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Formation of mesophase spherules in low-QI coal tar pitches and development of monolithic carbons therefrom

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Three coal tar pitches having different and low contents of primary quinoline insolubles (QI) were subjected to a series of thermal treatments at a predetermined temperature for different periods of soaking. The development of mesophase, in terms of its size and content in the heat-treated pitches, was studied as a function of the soaking time and content of primary quinoline insolubles in the original pitches. Mesophase spherules, with an average size of about 5 μm, formed in one of the coal tar pitches were separated using solvent extraction employing a suitable tar oil. These spherules, also called "mesocarbon microbeads (MCMB)", after being moulded into small rectangular plates, were carbonized at temperatures of 950 and 2700 °C to obtain fine textured monolithic carbons possessing apparent densities of 1.66 and 1.85 g cm^{-3}, respectively, at these heat-treatment temperatures.

1. Introduction

The development of carbonaceous mesophase (liquid–crystalline phase) in the early stages of carbonization of pitches was first reported by Brooks and Taylor [1, 2]. Since then, numerous contributions concerning the formation, growth and coalescence of mesophase spherules in pitches, as well as in their solvent fractions, have appeared in the literature [3–7]. Quinoline insolubles (QI) are an integral part of the coal tar pitches, and are often described as carbon black like particles. It is also reported that primary QI, or additives like carbon black or silica gel, retard the growth and coalescence of mesophase [1, 2, 8–11] resulting in a coke with more fine and isotropic carbon.

The mesophase spherules generated in a coal tar pitch by thermal treatment were first separated and called "mesocarbon microbeads (MCMB)" and used for the production of binderless isotropic high density carbon by Honda and Yamada in 1973 [12]. Since then, considerable interest has been shown in this type of carbon [13–17] because of its potential application as electrodes for electro-discharge machines and as material for hot-pressing dies, casting moulds, mechanical seals, crucibles, etc. However, little information is available in these papers regarding the development of this carbon. In view of this, the present authors initiated work on different developmental aspects of this specialty carbon [18–20]. In this paper, the authors report a systematic study of the development of mesophase (by heat treatment) in three coal tar pitches having different and low contents of QI, wherein the dependence of size and content of mesophase on the soaking time at a predetermined heat-treatment temperature (HTT) and the primary QI content in the pitch is investigated in detail. Mesophase spherules of suitable size, generated in one of the coal tar pitches by heat treatment, were separated out of the heat-treated pitch as insolubles by solvent extraction using a suitable tar oil; these were then used to develop a high density binderless carbon. The present paper gives a detailed account of the above study and the results obtained therein.

2. Experimental procedure

Three coal tar pitches having different and low contents of primary QI, and with other characteristics shown in Table I, were selected as the raw materials for the present study. Each of these three coal tar pitches were then heated in an inert atmosphere to a temperature of 420 °C at a rate of 150 °C h^{-1} for different periods of time, ranging from 1 to 7 h, resulting in overall ten experiments (experiments 1–10) of mesophase formation. The heat-treated (mesophase) pitches were characterized with respect to a number of parameters, and the results are given in Table II.

TABLE I Characteristics of precursor coal tar pitches

	Characteristics	CTP-1	CTP-2	CTP-3
1	Softening point (°C)	81	79	77
2	Quinoline insolubles (%)	6.5	3.3	0.5
3	Toluene insolubles (%)	21.2	20.7	20.2
4	Coking value (%)	48.6	48.0	47.7
5	Specific gravity	1.280	1.270	1.266

0022–2461

TABLE II Characteristics of the various heat-treated (mesophase) pitches

Experiment no.	Precursor pitch	Soaking time (h) at HTT 420 °C	Quinoline insolubles (%)	Toluene insolubles (%)	Coking value (%)	Size (μm) of mesophase spherules		
						Predominant range	Median	Mean
1	CTP-1	2.0	28.8	57.5	72.0	–	–	–
2	CTP-1	3.5	34.0	62.2	72.2	3.8–7.5	5.0	5.1
3	CTP-1	5.0	39.0	67.0	72.7	3.8–13.8	6.1	7.5
4	CTP-1	7.0	50.3	73.2	78.4	6.3–21.3	10.8	12.8
5	CTP-2	2.0	24.5	49.0	64.0	1.9–6.9	3.6	4.2
6	CTP-2	3.0	29.4	54.7	66.5	3.1–8.1	4.6	5.3
7	CTP-2	5.0	32.1	56.3	69.0	3.8–16.3	7.2	9.1
8	CTP-3	1.0	20.0	55.0	60.0	1.9–8.1	4.4	5.2
9	CTP-3	1.5	22.4	55.8	66.0	6.3–21.3	12.3	13.5
10	CTP-3	3.0	30.0	61.0	70.0	7.5–35.0	22.3	24.2

Anisotropic mesophase spherules were observed in polished specimens of mesophase pitches mounted in resin blocks, using a cross-polarized light optical microscope. Optical micrographs of the heat-treated pitches (experiments 1–10) are shown in Figs 1–3. The size (diameter) of the mesophase spherules was determined from these micrographs by counting 500–1000 points for each heat-treatment experiment. The mean size of the mesophase spherules formed in the three coal tar pitches as a function of soaking time is plotted in Fig. 4.

In the case of Experiment 6, MCMB were obtained from the heat-treated (mesophase) pitch by solvent extraction with a suitable tar-based oil. A histogram of the size distribution of mesophase spherules and the curve of their cumulative frequency versus size are shown in Fig. 5. These mesocarbon microbeads were also examined on a scanning electron microscope, and the micrograph obtained is shown in Fig. 6. These mesocarbon microbeads were also subjected to thermogravimetric analysis (TGA) up to 950 °C using a Mettler TA3000 thermogravimetric analyser, and the TGA curve obtained is shown in Fig. 7. The characteristics of the heat-treated pitch, as well as the mesocarbon microbeads obtained from this pitch, are given in Table III. These microbeads were hot-moulded into rectangular plates of 60 × 20 × 5 mm size at 110 °C, at a pressure of 1200 $kg\,cm^{-2}$ using a conventional hydraulic press. These plates were then carbonized at 950 and 2700 °C in atmospheres of high purity nitrogen and argon, respectively, to obtain monolithic carbon plates. These plates were tested for various physical characteristics, and were also subjected to optical microscopy. The values of the characteristics obtained are compiled in Table IV, and the optical micrographs are shown in Fig. 8.

3. Results and discussion

From Table II, it is clear that in the case of all three pitches, the different heat treatments invariably result in an increase in quinoline and toluene insoluble contents, as well as an increase in the coking values of resultant pitches. This is due to the removal of relatively lower molecular weight components from the precursor pitches, as well as to polymerization and condensation reactions taking place between the various planar aromatic molecules present in these pitches. Such reactions would obviously lead to the formation and growth of mesophase spherules. This is what has been observed in the polished samples of these heat-treated pitches examined using the optical microscope (Figs 1–3). It has, in fact, been found that the size and concentration of mesophase in any heat-treated pitch increases as the soaking time at the HTT (420 °C) increases. However, the increase in mesophase size with heat-treatment time is dependent upon the QI content in the precursor pitch. This is clearly seen from Fig. 4, showing the curves of mean size of mesophase spherules versus soaking time at the HTT of 420 °C for the three coal tar pitches. It is interesting to note that whereas in the case of CTP-3, having a QI content of 0.5%, the mean size of the spherules rises to as high as 24.2 μm for a heat-treatment period of 3 h; it reaches a value of only 12.8 μm for CTP-1, having a QI content of 6.5%, even after 7 h heat-treatment. For CTP-2, having a QI content of 3.3%, however, the mean size of the spherules is found to be 9.1 μm for a heat-treatment period of 5 h. These observations can be attributed to the presence of primary QI particles in the original pitches, which inhibit the coalescence and growth of mesophase spherules. Further, it may be worthwhile to mention here that some large non-spherical mesophase is also observed in the case of CTP-3 having a very low content of QI (0.5%) due to the incomplete coalescence of mesophase spherules, which is not desirable for producing high density monolithic carbons.

Further, as regards the monolithic carbon obtained from the mesophase spherules (MCMB), CTP-2 on heat-treatment at 420 °C for 3 h (experiment 6) was found to contain 40 wt % of these spherules, as given in Table III. The plots of differential (histogram) and cumulative frequencies of the mesophase spherules formed in this pitch versus their size (Fig. 5) indicate that the size of these spherules predominantly lies in the range 3.1–8.1 μm. This is consistent with the SEM photograph of the MCMB shown in Fig. 6. Further, it is also seen from Table III that these microbeads have quinoline and toluene insoluble contents of 93 and 96%, respectively, and have a coking yield of 82% (heating rate = 600 °C h^{-1}) as obtained using the ther-

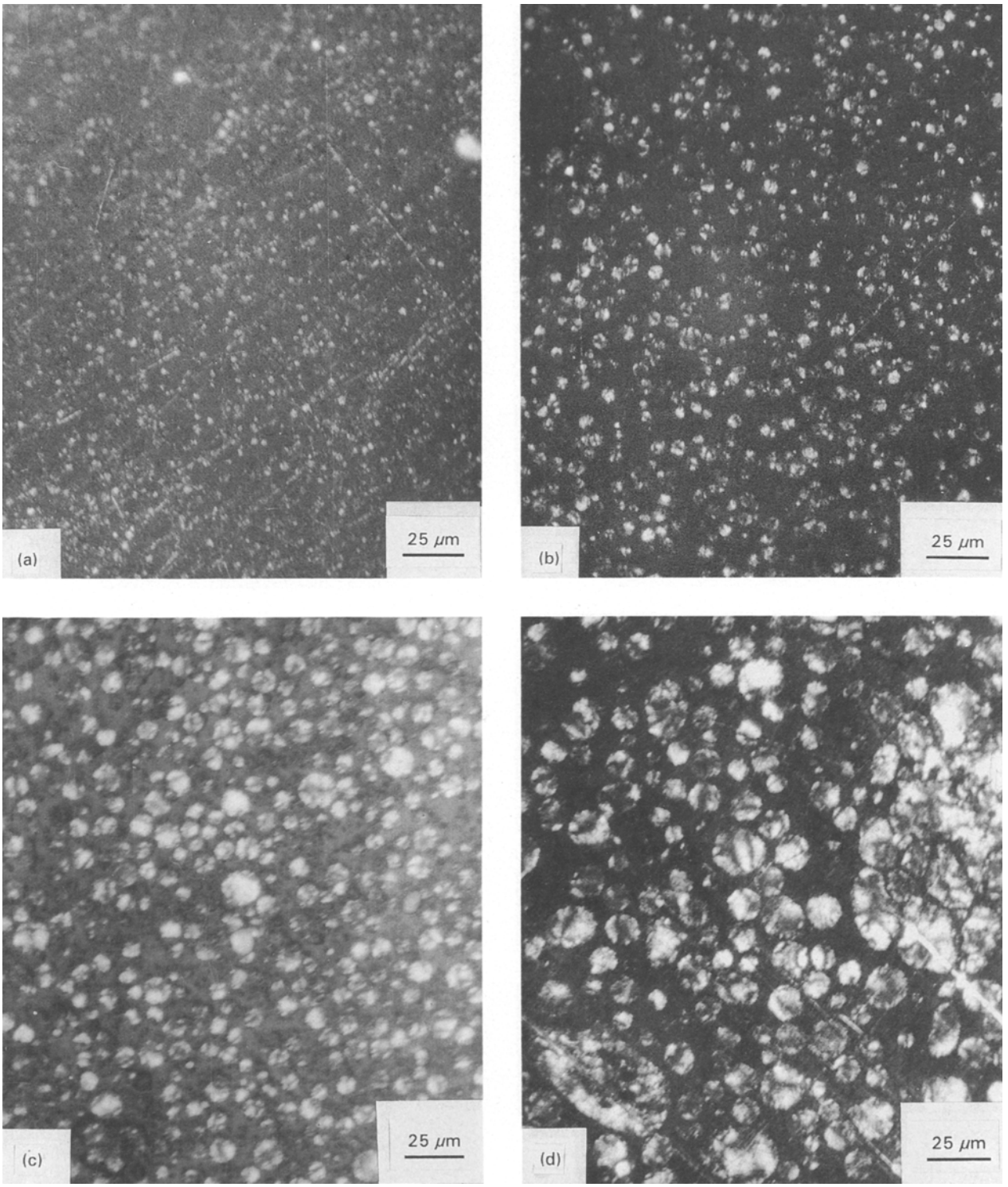
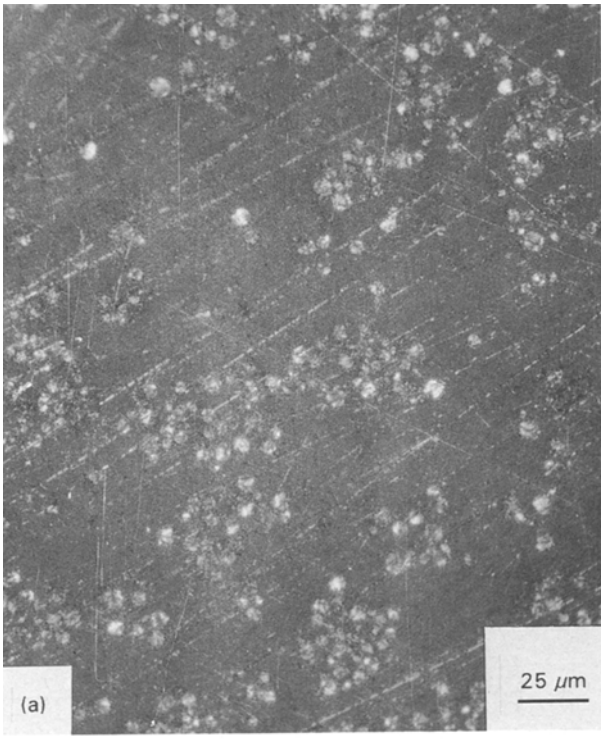
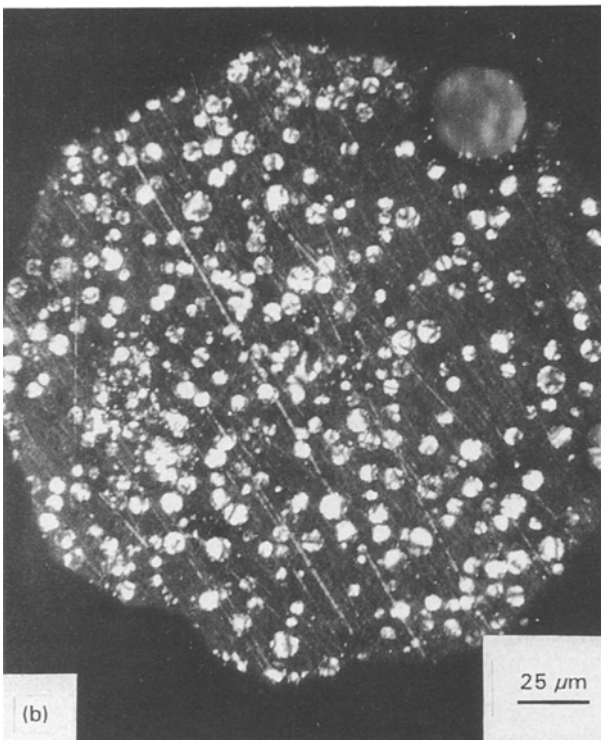


Figure 1 Optical micrographs of CTP-1 heat-treated at 420 °C for (a) 2 h, (b) 3.5 h (c) 5 h and (d) 7 h.

mogravimetric analyser. The TGA curve is shown in Fig. 7. However, this coking yield, as determined by another test procedure [21] employing a heating rate of 200 °C h^{-1}, is found to be 89%. The latter procedure gives a coking yield for heat-treated CTP-2 of 66.5%; a value significantly lower, compared to 89% obtained for the mesophase spherules isolated from this heat-treated (mesophase) pitch. The higher coking yield of MCMB compared to the heat-treated pitch is in agreement with the higher atomic C/H ratio of 2.65 of these MCMB, compared to a value of 2.26 for the heat-treated (mesophase) pitch, as shown in Table III.

The green plates made from the microbeads show an apparent density of 1.25 g cm^{-3}, which increases to 1.66 g cm^{-3} on carbonization of the plates to 950 °C. This increase in the apparent density on carbonization of the plates is due to an enormous volume shrinkage of 33.9% and a weight loss of only 13.7%, i.e. because of the dominance of volume shrinkage over weight loss. The carbonized (950 °C) plates have been found to have a high bending strength of 88.2 MPa and a Shore hardness of 95. On further heat treatment from 950 to 2700 °C, the plates show a cumulative weight loss of 20.5%, accompanied by cumulative volume





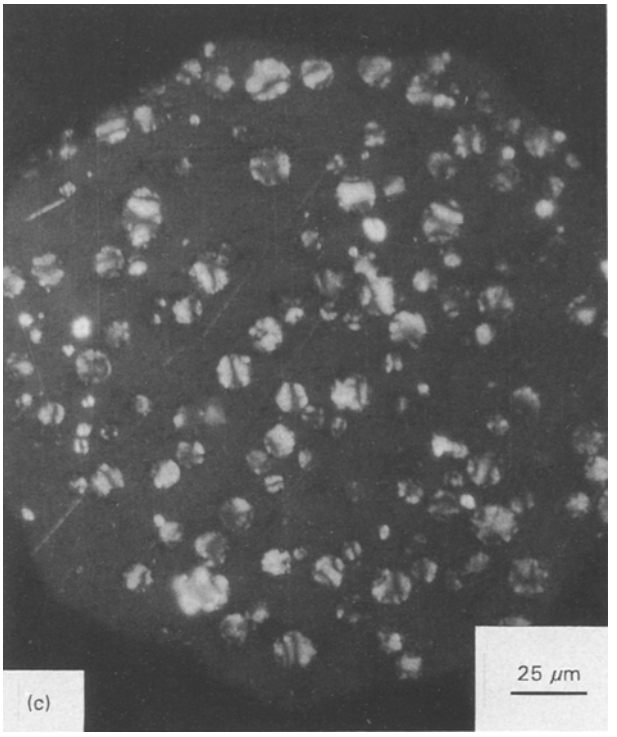


Figure 2 Optical micrographs of CTP-2 heat treated at 420 °C for (a) 2 h, (b) 3 h, and (c) 5 h.

and linear shrinkages of 45.8 and 18.6%, respectively. The apparent density, in turn, increases from 1.66 g cm^{-3} at a HTT of 950 °C, to a value of 1.85 g cm^{-3} at 2700 °C. This may again be attributed to continuing dominance of volume shrinkage over weight loss up to a HTT of 2700 °C. Further, however, the bending strength of the plates decreases from 88.2 to 68.3 MPa due to heat-treatment between 950 to 2700 °C; which may be due to a corresponding increase in the open porosity from a value of 7.9–14.5%, resulting from the growth of crystallites following removal of disorganized matter between crystallites and from an improvement in the alignment of the crystallites. The growth of crystallites during heat treatment from 950 to 2700 °C is clear from the increase in the value of L_c from 1.59 to 15.8 nm and the decrease in the value of $d_{0\,0\,2}$ spacing from 0.351 to 0.336 nm, as is seen from Table IV. The Shore hardness of the plates is found to have a similar pattern as

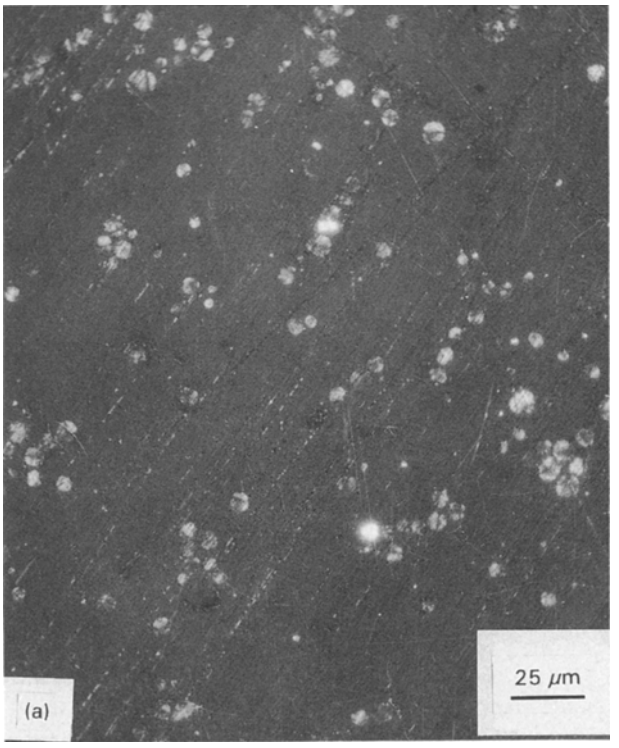
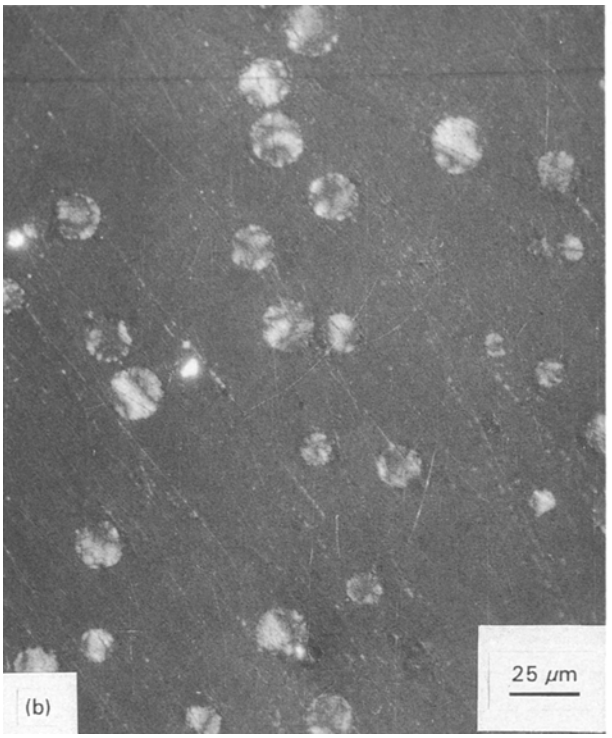
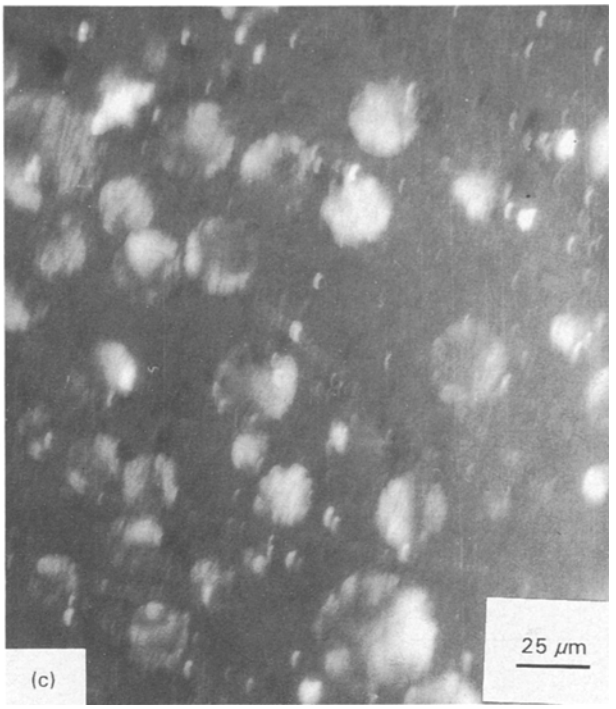


Figure 3 Optical micrographs of CTP-3 heat treated at 420 °C for (a) 1 h, (b) 1.5 h, (c) 3 h.





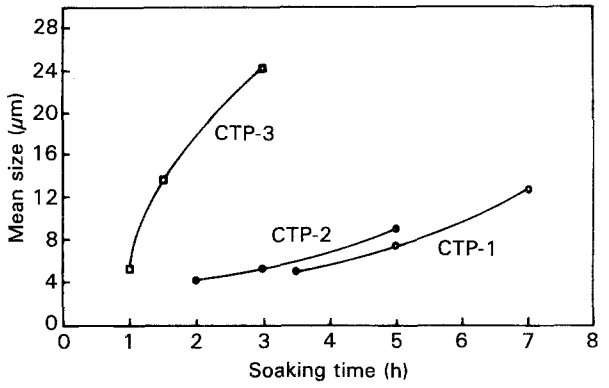


Figure 4 Mean size (dia.) of mesophase spherules formed in three coal tar pitches as a function of soaking time.

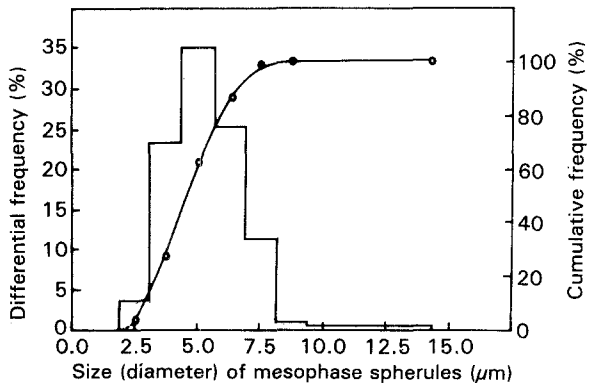


Figure 5 Differential (histogram) and cumulative frequencies of mesophase spherules formed in CTP-2 by heat-treatment at 420 °C for 3 h, as a function of their size.

the bending strength, and accordingly decreases from a value of 95 to 70 as the HTT increases from 950 to 2700 °C. Electrical resistivity is seen to have a pronounced fall from 6.7 m Ω cm at a HTT of 950 °C, to a

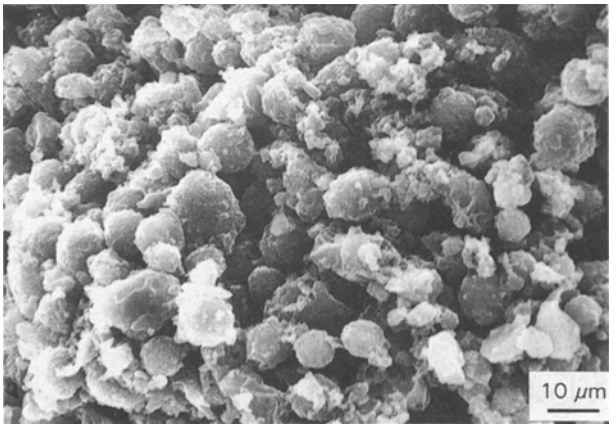


Figure 6 SEM photograph of mesocarbon microbeads obtained by heat treatment of CTP-2 at 420 °C for 3 h.

value of 2.7 m Ω cm at 2700 °C, which is a usual phenomenon for all polycrystalline carbons, and corresponds to the growth of crystallites constituting these carbons. Finally, the microstructure of the MCMB-based monolithic carbons, in both carbonized (HTT = 950 °C) as well as graphitized (HTT = 2700 °C) states, is found to be quite homogeneous with a fine isotropic texture, as shown in Fig. 8a, b.

4. Conclusions

1. The presence of some primary quinoline insolubles in the precursor coal tar pitch appears to be beneficial in controlling the growth of mesophase spherules to a desired size for ultimate use in the development of fine textured high density, high strength, isotropic carbons.

2. Monolithic carbons made from mesophase spherules (MCMB) having an average size of about 5 μm, generated in a coal tar pitch with a quinoline insoluble content of 3.3%, exhibit apparent densities of 1.66 and 1.85 g cm^{-3}, bending strengths of 88.2 and 68.3 MPa, Shore hardness of 95 and 70, electrical resistivities of 6.7 and 2.7 m Ω cm, and open porosities of 7.9 and 14.5% at heat treatment temperatures of 950 and 2700 °C, respectively.

3. The microstructure of the carbon, in both carbonized as well as graphitized states, reveals homogeneity and fine isotropic texture.

TABLE III Characteristics of mesophase pitch and mesocarbon microbeads obtained therefrom

	Characteristics	Mesophase pitch	Mesocarbon microbeads
1	Heat treatment/extraction yield (%)	84.0	40.0
2	Quinoline insolubles (%)	29.4	93.0
3	Toluene insolubles (%)	54.7	96.0
4	β-resins (%)	25.3	3.0
5	Coking yield (%)	66.5	89.0
6	Size of mesophase spherules (μm)		
	Predominant range	3.1–8.1	3.1–8.1
	Mean (average)	5.3	5.3
7	Carbon (C) content (%)	94.80	95.30
	Hydrogen (H) content (%)	3.52	3.02
	Atomic C/H ratio	2.26	2.65

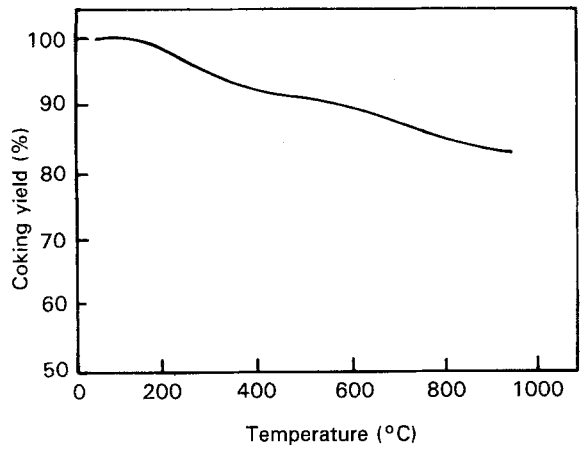


Figure 7 TGA curve of the mesocarbon microbeads.

TABLE IV Characteristics of the carbon plates heat treated to temperatures of 950 and 2700 °C

	Characteristics	HTT values (°C)	
		950	2700
1	Green apparent density (g cm^{-3})	1.25	1.25
2	Apparent density (g cm^{-3})	1.66	1.85
3	Specific gravity	1.68	1.86
4	Weight loss (%)	13.70	20.50
5	Volume shrinkage (%)	33.90	45.80
6	Linear shrinkage (%)	12.70	18.60
7	Bending strength (MPa)	88.20	68.30
8	Young's modulus (GPa)	15.20	27.00
9	Scleroscopic hardness	95	70
10	Electrical resistivity (m Ω cm)	6.70	2.70
11	Open porosity (%)	7.90	14.50
12	Crystallite parameters		
	d_{002} (nm)	0.351	0.336
	L_c (nm)	1.59	15.8

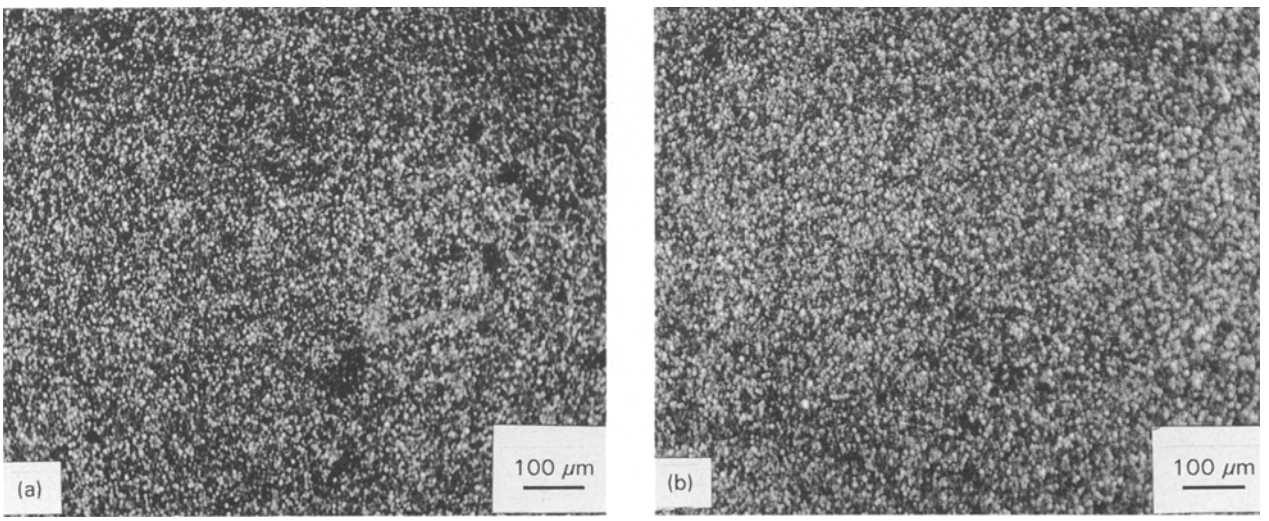


Figure 8 Optical micrographs of carbon plates heat treated to temperatures of (a) 950, and (b) 2700 °C.

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