) THE10A; (d) THE10F.

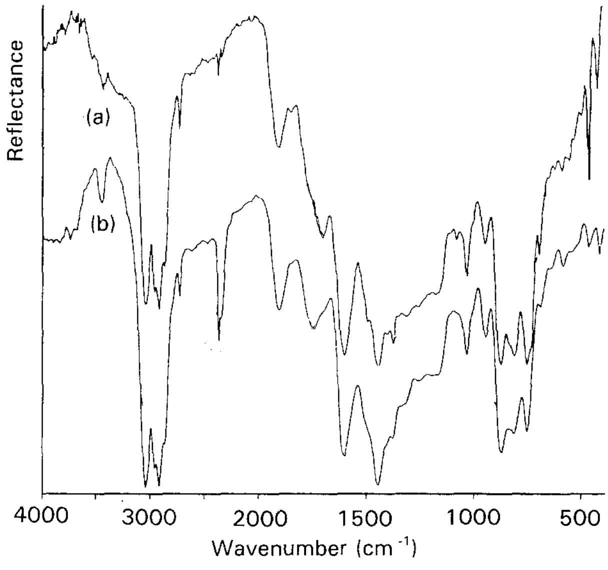


Figure 3 FT-IR spectra of THE10 pitches, (a) before heat treatment, (b) after heat treatment at 350 °C for 2 h.

anthracene has been consumed during the heat treatments. In Fig. 4, some quantitative differences are shown between anthracene- and acenaphthylene-added mesophase pitch which were heat treated at 350 °C for 2 h. Changes in the aromaticity represented by the peak height ratio at 3050–2920 cm^{-1} are listed in Table III. No correlation could be found in the aromaticity, with the exception of increasing aromaticity after blending of the nucleating agents.

3.2. Microstructure analysis

The mounted and polished mesophase samples were examined under a polarized reflected light microscope. The THE30F samples with 1% anthracene and 1% acenaphthylene (Fig. 5b and c) show an enhanced mesophase compared to THE30F, without the additives (Fig. 5a). Small size of anisotropic spheres are observed in a predominantly isotropic matrix of the mesophase pitch prepared from the original THE30F. In contrast, enhanced anisotropic mesophase from the THE30F modified with the nucleating agents, i.e. anthracene and acenaphthylene, is exhibited. It is well known that addition of fine particles as seeds enhances crystallization in ceramic materials with respect to the kinetics.

Thus blending of a catalytic amount of pure aromatic hydrocarbons of naphthenic structure as seeds, with pitch may enhance mesophase formation. This is because the naphthenic hydrogens in the pitch play an important role in the development of a liquid crystal state [12].

The enhanced mesophase formation phenomenon observed in this study must be attributed to HF acting as a catalyst for ring condensation of the pitch and aromatic hydrocarbon, analogous to acidic inorganic

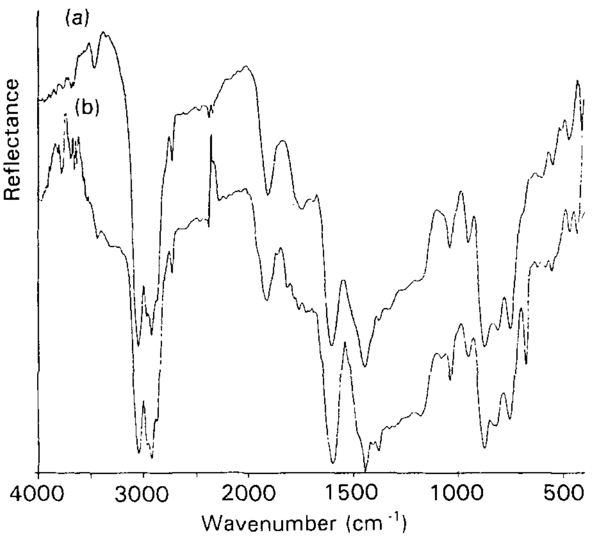


Figure 4 FT–IR spectra of 1 wt % nucleating agent-added THE10 mesophase pitches after heat treatment at 350 °C for 2 h: (a) 1 wt % anthracene added; (b) 1 wt % acenaphthylene added.

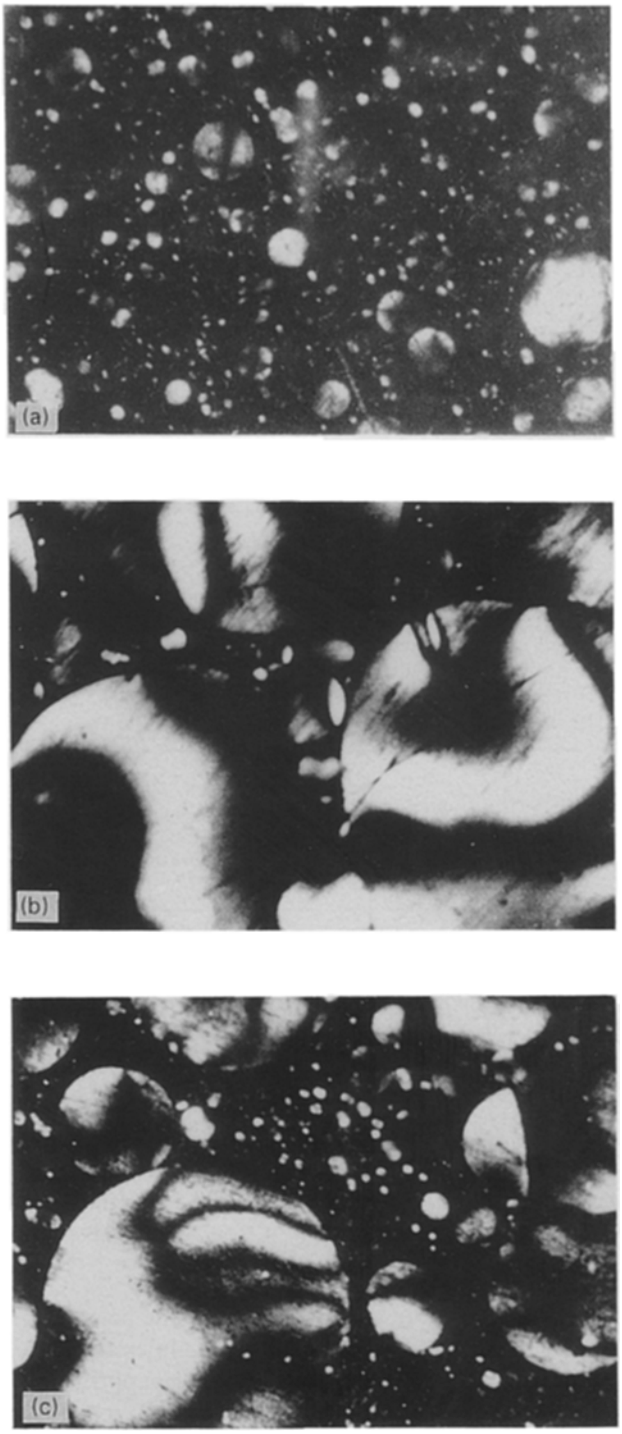


Figure 5 Mesophase microstructures of THE30F pitches after heat treatment in a nitrogen atmosphere at 350 °C for 2 h in the presence of 1 wt % nucleating agents (× 160): (a) THE30F; (b) THE30F with anthracene; (c) THE30F with acenaphthylene.

halides (e.g. $AlCl_3$), favouring condensation of aromatic hydrocarbon [6, 7]. The HF with ethanol is expected to perform selectively a Friedel–Crafts reaction with aromatic rings in the pitch and aromatic hydrocarbons, preserving methyl groups on the aromatic rings of mesophase pitch. New carbon–carbon bonds are formed by the Friedel–Crafts reaction. However, THE30 (30% hexane, 70% toluene-extracted pitch) with 1 wt % anthracene or acenaphthylene, did not show enhanced mesophase formation after heat treatment at 350 °C for 2 h, as shown in Fig. 6. Only 1 wt % nucleating agent was fully mixed with THE30 pitch without any effects, because this amount nucleating agent is too small to cause any change in the absence of proton from the acids. This is because a Friedel–Crafts reaction requires a source of protons, and hence the enhancement of mesophase formation by blending of pure aromatic hydrocarbons requires a strong Brönsted acid catalyst with alcohol. Fig. 7 shows the THE10A and 1 wt % acenaphthylene-added THE10A mesophase after heat treatment at 350 °C for 2 h. The THE10A with 1 wt % added acenaphthylene shows the well-developed spherical mesophase in the presence of Brönsted acids, i.e. HCl and HNO_3, which caused the condensation reaction during the heat treatment via the free radical mechanism, with the polycondensation of acenaphthylene [10]. HCl and HNO_3, which provided protons, affected the aromatic condensation reaction via the Friedel–Crafts reaction during the heat treatment.

Fig. 8 shows the change in anisotropic content in THE30 by the blending of pure aromatic hydrocarbons. An addition of 1 wt % anthracene and acenaphthylene to THE30 (Fig. 8b and c) shows no effect, compared with THE30 (Fig. 8a). On the other hand, the 3 wt % added THE30 (Fig. 8e and f) shows a large number of small nucleus spheres in the matrix. This indicates that the addition of 3 wt % anthracene hinders the mesophase formation in the pitch without a proton source, as previously observed. The sample with 3 wt % acenaphthylene added (Fig. 8d) shows no mesophase formation at 350 °C for 1 h. It is clearly shown that the aromatic hydrocarbon hinders mesophase formation when no proton source is present in the pitch. These results agree well with those of Stevens and Diefendorf [3]. They showed that the amount of mesophase formed decreased with the increase in the addition of aromatic hydrocarbons. Assuming the mesophase pitch is made up of molecules which show varying degrees of mesophase-forming potential, the addition of a new species in significant quantities will cause a repartitioning of components

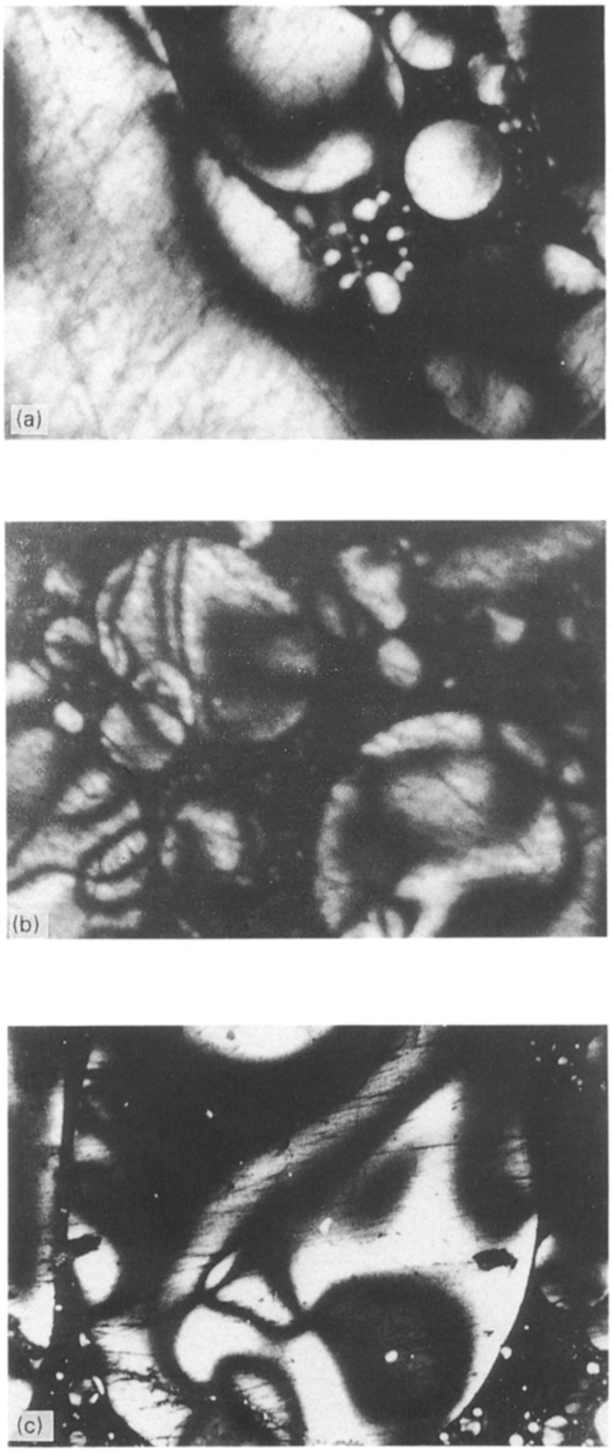


Figure 6 Mesophase microstructures of 1 wt % nucleating agents-added THE30 pitch after heat treatment at 350 °C for 2 h in a nitrogen atmosphere (× 160): (a) no additive; (b) anthracene added; (c) acenaphthylene added.

between the mesophase and the isotropic phase. The addition of aromatic hydrocarbons to pitch is found to be very effective in controlling the amount of mesophase in the resultant carbons. This is explained by the fact that any molecules present which are not mesophase formers, adversely affect the formation of mesophase. However, in the presence of protons, the aromatic hydrocarbons can be polymerized to become mesophase formers. The addition of aromatic hydrocarbons in quantities larger than the catalytic amount decreases the mesophase formation, because these molecules by themselves are unable to function as a nucleating agent [3, 13, 14].

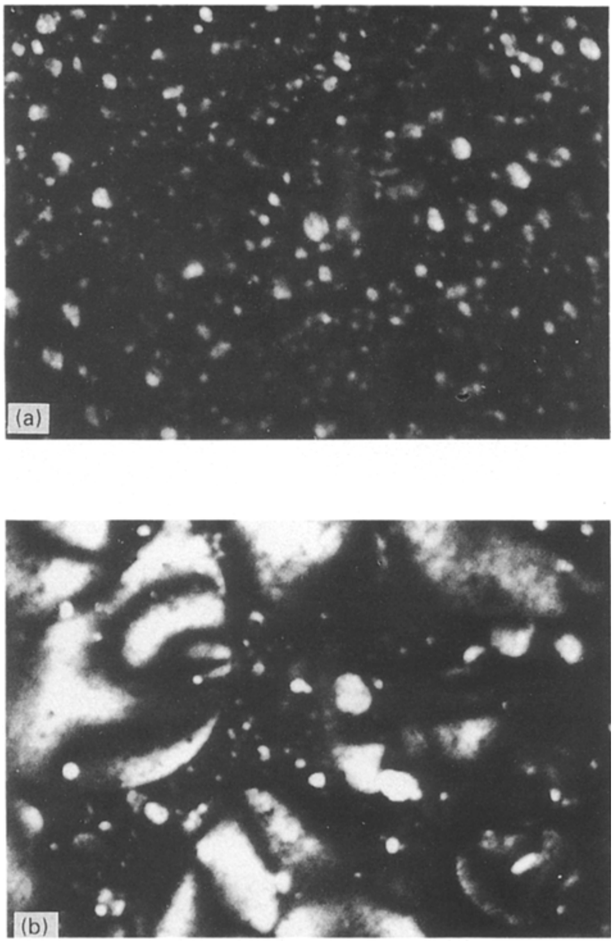


Figure 7 Microstructures of THE10A mesophase pitch after heat treatment at 350 °C for 2 h in a nitrogen atmosphere (× 160): (a) with no additive; (b) with 1 wt % acenaphthylene.

Fig. 9 shows the mesophase microstructure of the THE10F with 3 wt % anthracene and acenaphthylene at 350 °C for 2 h. As discussed previously, 1 wt % aromatic hydrocarbons gives enhanced mesophase formation in the presence of acid. However, pitches with 3 wt % aromatic hydrocarbons added, show no significant increase in mesophase formation, although the size of the spheres is a little larger than the pitch without the nucleating agents. Therefore, acids are needed as a catalyst for enhanced mesophase formation when a pitch is blended with a catalytic amount of aromatic hydrocarbons. The nature of the interaction between the aromatic hydrocarbons and the pitch, and its effects on mesophase development, appears to be closely related to the reactivity of the aromatic hydrocarbons and the catalytic conditions.

3.3. Softening temperatures and solubilities of mesophase with added nucleating agents

The softening temperature was measured by the polymer melt or stick-temperature test using fine-powder mesophase pitches. The results are given in Table IV. The softening temperatures of 1 wt % anthracene- and

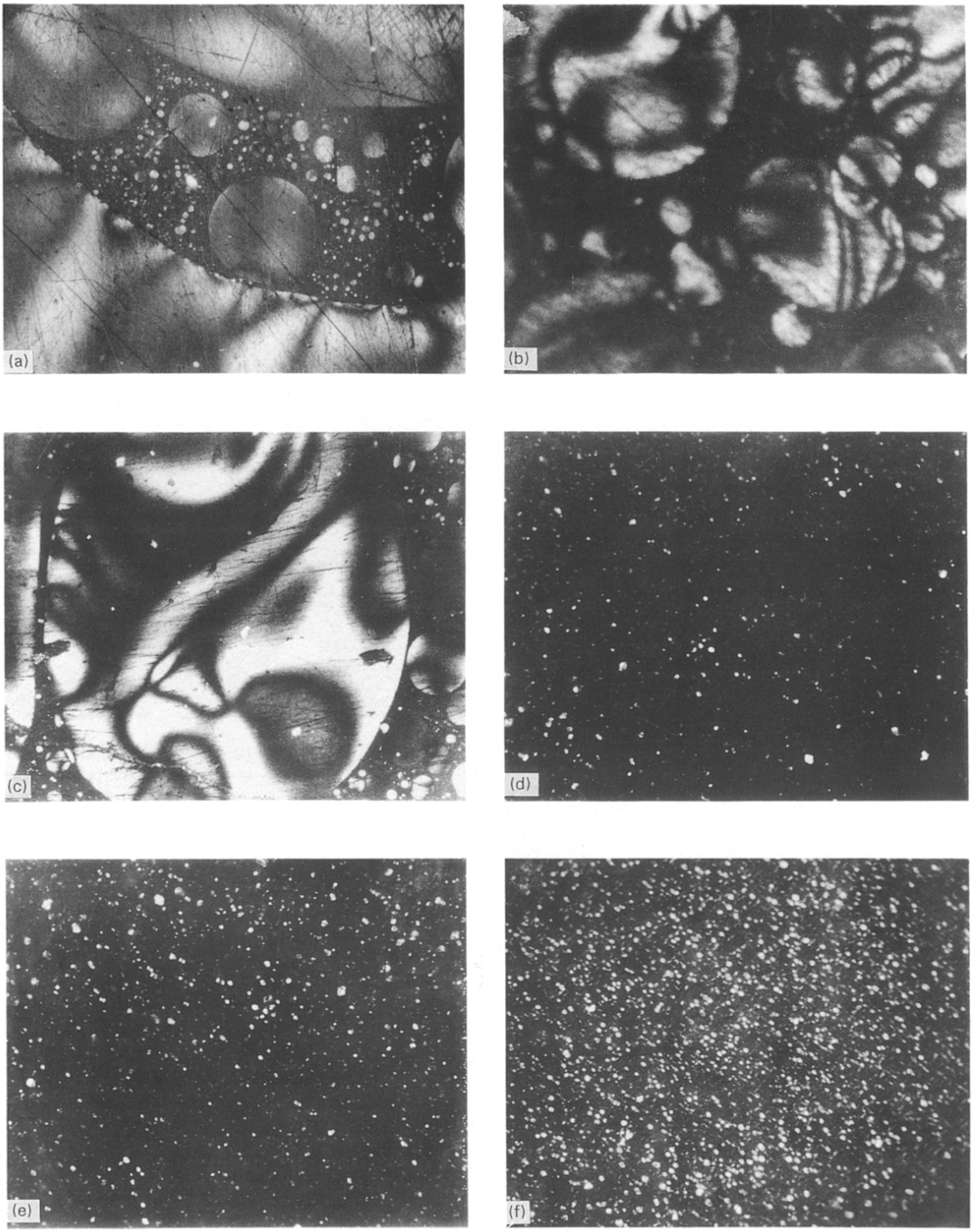


Figure 8 Mesophase microstructures of THE30 pitches after heat treatment under various conditions with anthracene (NU) and acenaphthylene (ACNU) at 350 °C (× 160): (a) THE30 (2 h); (b) 1 wt % Nu (2 h); (c) 1 wt % ACNU (2 h); (d) 3 wt % NU (1 h); (e) 3 wt % NU (2 h); (f) 3 wt % (2 h).

acenaphthylene-blended mesophase pitches were increased on addition of nucleating agents (NU and ACNU). This is because of the enhanced mesophase formation, as shown in Figs 5 and 7. As the amount of additives increased, the mesophase formation was hindered, as shown in Fig. 8d–f. This is reflected in the softening temperature of 3 wt % blended pitches in Table IV. It shows that the softening points are decreased by a 3 wt % addition. This trend is consistent with the observation of optical texture under the microscope. The solubilities of the mesophases in THF were obtained by Soxhlet extraction of finely crushed mesophase pitch powders at the boiling point of the THF. The results are given in Table V. Although

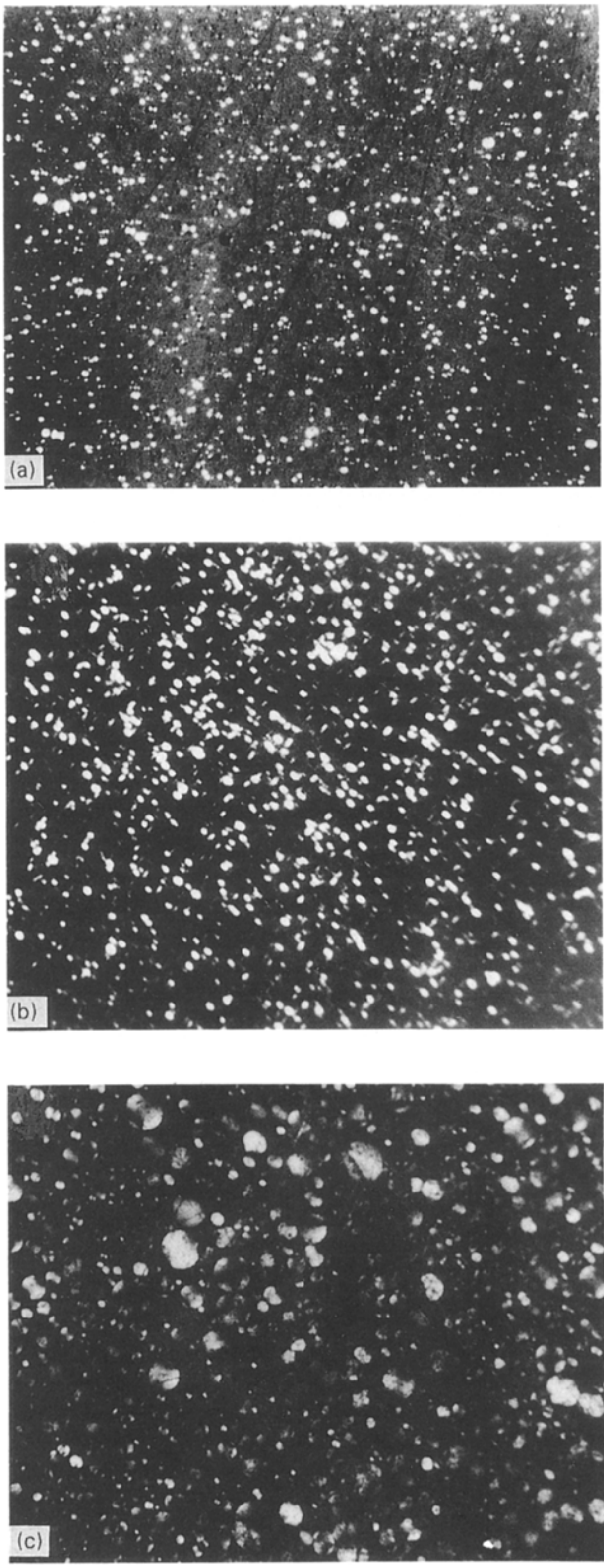


Figure 9 Mesophase microstructures of 3 wt % nucleating agents-added THE10F pitch after heat treatment at 350 °C for 2 h in a nitrogen atmosphere: (a) THE10F; (b) THE10F + anthracene; (c) THE10F + acenaphthylene.

TABLE IV Softening points of pitches with various nucleating agents after heat treatment at 350 °C for 2 h

	Softening points (°C)				
	Mesophase	1NU	1ACNU	3NU	3ACNU
A-240	157.3	216.2	150.8	133.5	147.8
THE10	245.9	331.7	303.9	269.8	276.4
THE30	220.7	253.3	295.6	259.9	255.3
THE10A	268.7		313.6	297.4	278.1
THE30A	252.6	255.0	302.7	271.7	273.7
THE10F	248.7	312.3	224.9	267.5	277.7
THE30F	228.3	296.5	256.7	269.3	280.8

Note: for abbreviations, see Table III.

TABLE V THF insolubles of mesophases (350 °C/2 h) obtained by Soxhlet extraction method for 2 h

	THF insolubles (%)		
	350 °C	1NU	1ACNU
A-240	23.81	32.46	33.33
THE10	89.10	81.36	85.45
THE10A	92.38	87.74	74.26
THE10F	87.48	91.23	69.57

Note: For abbreviations, see Table III.

well-developed spherical mesophase was exhibited by all of the THE10, the nucleating agent-added mesophase pitches (1NUTHE10 and 1ACNUTHE10) have a lower THFI than THE10 (350 °C/2 h) mesophase pitch. In the case of acidified solvent extraction, the nucleating agents-added mesophase pitches (1NUTHE10A, 1ACNUTHE10F and 1ACNUTHE10F) also show lower THFI than THE10A and THE10F without the nucleating agents, except 1NUTHE10 mesophase pitch. That is, 1 wt % blended mesophase was more soluble than the unblended mesophase. This is contradictory to the previous explanation that more mesophase indicates lower solvent solubility. The alkyl groups produced by the Friedel–Crafts alkylation reaction may be given the lower solvent insoluble in Soxhlet extraction. Thus, it is incorrect to say that the more mesophase, the less soluble is in the solvent.

4. Conclusions

1. A source of acid is required for the Friedel–Crafts reaction in the condensation reaction of aromatic rings.
2. The catalytic amounts of nucleating agents have been consumed completely during the heat treatment which increased the aromaticity of the pitch.
3. When 1 wt % pure aromatic hydrocarbons (anthracene and acenaphthylene) were added to the acidified solvent-extracted pitch, larger mesophase spherules were obtained compared with the mesophase formation without the pure aromatic hydrocarbons.

References

1. I. MOCHIDA, Y. KORAI, M. NAKAMURA, S. M. ZENG and M. KAMEYAMA, *Carbon* **27** (1989) 498.
2. I. MOCHIDA, Y. KORAI, M. NAKAMURA, S. IN and B. RHEE, *J. Mater. Sci. Lett.* **10** (1991) 121.

3. W. C. STEVENS and R. J. DIEFENDORF, in "Carbon 86", Proceedings of an International Conference on Carbon (German Ceramic Society, Baden-Baden, 1986) p. 61.
4. J. D. BROOKS and G. H. TAYLOR, in "Chemistry and Physics of Carbon", Vol. 4, edited by P. L. Walker Jr (Marcel Dekker, New York, 1986) p. 243.
5. Y. KORAI, M. NAKAMURA, I. MOCHIDA, Y. SAKAI and S. FUJIYAMA, in "20th Biennial Conference on Carbon", Santa Barbara, CA, (Amer. Carbon Soc., CA, Extended Abstracts, 1991) p. 158.
6. H. MARSH, J. M. FORSTER, G. HERMAN and M. ILEY, *Fuel* **52** (1973) 234.
7. J. H. CRANMER, I. G. PLOTZKER, L. H. PEEBLES Jr and D. R. UHLMANN, *Carbon* **21** (1983) 201.
8. I. C. LEWIS, in "20th Biennial Conference on Carbon, Extended Abstracts", Santa Barbara, CA, (Amer. Carbon Soc., CA, 1991) p. 156.
9. I. MOCHIDA, T. OYAMA, Y. KORAI and Y. Q. FEI, *Fuel* **67** (1988) 1171.
10. E. FITZER, K. MUELLER and W. SCHAEFER, in "Chemistry and Physics of Carbon", Vol. 7, edited by P. L. Walker Jr (Dekker, New York, 1971) p. 237
11. Y. S. LIM and B. I. LEE, *Carbon* **27** (1989) 739..
12. I. MOCHIDA, K. SHIMIZU, Y. KORAI, H. OTSUKA and S. FUJIYAMA, in "Carbon '88", Proceedings of the International Conference on Carbon, edited by B. McEnaney and T. J. Mays, University of Newcastle upon Tyne, UK (Joint carbon group of the Institute of Physics and the Royal Soc. of Chem., 1988) p. 259.
13. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. MATSUMOTO, *J. Mater. Sci.* **23** (1988) 670.
14. I. MOCHIDA, H. TOSHIMA, Y. KORAI and T. NAITO, *ibid.* **23** (1988) 678.

Received 2 January
and accepted 2 September 1992