

# Mesophase formation and chemical changes in petroleum pitch during low-temperature heat soaking

Y.-S. LIM, B. I. LEE\*

Center for Engineering Fibers and Their Composites, Department of Ceramic Engineering, Clemson University, Clemson, South Carolina 29631-0907, USA

A-240 petroleum pitch was used to study the mesophase formation. The mesophase formation of solvent and solvent-acid extracted pitch were controlled in terms of optical texture by adding aromatic hydrocarbon compounds as nucleating agents. It is possible to improve considerably the coking properties that are enhanced by the ring condensation tendency of the precursor. The mesophase yield of the HF-solvent extracted pitches in the presence of 1% anthracene was increased when compared with HF-solvent extracted pitch in the absence of anthracene. In this case, HF acted as a catalyst along with anthracene for ring condensation, similar to  $\text{AlCl}_3$  in the aromatic hydrocarbons.

## 1. Introduction

Most high-performance carbon fibres are produced from either a polyacrylonitrile (PAN) or a pitch precursor. Pitch-based carbon fibres have been recognized as a strategic material because of their excellent strength or modulus per unit weight [1]. Pitch-based carbon fibres are prepared by converting the pitch into a liquid crystalline state, mesophase, by heat-treatment. A pitch of high purity as well as higher coking value has been recognized as an appropriate precursor for high-performance pitch-based carbon fibres or matrix for advanced carbon-carbon composites [2].

In a previous paper [3], it was reported that A-240 pitch could be purified with solvents (toluene, toluene/hexane mixture) and solvent-acids ( $\text{HCl}$ ,  $\text{HNO}_3$ , HF) to extract the inorganic impurities in the pitch. However, the solvent-acid treated pitch was more difficult to form mesophase than that of just solvent-treated pitch at low temperature.

Inagaki *et al.* [4] added 10 to 20 wt % polyethyleneterephthalate (PET) to a petroleum pitch to enhance mesophase formation. PET was found to be effective for controlling the bulk mesophase texture of the pitch in argon under pressure above 10 MPa. Mochida *et al.* [2, 5] synthesized mesophase from a pure aromatic hydrocarbon with the aid of Bronsted acid ( $\text{HF}/\text{BF}_3$ ). They also examined blending of polyvinylchloride (PVC) pitch into a petroleum-derived mesophase pitch to produce superior mesophase texture [6]. The mesophase texture of the petroleum-derived mesophase pitch was not controlled by blending of PVC pitch. Isotropic droplets of the PVC pitch remained in the petroleum-derived mesophase pitch [6].  $\text{HF}/\text{BF}_3$  must have polymerized the aromatic hydrocarbons through their protonated intermediates into pitch of higher

naphthenic contents. This, in turn, appears to have catalysed the mesophase formation of the pure hydrocarbons.

The effects of a pure aromatic hydrocarbon (anthracene) addition to the acid/solvent extracted pitch was examined in order to purify the pitch and to enhance the mesophase formation. We have attempted to define the chemical changes during the solvent/solvent-acid extraction and the effect on the subsequent heat-treatments for formation of mesophase. Fourier transform-infrared spectroscopy (FT-IR) was used to monitor the chemical changes at the various stages of the treatment. Differential thermal analysis/thermogravimetric analyses (DTA/TGA) and an optical microscope were also used to monitor the physical/chemical changes during the heat treatments [7, 8].

## 2. Experimental procedure

**2.1. Solvent fractionation of petroleum pitch**  
Starting pitch material (A-240), that has high degree of aromaticity, was obtained from Ashland Petroleum Company. The organic phase in the pitch was fractionated by using different proportions of toluene and hexane. The trace inorganic impurities were eliminated by extracting with the solvent mixed with acids ( $\text{HF}$  or  $\text{HCl}/\text{HNO}_3$ ) prediluted in alcohol. 20 g pitch was stirred in the solvent or solvent-acid mixture for 5 h at room temperature followed by filtration of the residue. The residue was dried in a vacuum oven for 5 h at 60 °C, and then analysed using FT-IR. A portion of the residue was mixed with 1 wt % anthracene ( $\text{C}_{14}\text{H}_{10}$ ) as a nucleating agent in benzene. The flow diagram of the solvent extraction procedure is given in Fig. 1. Solvent extractions were carried out with different proportions of toluene and hexane or containing  $\text{HCl}/\text{HNO}_3$  mixture in proportion of 15 ml 1M  $\text{HCl}/$

\* Author to whom correspondence should be addressed.

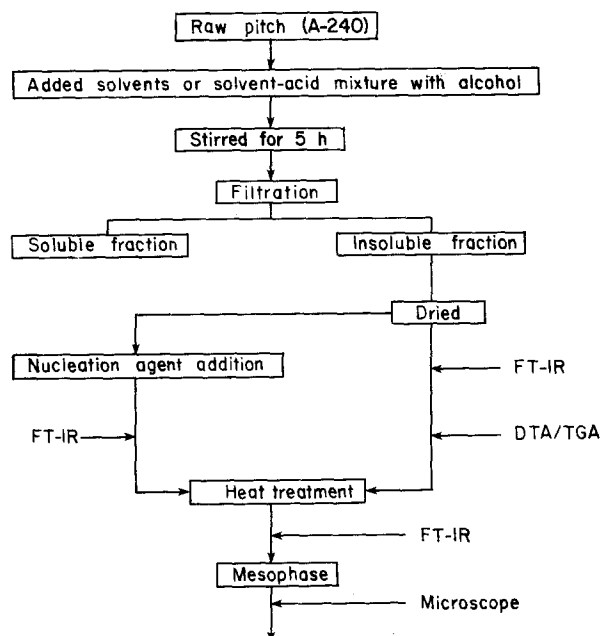


Figure 1 Processing map for the formation of mesophase from the petroleum pitch.

5 ml 1 M HNO<sub>3</sub> diluted in 20 ml EtOH or 20 ml of 6% HF solution diluted in 20 ml EtOH mixture. The extraction system and the resulting insolubles are listed in Table I.

## 2.2. Heat treatment for formation of mesophase

The fractionated pitch with or without the nucleating agent was heated to 350 °C and soaked for 2 h in a nitrogen gas atmosphere. The measured temperature of the pitch at steady-state soaking was within 5 °C of the intended temperature.

## 2.3. Microscopic observation

Heat treated pitch samples were mounted on pellets of polyester resin. These pellets were polished to obtain an optically flat cross-section. The sample pellets were then examined under a polarized reflected light microscope, Zeiss-ICM 405.

## 3. Results and discussion

### 3.1. Solvent extraction

The solvent systems had solubility parameters between about 7.3 and 8.9. Because the mesophase-forming fraction of an isotropic pitch is insoluble in solvents such as benzene and toluene, solvent extraction is employed to separate the mesophase forming fraction [9]. The results of solvent extraction are given in Table I. The amount of solvent-insoluble fraction increased with increasing amount of hexane because hexane (lower solubility parameter) is a worse solvent than toluene (higher solubility parameter). Acid(s)-solvent(s) extracted pitch has a larger amount of insoluble fraction than that of pitch extracted without acids except that of THE30F. The cause of the larger amount of insolubles in the presence of acids was studied by using the Soxhlet extraction method with tetrahydrofuran (THF). The added acid to EtOH may do two things. One is to lower the solvent solubility parameter and the other is to polymerize some of the soluble fraction of the pitch. The results of Soxhlet extraction for THF-insoluble (THFI) pitch samples are shown in Table II. On comparing the solvent insolubles of THE30 and THE30A in Table I, a slightly higher insolubility of THE30A is seen because of the lower solvent solubility parameter of THE30A due to 20 ml acid/20 ml EtOH. However the much lower solvent solubility parameter of THE30A increased to no more than 2 wt % insolubles. On the other hand, the percentage of THFI in Table II is reversed, i.e. lower percentage of THFI for THE30A. This suggests that the percentage of insolubles was affected mainly by the solvent solubility parameter rather than polymerization of the solubles. The solvent-HF treated system exhibited a different behaviour, as the solvent solubility parameter decreased, i.e. from THENOF to THE30F. It is shown in Table I that THE10F gave more insoluble than THE30F, despite the lower solvent solubility parameter of THE30F. This anomaly needs to be studied further.

### 3.2. DTA/TGA analysis

DTA/TGA thermograms were obtained using a Stanton-Redcroft DTA/TGA model STA-1500 in argon

TABLE I Insoluble residue (wt %) of A-240 pitch in various extractions

Samples	Extraction system (ml)/20 g A-240 pitch)	Insoluble (%)
THENO	200 ml toluene	15.0
THE10	20 ml hexane + 180 ml toluene	21.8
THE20	40 ml hexane + 160 ml toluene	25.0
THE30	60 ml hexane + 140 ml toluene	29.8
THENOA	200 ml toluene + A	20.7
THE10A	20 ml hexane + 180 ml toluene + A	28.3
THE20A	40 ml hexane + 160 ml toluene + A	30.5
THE30A	60 ml hexane + 140 ml toluene + A	31.5
THENOF	200 ml toluene + F	26.5
THE10F	20 ml hexane + 180 ml toluene + F	28.8
THE20F	40 ml hexane + 160 ml toluene + F	26.5
THE30F	60 ml hexane + 140 ml toluene + F	27.2

A = 1M HCl (15 ml) + 1M HNO<sub>3</sub> (5 ml) + EtOH (20 ml).

F = 6% HF (20 ml) + EtOH (20 ml).

TABLE II Insolubles (wt %) in solvent-extracted pitch by Soxhlet extraction method with THF solvent (%THFI)

Samples	THFI (%)
THE10	54.84
THE30	35.59
THE10A	32.73
THE30A	25.66
THE10F	28.00
THE30F	33.38

atmosphere at a heating rate of  $10^{\circ}\text{C min}^{-1}$  to a temperature of  $470^{\circ}\text{C}$ . The sample THE10, which has been extracted by 10% hexane and 90% toluene, gives the DTA/TGA thermogram in Fig. 2. For DTA the broad endothermic peak at 120 to  $230^{\circ}\text{C}$  represents evaporation of the low molecular weight volatile. The TGA shows the weight loss of about 5% up to the corresponding temperature. The endothermic peaks located in the temperature range 330 to  $430^{\circ}\text{C}$  may correspond to the formation of mesophase [10].

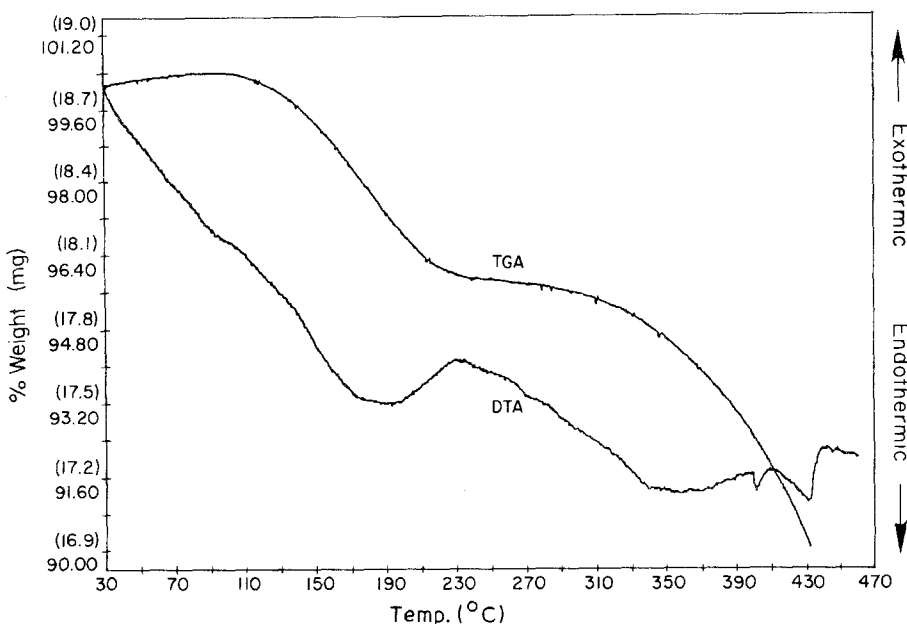


Figure 2 DTA/TGA thermogram of THE10 sample.

### 3.3. Infrared analysis

Infrared spectra were obtained using a diffuse reflectance stage in a Perkin-Elmer FT-IR 1600 spectrophotometer in the wave number range  $4000$  to  $400\text{ cm}^{-1}$ . The FT-IR spectra of A-240 parent pitch and toluene-extracted pitch are compared in Fig. 3. The qualitative differences between the parent pitch and the toluene-extracted pitch are hardly observable in these spectra. They show the characteristic bands corresponding to its aromatic structure ( $3050$ ,  $1611$ ,  $872$ ,  $811$ ,  $750\text{ cm}^{-1}$ ) and the aliphatic structure ( $2955$ ,  $2920$ ,  $2855$ ,  $1505$ ,  $1450\text{ cm}^{-1}$ ) [11-13]. The bands in the region  $900$ – $700\text{ cm}^{-1}$  are usually assigned to the out-of-plane bending of the aromatic C-H group. The bands in the region  $1611$  to  $1450\text{ cm}^{-1}$  are assigned to the stretching of aromatic C=C group. The  $3050\text{ cm}^{-1}$  bands have been mentioned as stretching of the aromatic C-H group. The  $1450$  to  $1300\text{ cm}^{-1}$  bands are allocated to bending of the aliphatic hydrocarbon. The other three bands at  $2955$ ,  $2920$ ,  $2855\text{ cm}^{-1}$  represent the stretching of the aliphatic hydrocarbons.

The relative peak height, found using the base-line method for infrared bands at  $3050\text{ cm}^{-1}$  (aromatic)

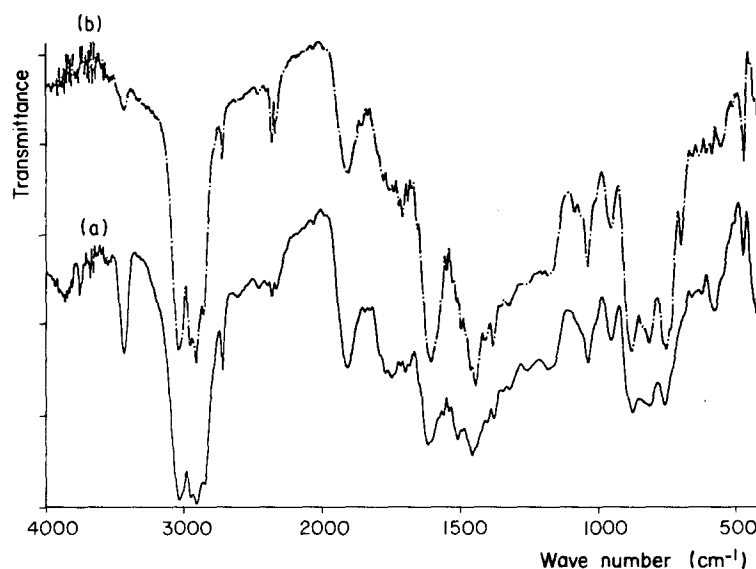


Figure 3 FI-IR spectra of (a) A-240 pitch and (b) THENO sample.

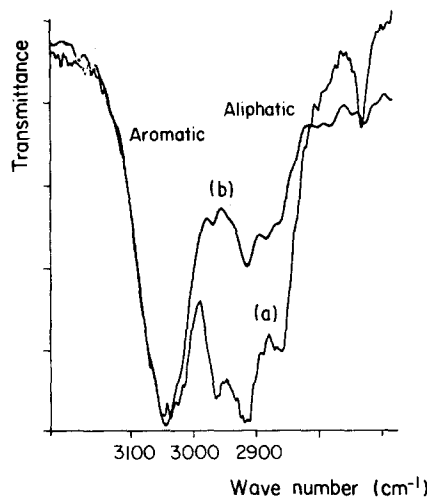


Figure 4 The relative intensity of FT-IR peaks at 3050 and 2920  $\text{cm}^{-1}$ . (a) The spectrum of THE10 sample at 25 °C, (b) the spectrum of THE10 sample after heat treatment (400 °C, 2 h).

and at 2920  $\text{cm}^{-1}$  (aliphatic), are shown to depend on the heat treatment conditions as shown in Table III and Fig. 4. These results show that the values of aromaticity are increased with heat-treatment temperature (HTT). This phenomenon suggests a greater proportion of condensed ring system as the HTT

increased [12]. The loss of alkyl and the gain of aromatic C-H groups can be explained by the initial cracking and aromatic polymerization reaction [14, 15]. Qualitative differences between the FT-IR spectra of pitch containing anthracene and the pitch without anthracene after heat treatment at 350 °C are hardly observable, as shown in Fig. 5. The small amount of anthracene must have reacted completely during the heat treatment. As shown in Table III, anthracene-added HF-solvent treated pitches (THE10F and THE30F) have larger aromaticities than that of HF-solvent pitch without anthracene at the same temperature 350 °C. This phenomenon must be attributed to HF acting as a catalyst for ring condensation of the pitch and anthracene, analogous to inorganic halide (e.g.  $\text{AlCl}_3$ ) favouring condensation of aromatic hydrocarbons [2, 5, 6].

### 3.4. Microstructure analysis

The mounted and polished mesophase samples were examined under a polarized reflected light microscope. Fig. 6 shows that the presence of a high molecular weight component is critical to mesophase formation. Increasing the high molecular weight component results in the formation of anisotropic phase. As can

TABLE III Evaluation of aromatics for various pitch samples with different heat treatments using the IR peak height ratios

Sample	Ratio of Aromatics			
	25 °C	350 °C	400 °C	NU350 °C
A-240	0.966	1.000	2.533	1.102
THENO	0.958	1.044	1.202	
THE10	0.960	1.056	2.103	1.111
THE20	0.951	1.127	1.018	1.061
THE30	0.966	1.087		1.042
THENOA	1.000		2.156	
THE10A	0.985		1.045	1.064
THE20A	0.938	1.117	2.196	1.604
THE30A	0.967		1.537	
THENOF	0.986		1.113	
THE10F	0.983	1.056	1.253	1.101
THE20F	0.986		1.075	
THE30F	0.987	1.033	1.168	1.085

NU = 1% anthracene-added samples.

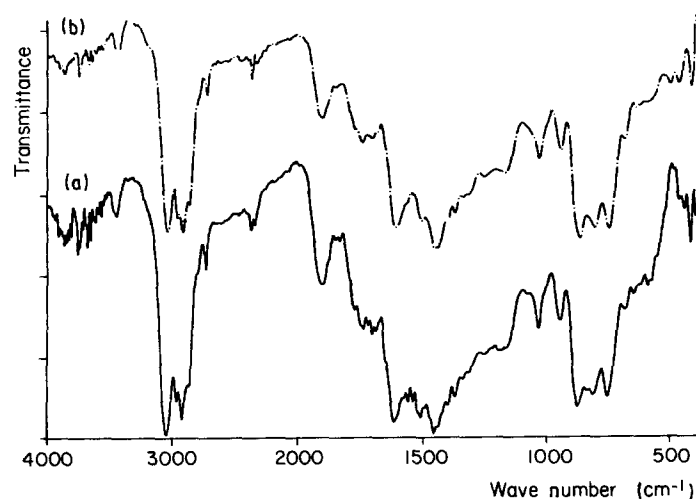
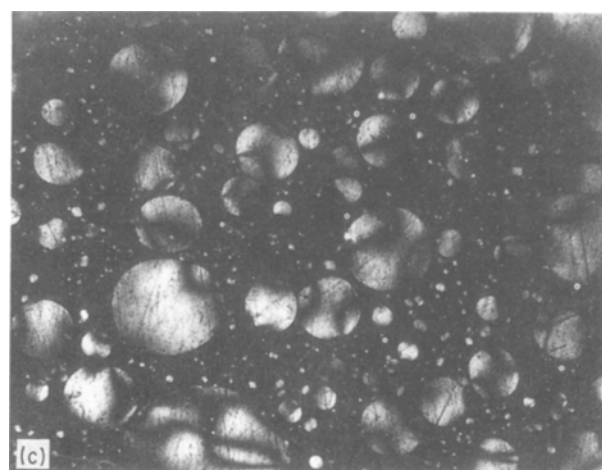
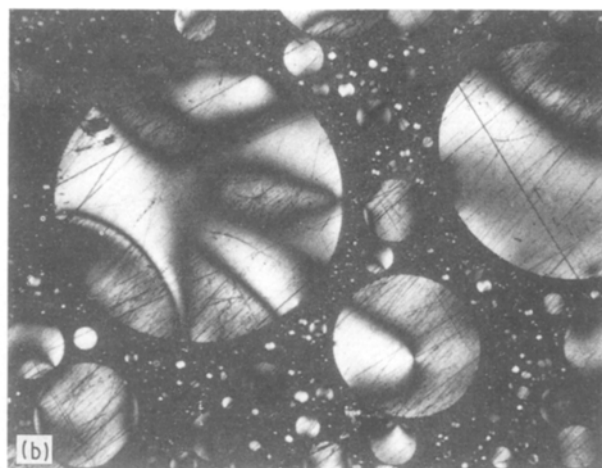
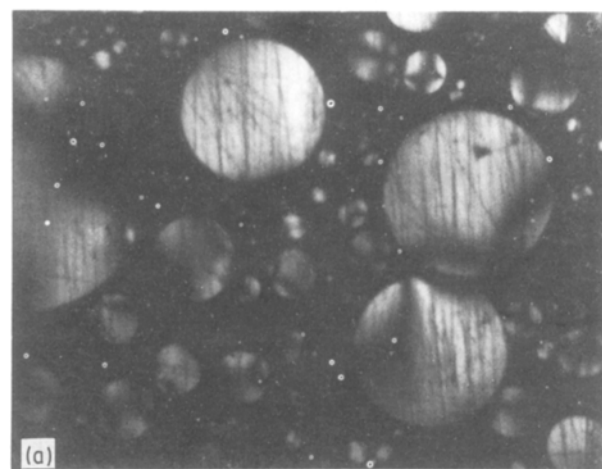


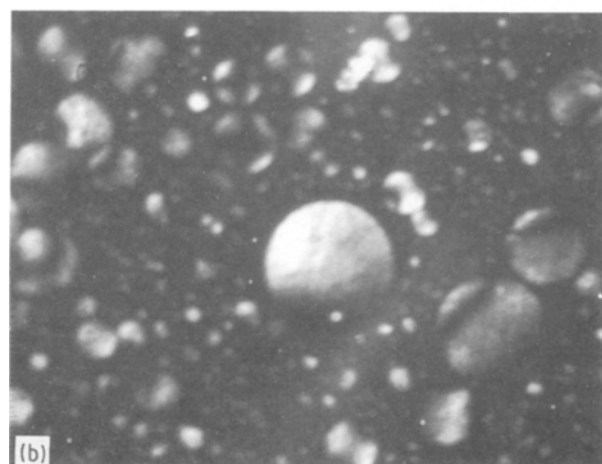
Figure 5 The FT-IR spectra of catalysed and non-catalysed THE20 sample after heat treatment (350 °C, 2 h). (a) 1% anthracene-added THE20 sample, (b) THE20 sample with no anthracene.



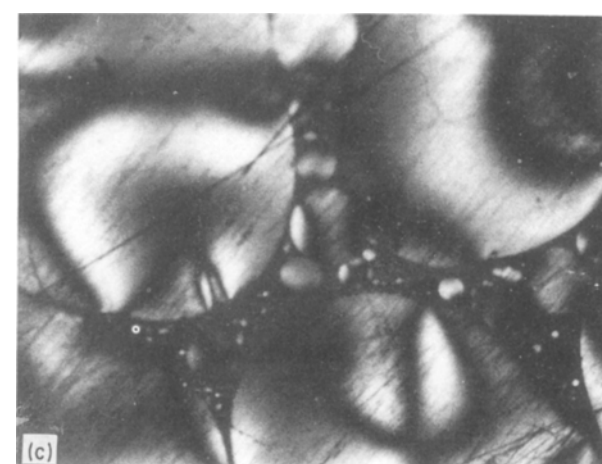
*Figure 6* Mesophase microstructures as a result of the presence of high molecular weight components at 350 °C for 2 h under nitrogen gas (X160). (a) A-240 pitch with no solvent extraction and no anthracene showing very small spherules of mesophase, (b) THE20 sample showing large spherules of mesophase, (c) THE20A sample showing medium-sized spherules of mesophase.



be seen from Table II, higher molecular weight component samples show a well-developed mesophase (Figs 6b and c) than that of parent A-240 pitch (Fig. 6a) at 350 °C under flowing nitrogen gas. Fig. 7 shows that mesophase seeds grew to larger spherical mesophase with anthracene as a nucleation agent. Figs 6a and 7a show the mesophase formed from A-240 pitch and the anthracene-added A-240 pitch, respectively, at 350 °C under flowing nitrogen gas. The A-240 pitch appeared with very small spheres of mesophase. However, 1% anthracene-added A-240 pitch shows the larger spherules of mesophase. Figs 7b and c are the pitch extracted with 6% HF solution with solvents. THE30F sample with no anthracene (Fig. 7b) has a larger amount of spherical mesophase than A-240 pitch (Fig. 6a). However, THE30F sample with 1% anthracene (Fig. 7c) shows larger spherules of



*Figure 7* Mesophase microstructures as a result of nucleating agent treatment and non-nucleating agent treatment at 350 °C for 2 h (X160). (a) A-240 pitch with 1% anthracene showing large spherules of mesophase, (b) THE30F sample with no anthracene showing medium-sized spherules of mesophase, (c) THE30F sample with 1% anthracene showing large spherules of mesophase.



mesophase. Solvent-HF treated pitch with 1% anthracene appeared to enhance mesophase formation. HF must have acted as a polymerization catalyst for anthracene, and in turn anthracene acted as a nucleating agent exhibiting enhanced mesophase formation.

#### 4. Conclusions

1. No qualitative difference in the FT-IR spectra band between parent pitch (A-240) and solvent-extracted pitch could be shown.

2. The presence of higher molecular weight components is critical to mesophase formation. Increasing the high molecular weight component results in the formation of anisotropic phase.

3. The percentage of insolubles of the pitch was affected mainly by the solvent solubility parameter rather than polymerization of the solubles of the pitch by the strong acid in the solvent-HCl-HNO<sub>3</sub>-EtOH mixture system.

4. When 1% anthracene was added to the solvent-extracted and/or solvent-acid extracted pitch, larger mesophase spherules were obtained than without anthracene. Solvent-HF treated pitch with 1% anthracene clearly showed enhancement of mesophase formation.

5. HF appeared to act as a polymerization catalyst for anthracene; in turn anthracene acted as a nucleating agent exhibiting enhanced mesophase formation.

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