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The effects of pressure on the carbonization of pitch and pitch/carbon fibre composites

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Three pitches which give carbons of varying optical texture have been carbonized singly and with different carbon fibres at pressures in the range 0.1 to 200 MPa. The effect of pressure on the carbonization system is to retard growth and coalescence of the growth units of mesophase, thus reducing the size of the optical texture of the resultant carbon. With increasing pressure botryoidal (spherical) structures are formed. On co-carbonization of pitches with carbon fibres the alignment of the basal planes of the matrix carbon parallel to the fibre length at the fibre/matrix interface is improved within a given pressure range. This range is dependent upon the parent pitch used and is experimentally determined. This effect is seen for all fibre types.

1. Introduction

Carbon fibre reinforced composites are important in engineering and scientific applications where high strength coupled with an ability to withstand high temperatures and thermal shock is necessary. Industrially prepared and commercially available carbon/carbon fibre composites are prepared by impregnation of the carbon fibre weave with e.g. fluid pitch under pressure [1]. Impregnation and carbonization under pressure have the effect of improving composite density.

Carbonization under pressures of about 100 MPa leads to the development of botryoidal (sphere-like) structures in pitches [2] and affects the development of transverse orientated graphite (TOG) around carbon vapour deposited (CVD) coated PAN (polyacrylonitrile) fibres when these are used in composite manufacture [3]. It is also reported that carbonization under pressures of about 100 MPa accelerates the graphitization of carbons (pitch cokes) [4, 5].

Orientation of the basal planes of the matrix carbon in carbon/carbon fibre composites is of importance when considering composite properties such as thermal conductivity, electrical conductivity and mechanical strength [3, 6, 7]. The effects of pressure on the formation and structure of the matrix carbon is, therefore, also of considerable interest in so far as pressure affects the structure of matrix carbon.

A systematic study of the effects of pressure on the carbonization of pitches and on the co-carbonization of pitches with carbon fibres is not available. The overall objective of this study is therefore to investigate the effects of pressure, in the range 0.1 to 200 MPa, upon the carbonization of pitches with high and low viscosities with and without PAN and CVD coated PAN fibres, and with PAN fibre cloths added to the carbonization system.

Specific objectives include the effects of this range of pressure upon the growth and coalescence of mesophase and upon the optical texture [2, 8] of resultant carbon.

For carbon/carbon fibre composites, it is necessary to know the effects of pressure on the alignment of the basal planes of the matrix carbon (as deduced from reflection interference colours [9]) at the fibre/matrix interface. The use of CVD coatings increases the amount of TOG (transverse orientated graphite) formed in the matrix carbon at the fibre/matrix interface;

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therefore the effect of carbonization under pressure on this alignment is investigated.

2. Experimental details

2.1. Materials used

2.1.1. Pitch matrix precursors

A240 Ashland petroleum pitch

Esso CP1510 petroleum pitch

D112 coal extract

2.1.2. Fibres/fibre cloths

HMU PAN fibres

CVD coated PAN fibres

G2206 PAN fibre cloth

2.1.3. Carbonizations at 0.1 MPa (atmospheric pressure)

Each of the three ptich matrix precursors used was ground to particle sizes of 212 to 600 μm and carbonized singly and co-carbonized with HTU PAN, CVD coated PAN fibres and G2206 PAN fibre cloth (not with coal extract). All carbonizations were carried out in a Carbolite horizontal electrical tube furnace under nitrogen to heat treatment temperatures (HTT) of 1173 K (900° C) at heating rates of 3 K min^{-1}.

2.2. High pressure carbonizations

2.2.1. Pressures to about 13.3 MPa

Carbonizations were carried out in a stainless steel pressure reaction vessel, constructed from grade 304 OD16 gauge stainless steel tubing with Hoke International Gyrolok stainless tube fittings and a Hoke valve. Pressure was measured using a Bell and Howell strain gauge pressure transducer with an Anadex digital indicator.

The reaction vessel was loaded with about 2 g pitch or pitch + fibre to give pressures of about 0.67 MPa (from volatile evolution). For pressures of about 6.7 and about 13.3 MPa, 1 or 2 g, respectively, of solid carbon dioxide was packed in the reaction vessel with the pitch. The loaded reaction vessel was placed for 2 h in a vertical electrical tube furnace preheated to 823 K (550° C).

Each pitch matrix precursor was carbonized with each fibre in this way. The resultant carbons were removed from the reaction vessel and heat treated in a horizontal electrical tube furnace to 1173 K (900° C) under nitrogen.

The above system could not be used for carbonization of carbon fibre cloths as the internal dimensions were too small. To carbonize pitch + fibre cloth systems, carbonizations were carried out in a 300 ml stainless steel autcoclave. This unit, supplied by Autoclave Engineers Inc., was fitted with a direct reading pressure gauge fitted to the autoclave body via stainless steel tubing. Also fitted to the unit was a safety valve consisting of a stainless steel rupture disc designed to rupture at pressures in excess of 33.3 MPa. The entire unit was surrounded by an electrical furnace capable of heating to temperatures of up to 750° C. Samples to be carbonized were placed in a pyrex tube (about 3 cm × 15 cm) which was inserted into the autoclave body.

Approximately 10 to 12 g of A240 and Esso CP1510 pitches in turn were carbonized with 2 to 3 cm^2 carbon fibre cloth. Since volatiles from the pitch raised the pressure only to 1.33 MPa solid carbon dioxide was added (approximately 25 to 30 g) to give a total pressure of 13.3 MPa at 973 K (700° C).

2.2.2. Pressures up to about 200 MPa

Carbonizations were carried out in a stainless steel pressure reaction vessel connected to a hydraulic pump capable of pressurizing the apparatus to 235 MPa. White water (soluble oil and water in the ratio 1:5) was used as the hydraulic fluid. The sample (weight about 0.05 g) was sealed inside a 3 cm gold tube of diameter 3 mm. The ends of this tube were sealed by pressure welding. The tubes were placed inside the reaction vessel of Stellite 25 stainless steel [2].

The loaded reaction vessel was placed in a vertical electrical tube furnace and heated to 873 K (600° C) at 5 K min^{-1}, with a 1 h soak period. All carbons were heat treated to 1173 K (900° C) under nitrogen at atmospheric pressure in a horizontal electrical resistance furnace to facilitate polishing. The A240 and Esso pitches were carbonized singly and together with each fibre at hydraulic pressures of 100 and 200 MPa.

2.3. Sample examination by microscopy

Each carbon was mounted in resin, polished and examined and photographed using a Vickers M41 polarizing microscope. Fracture surfaces of each carbon were examined by scanning electron microscopy. Optical examination of carbons from the A240 and Esso pitches carbonized with G2206 cloth at atmospheric pressure and at 13.3 MPa showed differences in porosity. This porosity was investigated as described in the following Section.

2.4. Image analysis of porosity

A quantitative analysis of pore size, area and Feret diameter of composites prepared at atmospheric and higher pressures used a semi-automatic image analyser to determine if carbonization under pressure had caused changes in the porous structure of the matrix carbon. The image analyser was an Optomax System III based on an Apple system. The polished composite was examined using the × 4 objective on a Vickers M17 polarizing microscope in conjunction with a Philips TV camera. The image was displayed on a Hitachi TV monitor linked to an Apple graphics tablet. An electronic stylus was used to draw desired shapes on the tablet; the drawn shape was displayed on the TV monitor superimposed on the sample image. The stylus could, therefore, be used to draw around pores in the sample.

The image analyser analysed the outline of the pores and recorded pore area, perimeter, form factor and Feret *x* and *y* diameters. These data were stored in named files. A total of 50 pores (50 representing the smallest statistically representative number for data analysis) was sampled from each of the two atmospheric pressure composites and from each of the two 2000 psi (13.3 MPa) composites.

3. Results

3.1. The effects of pressure upon optical texture of carbon

The effects of pressure on the optical texture of the A240 and Esso pitches and the D112 coal extract using the nomenclature of Table I are summarized in Tables II to IV.

TABLE I Nomenclature to describe optical texture in polished surfaces of cokes

Isotropic (I)	No optical activity
Very fine-grained mosaics (VMf)	< 0.5 µm in diameter
Fine-grained mosaics (Mf)	1.5 > diameter > 0.5 µm
Medium-grained mosaics (Mm)	5.0 > diameter > 1.5 µm
Coarse-grained mosaics (Mc)	10.0 > diameter > 5.0 µm
Supra mosaics (SM)	Mosaics of anisotropic carbon oriented in the same direction to give a mosaic area of isochromatic colour
Medium-flow anisotropy elongated (MFA)	< 30 µm in length; < 5 µm in width
Coarse-flow anisotropy elongated (CF)	60 > length > 30 µm; 10 > width > 5 µm
Acicular flow domain anisotropy (AFD)	> 60 µm in length; < 5 µm in width
Flow domain anisotropy elongated (FD)	> 60 µm in length; > 10 µm in width
Small domains, isochromatic (SD)	60 > diameter > 10 µm
Domains, isometric (D)	> 60 µm in diameter
D_b is from basic anisotropy of low-volatile coking vitrains and anthracite	
D_m is by growth of mesophase from fluid phase	
Ribbons (R)	Strands of mosaics inserted into an isotropic texture

Figs. 1 and 2 are optical and scanning electron microscope (SEM) micrographs of polished and fracture surfaces, respectively, of carbon from A240 carbonized at 200 MPa showing the botryoidal structures mentioned above. The carbon formed from A240 carbonized at 200 MPa consisted entirely of semi-coalesced spheres, of typical size up to about 50 µm (Fig. 2, position A).

Figs. 3 and 4 are optical and SEM micrographs of polished and fracture surfaces, respectively, of carbon from Esso CP1510 carbonized at 100 MPa showing developed botryoidal structures.

TABLE II A240 pitch

Pressure (MPa)	Description of resultant optical textures
Atmospheric	Flow domain anisotropy
0.6	Flow domain anisotropy
13.3	Flow domain anisotropy
16.6	Domain anisotropy
100	Small domain anisotropy; some botryoidal (spherical) structures formed at pore perimeters.
200	Coarse-grained mosaic; the carbon consists entirely of botryoidal structures.

TABLE III Esso CP1510 Pitch

Pressure (MPa)	Description of resultant optical texture
Atmospheric	Flow domain anisotropy
0.6	Flow domain anisotropy
6.7	Coarse flow anisotropy
13.7	Medium flow anisotropy
100	Coarse-grained mosaic; the carbon consists entirely of botryoidal structures of size ~ 40 μm diameter
200	Medium-grained mosaic; the carbon consists entirely of botryoidal structures of size ~ 15 μm diameter

At this pressure, the carbon formed consisted entirely of these structures, of typical size up to about 50 μm (Fig. 4, position B).

Fig. 5 is a SEM micrograph of a fracture surface of carbon from D112 coal extract carbonized at 90 psi (0.6 MPa); even at this relatively low pressure, botryoidal structures exist in the surface, of typical size up to 10 μm (position C).

Fig. 6 is a SEM micrograph of a fracture surface of carbon from D112 coal extract carbonized at 13.3 MPa. At this pressure the entire carbon is composed of semi-coalesced botryoidal spheres, of typical size up to 10 μm (position D).

3.2. The effects of pressure upon the co-carbonization of pitches with carbon fibres

3.2.1. A240 pitch + HMU fibres

The orientation of the basal planes of the matrix carbon at the fibre/matrix interface is deduced from the reflection interference colours (RIC). The co-carbonization of A240 + HMU PAN fibres at pressures ranging from atmospheric to 13.3 MPa produced composites in which basal plane orientation of the matrix carbon within about 5 μm of the fibre/matrix interface is parallel to the fibre length. Figs. 7 and 8 are optical micrographs of A240 + HMU PAN fibres carbonized at atmospheric pressure and at 13.3 MPa, respectively. Positions E and F show that the alignment of the basal planes of the matrix carbon is parallel to the fibre lengths.

At carbonization pressures of 100 and 200 MPa the RIC indicate alignment of basal planes of the matrix carbon parallel to the fibre length within about 5 to 10 μm of the fibre surface. Fig. 9 is an optical micrograph of the composite prepared at 200 MPa where the entire carbon is composed of porous, semi-coalesced botryoidal structures. The fibres are, however, completely sheathed (position G).

3.2.2. A240 pitch + CVD coated fibres

At carbonization pressures ranging from atmospheric to 13.3 MPa the RIC reveal no significant alignment of basal planes of the matrix carbon parallel to the fibre length. Fig. 10 is an optical micrograph showing carbon from A240 pitch co-carbonized with CVD coated fibres at atmospheric pressure; position H shows the random alignment of basal planes of the matrix carbon at the fibre/matrix interface.

At pressures of 100 and 200 MPa, the RIC indicate that the A240 + CVD coated fibres formed a composite in which the basal planes of the matrix carbon are aligned parallel to the fibre length within about 10 μm of the fibre/matrix interface. Fig. 11 shows the composite carbonized under 200 MPa; the carbon is formed entirely of botryoidal structures but these completely sheath the fibres (position I).

3.2.3. Esso CP1510 pitch + HMU fibres

At pressures ranging from atmospheric to 13.3

TABLE IV D112 coal extract

Pressure (MPa)	Description of resultant optical texture
Atmospheric	Coarse-grained mosaics
0.6	Medium-grained mosaics
6.0	Medium-grained mosaics
14.0	Small-grained mosaics; the carbon consists entirely of botryoidal structures

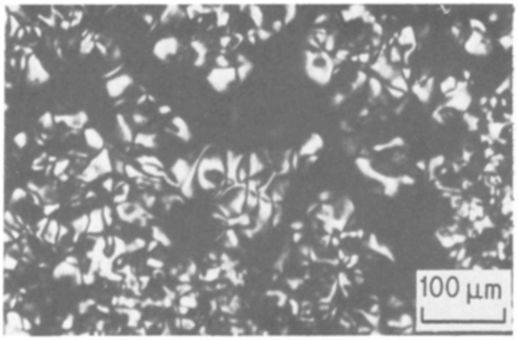


Figure 1 Optical micrograph of carbon from A240 petroleum pitch; 200 MPa.

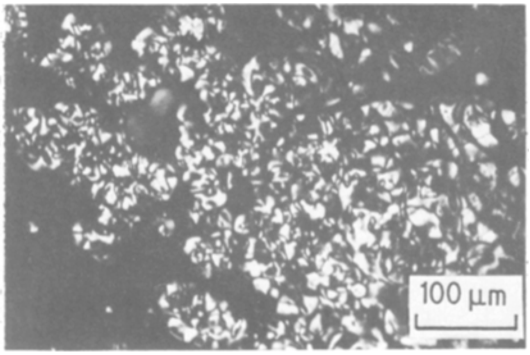


Figure 3 Optical micrograph of carbon from Esso CP1510 petroleum pitch; 100 MPa.

MPa, the Esso CP1510 pitch + HMU fibre composites showed the same features as for A240 pitch, i.e. basal plane orientation of the matrix carbon is predominantly parallel to the fibre length. Botryoidal structures tend to form at pressures which are lower for the Esso CP1510 than for the A240 pitches; at 100 MPa the carbon is entirely botryoidal, with fibres sheathed in the semi-coalesced spheroids. RIC indicate that basal planes of the matrix carbon are parallel to the fibre length within about 5 μm of the fibre surface. However, at 200 MPa, Fig. 12, RIC indicate no overall preferred orientation of the basal planes of the matrix carbon at the fibre interface (position J).

3.2.4. Esso CP1510 + CVD coated fibres

Again, as with the A240 pitch, RIC indicate no preferred orientation of basal planes of the matrix carbon at the interface with the fibres for Esso CP1510 + CVD coated fibres carbonized at pressures ranging from atmospheric to 13.3 MPa. At 100 MPa, however, Fig. 13, RIC indicate a preferred orientation of basal planes of matrix carbon parallel to the fibre length within about 5 μm of the fibre surface (position K). This preferred orientation is lost at pressures of 200 MPa (Fig. 14, position L). At both of these pressures, the carbon is composed entirely of botryoidal structures which sheath the fibres.

3.2.5. D112 coal extract + HMU fibres

In the D112 + HMU fibres composite carbonized at atmospheric pressure, the orientation of the matrix carbon was predominantly random at the fibre matrix interface, although some areas existed where orientation of the basal planes was parallel to the fibre length (Fig. 15, position M). For the same composite carbonized under a pressure of 0.6 MPa the basal planes of the D112 matrix carbon are aligned along most of the fibre length within about 1 to 5 μm of the fibre (Fig. 16, position N). However, when carbonization pressures are increased to 13.3 MPa this alignment

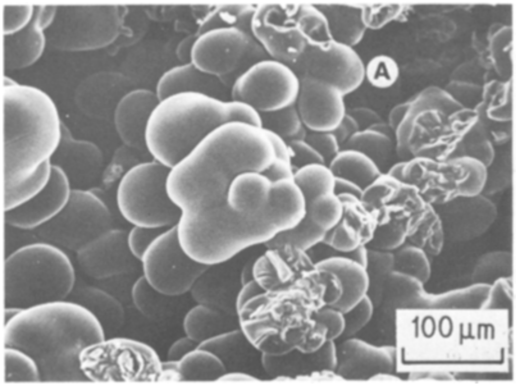


Figure 2 SEM micrograph of carbon from A240 petroleum pitch; 200 MPa.

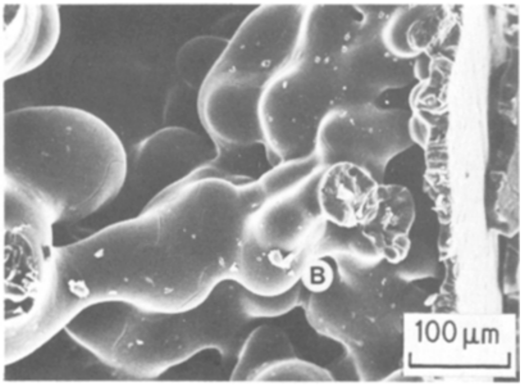


Figure 4 SEM micrograph of carbon from Esso CP1510 petroleum pitch; 100 MPa.

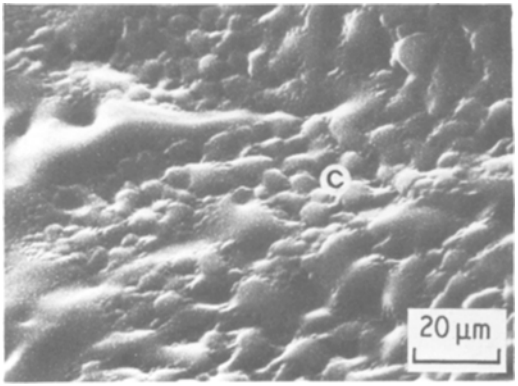


Figure 5 SEM micrograph of a fracture surface of carbon from D112 coal extract; 0.6 MPa.

is lost and orientation of the basal planes of the matrix carbon at the fibre/matrix interface again becomes predominantly random.

3.2.6. D112 coal extract + CVD coated fibres

For D112 + CVD fibres carbonized at pressures ranging from atomospheric to 100 psi (0.6 MPa), there is no significant alignment of basal planes of the matrix carbon parallel to the fibre length as deduced from RIC (Fig. 17, position O). However, at 6.7 MPa, RIC indicate that such alignment is found at the fibre/matrix interface over significant distances (up to 5 μm); e.g. Fig. 18, position P. However, at carbonization pressures of 13.3 MPa, alignment is again random.

3.3. The effects of pressure upon the co-carbonization of pitches with a woven carbon fibre cloth (G2206)

The composites prepared by carbonization of G2206 cloth and A240 and Esso CP1510 pitches at atmospheric pressure (Figs. 19 and 20, respectively) show the following features:

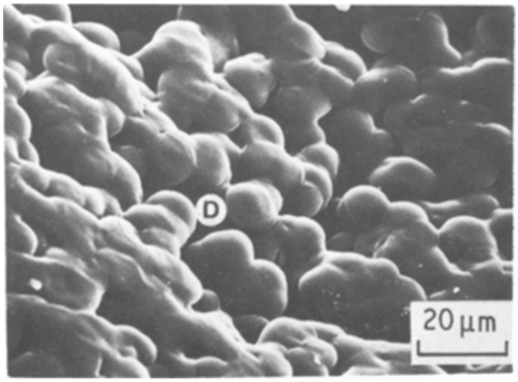


Figure 6 SEM micrograph of a fracture surface of carbon from D112 coal extract; 13.3 MPa.

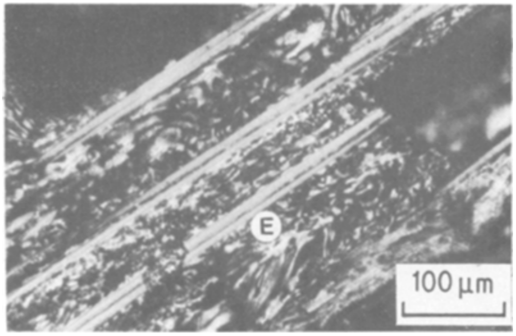


Figure 7 Optical micrograph of HMU fibres in matrix carbon from A240 pitch; atmospheric.

1. The orientation of the basal planes of the matrix carbon close to the fibre within each fibre bundle as deduced from the reflection interference colours (RIC) is parallel to the fibre length (positions Q and R).
2. There is rapid change in the basal plane orientation within a distance of about 5 μm at the fibre bundle interface (position T). Basal planes orientated parallel to the longitudinal direction of one fibre bundle change orientation between fibre bundles and re-orientate parallel to the second fibre bundle.
3. The matrix carbon between fibre bundles is often associated with fissuring of typical width about 5 to 10 μm and length up to about 200 μm, running between the fibre bundles (positions U and V).

The G2206 cloth in an A240 pitch matrix carbon (Fig. 21) and in an Esso CP1510 pitch matrix carbon (Fig. 22) carbonized under

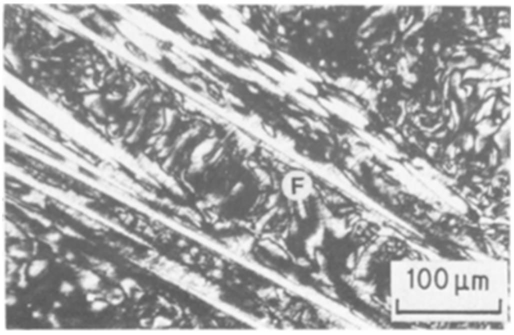


Figure 8 Optical micrograph of carbon from A240 pitch + HMU fibres; 13.3 MPa.

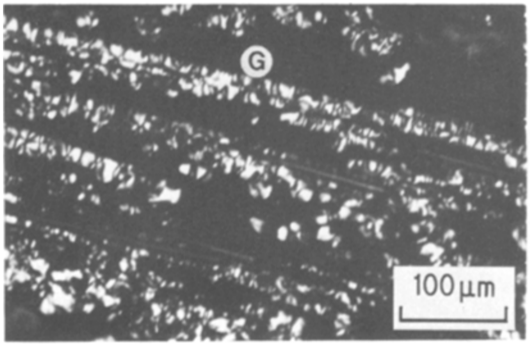


Figure 9 Optical micrograph of HMU fibres in a matrix carbon from A240 petroleum pitch; 200 MPa.

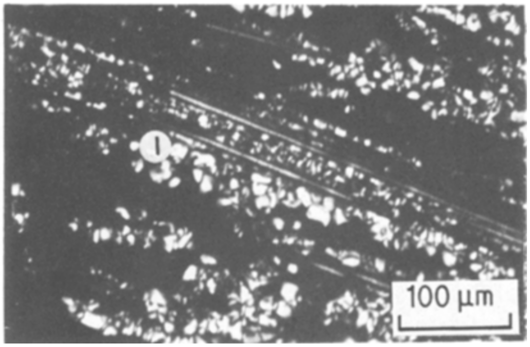


Figure 11 Optical micrograph of CVD coated fibres in matrix carbon from A240 pitch; 200 MPa.

pressures of 13.3 MPa show the same features as described above for the composites prepared at atmospheric pressure.

However, two differences are seen between the two composites carbonized at atmospheric pressure and at 13.3 MPa. Firstly, in all four composites the RIC indicate that basal plane orientation of the matrix carbon is predominantly parallel to the fibre length within fibre bundles. In the composites prepared at 13.3 MPa, however, there appear to be fewer areas in which RIC indicate basal plane orientation of the matrix carbon to be perpendicular to fibre length in the vicinity of the fibres than there are in the atmospheric pressure composites. This indicates that basal plane orientation of the matrix carbon in the high pressure composites is more closely parallel to the fibre length than in the composites prepared at atmospheric pressure.

Secondly, optical examination and comparison of the two atmospheric pressure composites with the two higher pressure ones suggest that changes have occurred in the porous structure of the higher pressure composites.

Pores of typical diameter up to about 50 μm are frequently seen in the atmospheric pressure composites (Fig. 19, position W; Fig. 20, position Z). Such pores are not found so frequently in the composites prepared at 13.3 MPa. The quantitative analyses of 50 pores from each of the four composites are with Figs. 23 to 30. All measurements are in micrometers. 50 pores form a statistically representative group for an initial study such as this but it should be emphasized that for greater reliability in future studies a larger number of pores should be analysed (about 500).

In the A240 atmospheric pressure composites, Figs. 23 and 24, 94% of the pores have Feret x diameters $\leqslant 400\,\mu$m and 92% have Feret y diameters $\leqslant 450\,\mu$m. The A240 13.3 MPa composite, Figs. 25 and 26, has 92% of pores with Feret x diameters $\leqslant 250\,\mu$m, and 100% with Feret x diameters $\leqslant 400\,\mu$m. It also has 92% of pores with Feret y diameters $\leqslant 300\,\mu$m and with

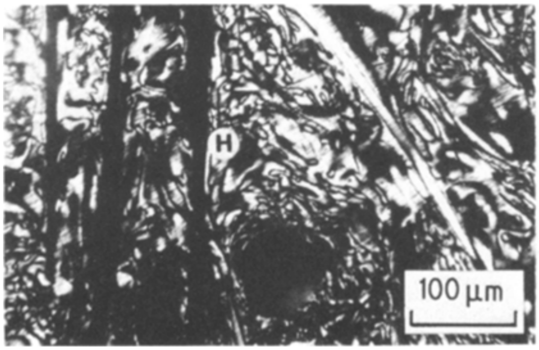


Figure 10 Optical micrograph of CVD coated fibres in matrix carbon from A240 pitch; atmospheric.

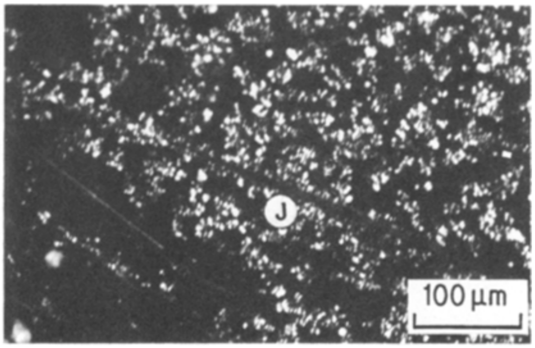


Figure 12 Optical micrograph of HMU fibres in a matrix carbon from Esso CP1510 pitch; 200 MPa.

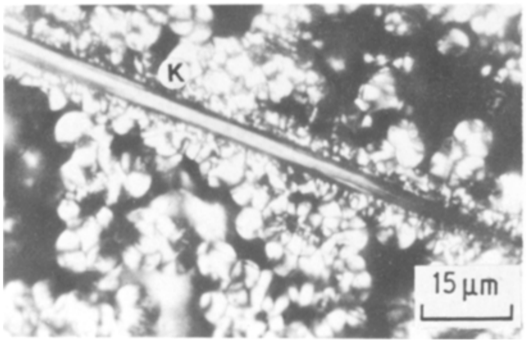


Figure 13 Optical micrograph of CVD coated fibres in a matrix carbon from Esso CP1510 pitch; 100 MPa.

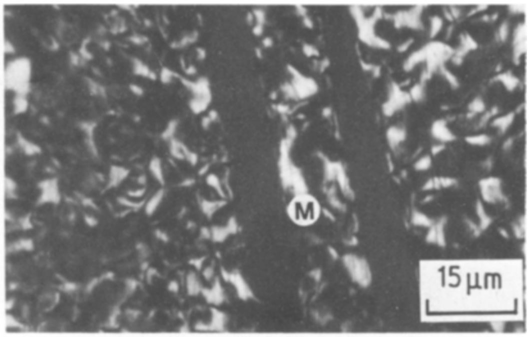


Figure 15 Optical micrograph of HMU fibre matrix carbon from D112 coal extract; atmospheric.

100% ⩽ 450 µm. The trend is for Feret diameters to decrease with increasing pressure of carbonization.

In the Esso CP1510 atmospheric pressure composite, Figs. 27 and 28, 92% of the pores have Feret x diameters ⩽ 450 µm, and 96% have Feret y diameters ⩽ 500 µm. The Esso CP1510 13.3 MPa composite, Figs. 29 and 30, has 98% of pores with Feret x diameters ⩽ 300 µm, and 98% Feret y diameters ⩽ 350 µm. The trend is again for Feret diameters to decrease with increasing pressure of carbonization.

4. Discussion

4.1. The effects of pressure upon optical texture of carbon

The effects of carbonization under pressure are to reduce the size of the optical texture of carbons produced from the flow-textured A240 and Esso CP1510 petroleum pitch cokes (carbons), and the smaller textured D112 coke. In the former, significant reduction in the size of the optical texture occurs at pressures in excess of 100 MPa; with the D112 coal extract the same effect is seen at much lower pressures (about 0.67 MPa).

At approximately the same pressures at which a change in size of optical texture is seen, botryoidal structures begin to develop in the coke. These represent semi-coalesced growth units of mesophase, and ultimately, as the pressure of carbonization is increased, the coke is formed entirely of these structures. It therefore appears that the effects of carbonization under pressure are to retard the growth and coalescence of mesophase growth units ultimately leading to a considerable reduction in optical texture of the resultant coke and to the formation of botryoidal structures. If carbonization pressures are further increased, the size of the botryoidal spheres themselves is decreased and they are prevented from fully coalescing.

It is important to note that the pressures at which these effects can first be seen is dependent upon the optical texture (viscosity) of the parent material. The smaller the optical texture (the higher the viscosity), the lower the pressures

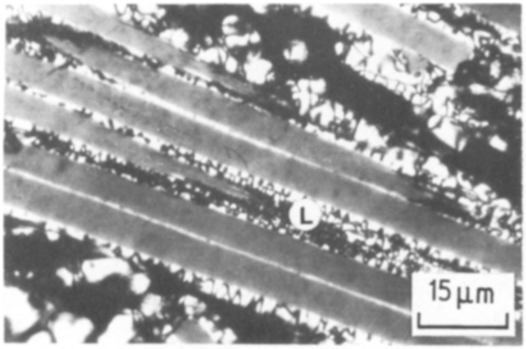


Figure 14 Optical micrograph of CVD coated fibres in a matrix carbon from Esso CP1510 pitch; 200 MPa.

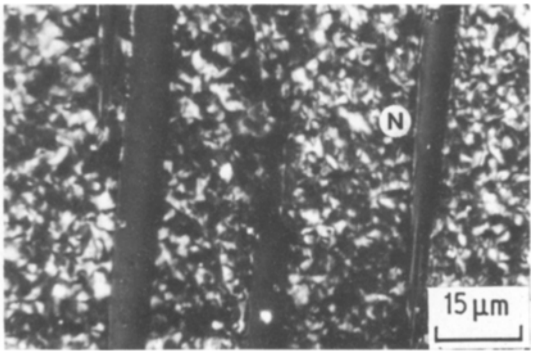


Figure 16 Optical micrograph of HMU fibres in matrix carbon from D112 coal extract; 0.6 MPa.

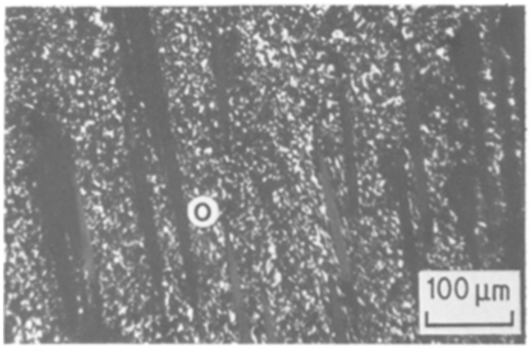


Figure 17 Optical micrograph of CVD coated fibres in matrix carbon from D112 coal extract; 0.6 MPa.

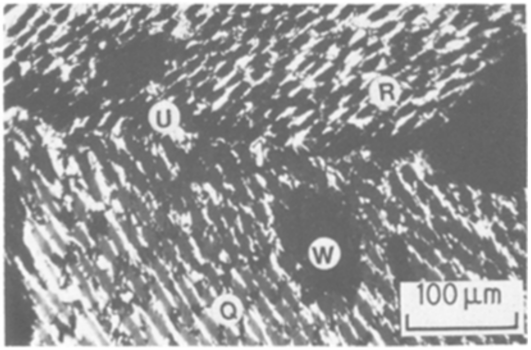


Figure 19 Optical micrograph of G2206 cloth in matrix carbon from A240 pitch; atmospheric.

needed to reduce size of optical texture and cause the formation of botryoidal structures.

4.2. The effects of pressure upon the co-carbonization of pitches with carbon fibres

In co-carbonizations of pitches and fibres, pressures up to a given value (dependent on the pitch viscosity) increase the amount of alignment of the basal planes of the matrix carbon (as deduced from RIC) for both fibre types. Alignment becomes random above this value. For the high viscosity D112 coal extract, alignment begins to be randomized at pressures of 13.3 MPa. For A240 and Esso CP1510 pitches, however, alignment is improved, even for CVD coated fibres, at pressures up to 100 MPa (Esso CP1510) and 200 MPa (A240). Above 100 MPa, basal plane alignment of matrix carbon is randomized for the Esso CP1510.

There appears to be an optimum pressure range within which alignment of the basal planes of the matrix carbon is improved for all fibre types and above which the alignment becomes random. This range depends upon the properties of the matrix precursor. The effect may be dependent upon the fluid properties of coalesced mesophase within the interstices between the carbon fibres and fibre bundles.

It is thought that the alignment of basal planes of the matrix carbon parallel to the fibre length is produced by flow of the mesophase past the fibre surface. This produces shear forces which tend to align the lamellar molecules of the mesophase in the direction of easiest slip, i.e. parallel to the fibre length. The effect of carbonization under pressure is to increase the viscosity of the pitch, i.e. the normal effect of pressure on a fluid (as is evident in the decrease in size of optical texture and formation of botryoidal structures) [2]. This increase in viscosity should decrease flow velocities in the carbonization system and should tend to prevent the alignment of matrix basal planes by shearing forces. That the opposite effect is actually seen (at least up to about 100 MPa for the lower viscosity pitches) suggests that the retention of

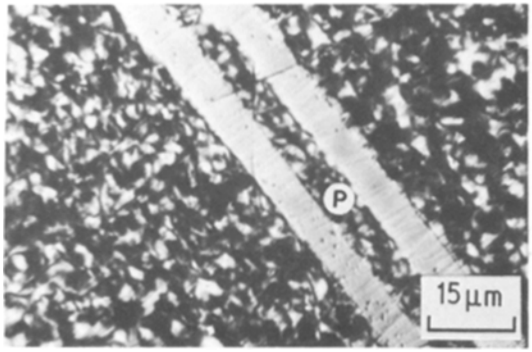


Figure 18 Optical micrograph of CVD coated fibres in matrix carbon from D112 coal extract; 6.7 MPa.

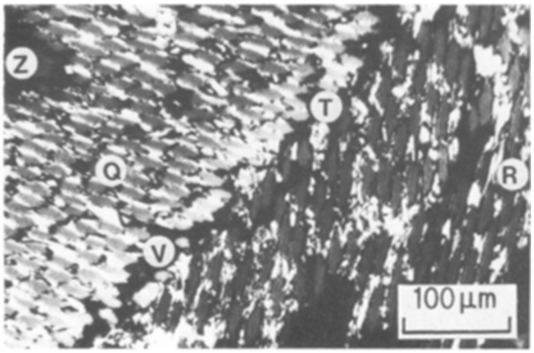


Figure 20 Optical micrograph of G2206 cloth in a matrix carbon from Esso CP1510 pitch; atmospheric.

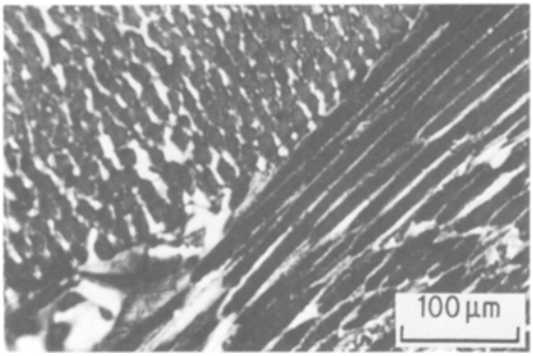


Figure 21 Optical micrograph of G2206 cloth in a matrix carbon from A240 pitch; 13.3 MPa.

volatile material in the carbonization system has the effect not only of producing yields of nearly 100% but also of acting as a "solvent", so reducing pitch viscosity. At pressures up to about 100 MPa this more than counteracts the increase in viscosity due to pressure and a more fluid system results. In such a system, basal planes of the matrix carbon become aligned parallel to fibre length because of the shearing forces produced by flow in the mesophase during carbonization. (This flow is caused by thermal gradients in the system and stirring due to volatile evolution). This effect is also seen with CVD coated fibres; pressures of this order improve alignment of the basal planes of the matrix carbon parallel to the length of these fibres.

At pressures above a value dependent on the properties of the matrix precursor, the effects of pressure begin to outweigh the effects of volatile retention, the viscosity of the pitch is increased and the alignment of basal planes of matrix carbon parallel to the fibre length is decreased.

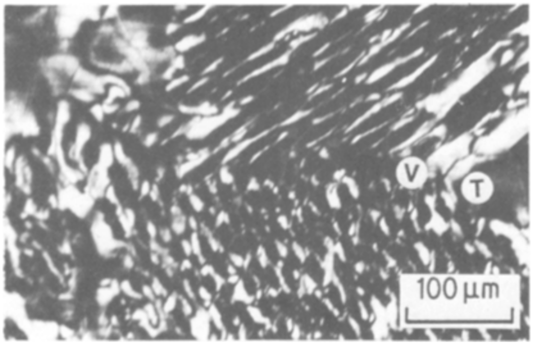
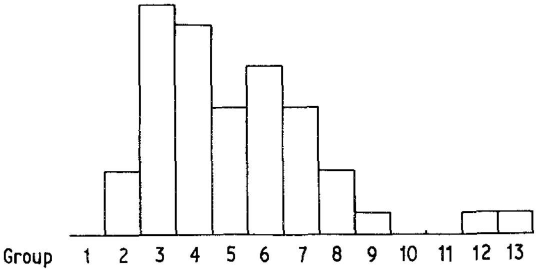
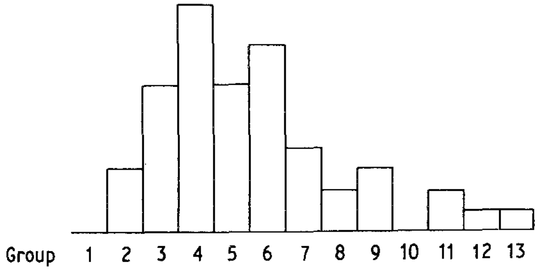


Figure 22 Optical micrograph of G2206 cloth in a matrix carbon from Esso CP1510 pitch; 13.3 MPa.



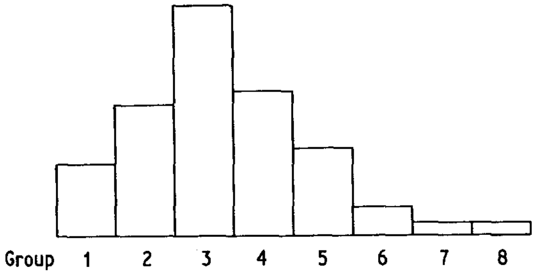
Group	Pores size range (μm)	Number of pores	Cumulative %
1	0–50	0	0
2	50–100	3	6
3	100–150	11	28
4	150–200	10	48
5	200–250	6	60
6	250–300	8	76
7	300–350	6	88
8	350–400	3	94
9	400–450	1	96
10	450–500	0	96
11	500–550	0	96
12	550–600	1	98
13	600–650	1	100

Figure 23 Histogram showing distribution of Feret *x* diameters for pores in composite from A240 pitch + G2206 cloth; atmospheric.



Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	0	0
2	50–100	3	6
3	100–150	7	20
4	150–200	11	42
5	200–250	7	56
6	250–300	9	74
7	300–350	4	82
8	350–400	2	86
9	400–450	3	92
10	450–500	0	92
11	500–550	2	96
12	550–600	1	98
13	600–650	1	100

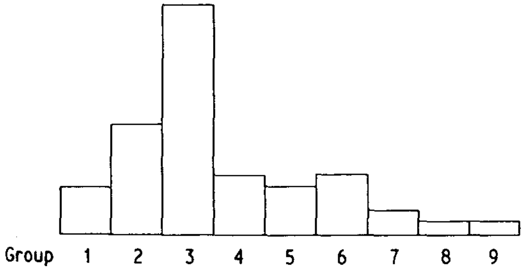
Figure 24 Histogram showing distribution of Feret *y* diameters for pores in composite from A240 pitch + G2206 cloth; atmospheric.



Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	5	10
2	50–100	9	28
3	100–150	16	60
4	150–200	10	80
5	200–250	6	92
6	250–300	2	96
7	300–350	1	98
8	350–400	1	100

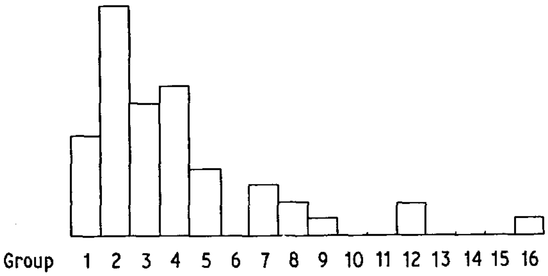
Figure 25 Histogram showing distribution of Feret x diameters for pores in composite from A240 pitch + G2206 cloth; 13.3 MPa.

It therefore appears desirable, for impregnation of carbon fibre composites under pressure, that the viscosity of the matrix pitch during carbonization should be low. There appears to be an optimum pressure for each pitch system used. In addition, the pitches carbonized here all formed semi-coalesced, porous botryoidal structures as the pressure of carbonization was increased. However, when fibres are added to carbonization systems, they appear to act as "condensation nuclei" for the anisotropic fluid matrix of mesophase and become fully coated with a sheath of the mesophase. This suggests that although the mesophase is not very cohesive within itself when carbonized at high pressures, addition of closely packed fibres to the carbonization system may help to prevent the formation of botryoidal structures and so to promote a more cohesive matrix.



Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	4	8
2	50–100	9	26
3	100–150	19	64
4	150–200	5	74
5	200–250	4	82
6	250–300	5	92
7	300–350	2	96
8	350–400	1	98
9	400–450	1	100

Figure 26 Histogram showing distribution of Feret y diameters for pores in composite from A240 pitch + G2206 cloth; 13.3 MPa.



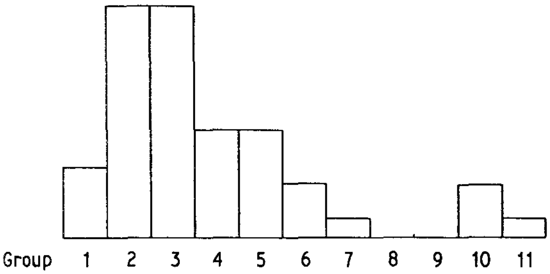
Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	6	11
2	50–100	14	39
3	100–150	8	54
4	150–200	9	72
5	200–250	4	80
6	250–300	0	80
7	300–350	3	86
8	350–400	2	90
9	400–450	1	92
10	450–500	0	92
11	500–550	0	92
12	550–600	2	96
13	600–650	0	96
14	650–700	0	96
15	700–750	0	96
16	750–800	1	98

Figure 27 Histogram showing distribution of Feret x diameters for pores in composite from Esso CP1510 pitch + G2206 cloth; atmospheric.

4.3. The effects of pressure upon the co-carbonization of pitches with a woven carbon fibre cloth (G2206)

4.3.1. Examination of composites by optical microscopy

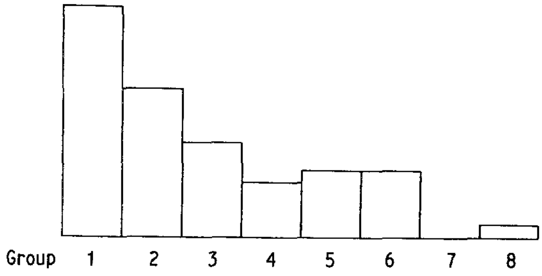
The results of the examination of composites prepared using A240 and Esso CP1510 petroleum pitches with G2206 fibre cloth at atmospheric pressure and at 13.3 MPa indicate that at both



Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	4	7
2	50–100	13	33
3	100–150	13	58
4	150–200	6	70
5	200–250	6	82
6	250–300	3	88
7	300–350	1	90
8	350–400	0	90
9	400–450	0	90
10	450–500	3	96
11	500–550	1	98

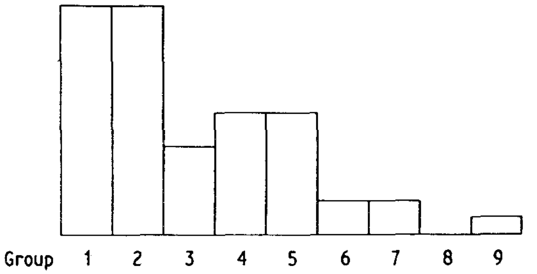
Figure 28 Histogram showing distribution of Feret y diameters for pores in composite from Esso CP1510 pitch + G2206 cloth; atmospheric.

carbonization pressures, basal plane alignment of the matrix carbon is parallel to the fibre length in fibre bundles and undergoes rapid changes in structural orientation between fibre bundles. Where it undergoes such rapid changes in orientation it is prone to fissuring; fissures in the matrix carbon are frequently found between fibre bundles. Carbonization under pressure, however, appears to increase the amount of matrix carbon in which basal planes are orientated parallel to the fibre length within fibre bundles; less variations in the RIC are seen indicating orientation to be more nearly parallel to the fibre length.



Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	17	34
2	50–100	11	56
3	100–150	7	70
4	150–200	4	78
5	200–250	5	88
6	250–300	5	98
7	300–350	0	98
8	350–400	1	100

Figure 29 Histogram showing distribution of Feret x diameters for pores in composite from Esso CP1510 pitch + G2206 cloth; 13.3 MPa.



Group	Pore size range (μm)	Number of pores	Cumulative %
1	0–50	13	26
2	50–100	13	52
3	100–150	5	62
4	150–200	7	76
5	200–250	7	90
6	250–300	2	94
7	300–350	2	98
8	350–400	0	98
9	400–450	1	100

Figure 30 Histogram showing distribution of Feret y diameters for pores in composite from Esso CP1510 pitch + G2206 cloth; 13.3 MPa.

4.3.2. Analysis of porous structure using a semi-automatic image analyser

The results obtained using the semi-automatic image analyser to analyse pore diameters indicate that the effects of carbonization under pressure are to reduce the Feret x and Feret y diameters of the pores for both matrix precursors. This shows that the effect of pressure is to limit the growth of the pores developing during carbonization; the volatiles given off which cause pore growth are increasingly compressed with increasing pressure of carbonization. It is to be noted that this effect is seen at relatively low pressures; at pressures in excess of 100 MPa both the A240 and Esso CP1510 form carbons consisting of semi-coalesced botryoidal structures with a considerable amount of porosity. This porosity has not yet been quantified.

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